GLASSY VISCOELASTICITY OF
DENSE SUSPENSIONS OF SOFT COLLOIDS AND
STRUCTURE & MISCIBILITY OF
SOFT FILLER POLYMER NANOCOMPOSITES

BY

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DISSEPTION

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In this thesis, we studied two soft condensed matter systems. The first part of the thesis studied the glassy viscoelasticity of dense suspensions of soft colloids and the second part of the thesis studied the structure and miscibility of soft filler polymer nanocomposites (PNCs).

In the first part of the thesis, we have presented the first microscopic theoretical study of activated glassy dynamics in dense fluids of finite range soft repulsive particles (many arm star polymers and microgel-like Hertzian spheres). The alpha relaxation time in the activated hopping regime is a rich function of volume fraction and temperature, including exhibiting a maximum value at ultra-high volume fraction due to a soft jamming crossover that signals local packing disorder due to particle overlap. A kinetic arrest diagram is constructed, and its qualitative features agree with the dynamic crossover (MCT) analog. The isothermal dynamic fragility varies over a wide range, and soft particles are predicted to behave as strong glasses. The highly variable dependences of the relaxation time on temperature and volume fraction are approximately collapsed onto two distinct master curves. We have applied NLE theory to study how particle softness influences the elastic shear modulus, the connections between the modulus (a short time property) and activated relaxation (a long time property), and the nonlinear rheological effects of stress-induced yielding, shear thinning of the relaxation time and viscosity, and stress versus shear rate flow curves of the repulsive Hertzian contact model of soft sphere fluids.
In the second part of the thesis, we have presented representative results based on a new minimalist multi-scale model constructed for soft nanoparticle fillers. This is the first theoretical study of the role of nanoparticle morphology associated with surface corrugation and fluctuation at one and two particle limit in polymer melts with/without interfacial cohesion.

Our results provide a physical basis for the unexpected ability to disperse chemically matched crosslinked polystyrene in linear polystyrene melt. The surface corrugation in the frozen surface regime results in a favorable entropic driving force for mixing which competes with unfavorable depletion, resulting in a major enhancement of nanoparticle dispersion, including a much larger spinodal solubility limit. Smooth hard sphere behavior is recovered when the number of beads are significantly large (N=282) and the relative corrugation size significantly reduced (from 20% to 10% of particle size). When surface fluctuation exists, the dependence of solubility limit on fluctuation magnitude is somewhat subtle, due to the relevance of multiple length scales. We find fluctuation suppresses dispersion for all particles sizes (or surface curvature) studied, and this effect is most pronounced when the monomer size is smaller than corrugation size. The extreme coherent fluctuation model shows dramatically enhanced dependence on fluctuation magnitude at large fluctuation magnitude and less miscibility. When interfacial cohesion exists, we develop a model for local bead-monomer level attraction, which explicitly connects to particle-monomer level attraction through potential mapping strategies. By varying the interfacial attraction strength, we can still observe all three regimes reported in prior PRISM studies of smooth HS filler PNCs. The steric stabilization regime is not sensitive to surface fluctuation magnitude, while the contact
clustering and strong bridging regimes are very sensitive to surface fluctuation magnitude. Surface fluctuation smears out surface corrugation and reduces interfacial cohesion, leading to stronger depletion attraction and more negative second virial coefficients.
To mom and dad
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CHAPTER 1

INTRODUCTION

1.1 Background and Motivation

The term “soft particle” refers to objects with tunably soft repulsive interactions of size that range from several nanometers to greater than a micron. Soft particles can be obtained conceptually in two ways. One is by exploiting the softness of an electrostatic or magnetic repulsive potential. Another way is to modify the synthesis of the particles, e.g. use many arm star polymers, crosslinked nanogels or microgels, micellar diblock copolymers based on self-assembly, a solid particle covered with adsorbed or grafted polymer chains, emulsion droplet, multilamellar vesicle and liposome (see Fig. 1.1) [1].

Dense fluids of soft particles, or soft particle pastes, are generally deformable objects dispersed in a solvent and in many materials applications are at large volume fractions, often above closepacking. They form an important class of materials at the interface between polymer solutions, granular materials, and colloids, for example, as rheology modifiers in ceramic processing, surface coating of submicron particles [2], and the food and pharmaceutical industries. All these materials exhibit both solid-like and liquid-like mechanical properties, with the solid-to-liquid transition taking a variety of forms. Such behavior is exploited industrially to formulate food or personal care products and to process high performance materials such as films, coatings, solid inks, and ceramics.

Compared to conventional hard sphere colloidal suspensions and glasses, soft particles exhibit additional new and interesting structural and dynamical features. A key
issue in repulsive dense systems is the topological caging constraints a tagged object feels due to its neighbors. Linear flexible polymers in solution at very high volume fraction or in the melt can be entangled and experience the so-called tube confinement, while long time dynamics proceeds via anisotropic reptation motion [3, 4]. On the other hand, when hard spheres reach a volume fraction of about 0.58, they are sufficiently constrained by neighbors (a small number not exceeding 12) that motion (on the scale of its size) becomes arrested, forming an effective cage [5-7], a “kinetic” glass transition occurs. Soft particles lie in between these two extremes, and a modified cage effect exists [8]. The particles interact through potentials that can be tuned over very wide range via the chemical composition and architecture, changing from polymer coils to hard sphere colloids. Either because of their (limited) interpenetration (many arm stars) and/or deformability (crosslinked microgels), suspensions of such particles can reach very high volume fractions, even beyond random close packing of hard spheres ($\phi_{rcp} \approx 0.64$). The particles then develop repulsive forces of elastic origin at contact, which control the cage elasticity and other macroscopic properties [1].

Two types of soft particles are of particular interest in this thesis. One is many arm stars, and the other is crosslinked microgels (see Fig.1.1). Many arm star polymers are a pristine model system for soft particles with many unique advantages. (1) Superior structural control compared with most soft particle systems, which are not so well characterized: polydispersity, limited control of aggregation or grafting density, difficulty in reproducing exactly the same composite particle, particle stability (particularly with respect to time and to temperature). Many arm stars can be tuned from polymer coils to almost hard spheres by increasing arm number. (2) For most soft particle systems, the
softness is tuned by various external parameters, e.g. temperature, pH, solvent, and additives, while for stars, varying the number and/or size of the ‘grafted’ chains is enough.

(3) Stars have a well-established microscopic description interaction potential at the center of mass level. Given the complexity of interactions, model systems with as simple as possible, well-understood interactions, are highly appreciated, e.g. no charges, no enthalpic, only entropic (excluded volume) interactions of tunable strength and spatial range [8].

Microgel particles are cross-linked latex or collapsed polymer particles that are swollen in a good solvent. Microgels have become one of the most popular soft matter systems to study because they can be conveniently prepared by surfactant-free emulsion polymerization (SFEP), and because their softness can be manipulated by varying the amount of crosslinking or temperature. The influence of the softness of concentrated microgel suspension dynamics has been studied in detail by Dynamic Light Scattering (DLS) [9]. Quite remarkably, the authors find that particle softness correlates with dynamic fragility, defined as the rate of increase of the structural relaxation time, $\tau_a$, with particle concentration. Very soft particles have an Arrhenius-like (exponential in concentration) growth of $\tau_a$, and increasing nonexponential growth (more fragile) as particle stiffen. As a result, soft colloids appear as a promising system for understanding the origin of fragility in glasses. Another long standing problem is the pursuit for a unified picture for the ergodic-to-nonergodic glass transition in a wide range of soft matter systems. Recent simulations and experiments [10] use microgels (or Hertzian sphere modeling based on elastic contact mechanics [11]) as a pristine model system to construct a jamming phase diagram [10]. A so called “soft jamming” transition has been
discovered corresponding to the non-monotonic change of the primary peak of the interparticle pair correlation function, \( g(r) \), with increasing particle concentration.

Soft particle suspensions exhibit remarkable nonlinear shear rheology. They respond either like an elastic solid when the applied stress is below the yield stress, or like a viscoelastic fluid when a stress greater than the yield value [12]. Thus they are very important for processing and applications. It is well documented that dense suspensions of soft particles are shear thinning fluids, and very often the shear stress increases with the shear rate when above their yield stresses for the cases of concentrated emulsions [13-15], microgel suspensions [16], and multilamellar vesicles [17]. Systematic rheological studies of concentrated microgel suspensions, compressed emulsions [18-19], diblock copolymer micellar solutions [20] and star polymers [21] have shown that the flow properties of these materials are described by a universal flow curve.

All of the above novel phenomena call for a microscopic theory which can help us to understand and provide materials design rules. Concerning microscopic theoretical studies of soft repulsive sphere glass dynamics, there has been very little work. The only study of glassy dynamics has applied standard ideal Mode Coupling Theory (MCT) [22], which has several qualitative discrepancies: critical power law growth of relaxation times with temperature and volume fraction instead of the observed strongly activated form indicative of barrier hopping dynamics, and incorrect dynamic fragility trends with particle stiffness. Such failures are no doubt due to the fact MCT does not capture activated dynamics while the Nonlinear Langevin Equation (NLE) theory [23-26] is a promising tool that includes the fundamentally important role of activated hopping events.
Adding nanoparticles or fillers to dense polymer melts can profoundly modify the mechanical, thermal, optical and/or other material properties. These so-called polymer nanocomposite (PNCs) are the subject of the second half of this thesis. They have a large surface to volume ratio of nanoparticles which results in large modification of the matrix polymer properties. Such property changes are strongly influenced by particle spatial dispersion and PNCs structure, which is poorly understood. Recently, the use of nanogel soft filler particles in PNCs revealed a host of intriguing phenomena, such as unexpected high dispersion in the absence of polymer-particle attraction [27] (will be discussed in Chapter 5), decrease of viscosity upon addition of the particles to the polymer matrix, and striking particle size dependence of shear elasticity [28] (will be briefly discussed in Chapter 7). These effects confirm the importance of these systems as rheological research tools. To achieve such novel properties, the role of soft particle surface morphology must be understood. The surface morphology can be viewed as a combination of surface corrugation (roughness) and fluctuation (softness). Thus, a multi-scale modeling approach is needed to fully understand the role of surface morphology at roughly the monomer length scale which is most relevant to polymer mediated depletion attraction forces between fillers which is a key driving force of undesirable macroscopic scale clustering and phase separation.

The development and initial application of predictive theories of the equilibrium structure and phase behavior of polymer nanocomposites based on hard filler has undergone dramatic progress in the past decade [29]. However, much remains to be done, and it seems fair to say that the development of broadly applicable microscopic theories that can balance computation complexity inherent of real PNCs but still capture the key
physics is in its early stages. Many theoretical challenges and key questions remain open for the PNCs based on the novel soft fillers described above, some of which are the following. (1) What is the role of coarse graining of nanometer scale chemical structure? (2) How do different length scales interfere in dense PNCs? What are their roles in nanoparticle dispersion? (3) How do the major states of polymer-mediated organization (depletion clustering, steric stabilization via polymer adsorption, and polymer-mediated bridging and network formation) change for nonsmooth fillers of varying corrugated surface, size and dynamic fluctuation? (4) How does the effective interfacial cohesion between homopolymers and fillers change thermodynamics at different level of description, i.e. from surface local interaction to particle center of mass level interaction? (5) Does filler surface softness and shape fluctuations on the nanometer scale perturbatively modify the states of organization and miscibility found for hard fillers, or qualitatively new and unique behavior emerge?

The general goal of this thesis follows two tracks (see Fig.1.2). The first one studies dense colloidal suspensions of soft particles. We first obtain the equilibrium structure and then use it as an input to activated barrier hopping NLE theory to study the slow activated dynamics, elasticity, and nonlinear rheology. The other track studies polymer nanocomposites. First, we also obtain the equilibrium structure for two-component system, and then we use it to study thermodynamics and equilibrium phase diagrams.
1.2 Dissertation Overview

Chapter 2 presents the theoretical basis and methodology used to study the equilibrium structure, glassy dynamics, and mechanical response of dense fluids of soft repulsive particles, including Ornstein–Zernike integral equation theory to obtain equilibrium liquid state structure, Naïve single particle MCT for the dynamical crossover, and quiescent NLE theory for the activated hopping are summarized under quiescent and stress-driven conditions. This methodology has been extensively developed in the group and is general such that it can be applied to any spherical soft repulsive particle system.

Two representative types of model soft particle suspensions are studied in detail in Chapters 3 (many arm stars) and 4 (Hertzian spheres mimicking crosslinked microgels) applying the methodology of Chapter 2. We first consider the real space structural consequences of single particle softness (interpenetrability for many arm stars and elastic overlapping for Hertzian spheres) to study the “soft jamming” transition. Then we study the NMCT dynamic crossover, glassy dynamical regime and activated barrier hopping, and dynamic fragility. Lastly, calculations for the linear elasticity and nonlinear rheology (for Hertzian sphere only) are presented. Qualitative and quantitative comparisons to experiment are given.

In Chapter 5, a new hybrid small scale Monte Carlo (MC) simulation plus Polymer Reference Interaction Site Model integral equation theory (PRISM) is proposed. The methodology is applied to model soft particle polymer nanocomposites to understand structure, thermodynamics and miscibility in Chapter 6. We first construct a minimalist multi-scale model, which explicitly studies the role of surface corrugation and fluctuation by introducing the dimensionless length scales for particle-monomer size asymmetry,
surface corrugation and fluctuation magnitude. Then we perform small-scale MC simulation to correctly capture the effective interactions among particles and monomers. We then employ PRISM theory to study the spatial statistical correlation functions of the mixture to understand how the surface morphology affects depletion attraction and bridging and whether it stabilizes dispersion.

Chapter 7 utilizes the multi-scale modeling developed in Chapter 5 in conjunction with the Naïve MCT and NLE theory of dynamics and elasticity to study the shear elasticity and glassy dynamics of dense fluids of soft nanoparticles of crosslinked polymeric nature and understand the particle size dependence of kinetic vitrification and the shear modulus.

Chapter 8 concludes the dissertation by summarizing the key results and briefly sketches possible future directions.

1.3 References


1.4 Figures

**Soft Colloids & Nanoparticles**

![Diagram of soft colloids and nanoparticles](image)

- **a**: Solid particle covered with adsorbed or grafted polymer chain
- **b**: Crosslinked Microgels/Nanogels
- **c**: Many arm stars
- **d**: Block copolymer micelle
- **e**: Emulsion droplet
- **f**: Multilamellar vesicle
- **g**: Liposome

**Fig. 1.1**

Fig. 1. 2

Schematic representation of the general goal of thesis: for colloidal suspension (top), we first obtain the equilibrium structure and then use it as a input to activated barrier hopping and mechanical response theories. For polymer nanocomposites, we also first determine its equilibrium structure then use it to study thermodynamics and phase diagram.
CHAPTER 2

GLASSY DYNAMICS AND MECHANICAL RESPONSE IN DENSE FLUIDS OF SOFT REPULSIVE SPHERES: METHODOLOGY

2.1 Introduction

The hard sphere fluid or colloidal suspension is a pristine model system to investigate glassy dynamics due solely to singular repulsive excluded volume forces and crowding [1,2]. Many ensemble-averaged aspects are well described by ideal mode coupling theory (MCT) [2] in the initial (or precursor) slowing down regime that covers a few orders of magnitude of relaxation based on adjustment of the critical nonergodicity volume fraction. Ideal MCT self-consistently describes collective time-dependent density fluctuations based on the confining cage concept and continuous small amplitude cooperative motions within a dynamical Gaussian approximation [2]. However, confocal microscopy [3] and computer simulations [4] both find single particle trajectories display intermittent large amplitude activated hopping events at high volume fractions, even in the dynamical precursor regime. A recent experimental and simulation study [5] suggests activated dynamics is dominant well below random close packing (RCP). The many highly nongaussian phenomena observed [6] are not captured by ideal MCT, but are well described by the nonlinear Langevin equation theory (NLE) as a consequence of thermally activated barrier hopping and intermittent trajectories [6-9]. Hence, the prediction of ideal MCT, a dynamical Gaussian approach that ignore large amplitude hopping of complete arrest is now understood to actually indicate a dynamic crossover
from collective but smooth Gaussian like dynamics to a slower form of activated transport and relaxation.

Perhaps the simplest variation away from hard spheres are soft repulsive spherical particles. Experimentally, distinct families of such colloids or nanoparticles have been created where the degree of softness, and functional form of the interparticle potential, are different and widely tunable. For example, recent experimental studies have appeared for dense suspensions of many arm star polymers [10,11], crosslinked microgels [12-19], and copolymer micelles [20]. The repulsive interaction between many arm stars in a good solvent are mediated by the underlying polymer chains, and at the center-of-mass level consist of an arm-number-dependent longer range Yukawa repulsion and a logarithmic repulsion at small separations (see Fig.2.1). In contrast, a popular simple model for microgels is the finite range, repulsive Herztian contact interaction [21,22] which remains finite at full particle overlap (see Fig.2.1). This potential, or minor variants of it, have also seen much simulation study as a model system for athermal granular jamming [23].

What all dense fluids of soft repulsive particles have in common is the emergence of intermittent dynamics and glass-like viscoelasticity at high enough concentrations with qualitatively distinct features not present in hard sphere suspensions. Besides the broad relevance to materials science, soft particles are ubiquitous in other areas such as polymer nanocomposites [24] and vesicle diffusion in biopolymer networks [25].

Recent experiments have uncovered a wealth of fascinating phenomena including: (i) non-Arrhenius variation of the relaxation time with particle stiffness (or effective inverse temperature) and fluid volume fraction [13,14], (ii) massive variability of the dynamic fragility associated with relaxation and viscous flow [13,17], (iii) non-
monotonic variation of local packing structure with volume fraction due to the avoidance of strict jamming (so-called “soft jamming crossover”) [14], (iv) a direct connection between vitrification volume fraction and the elastic shear modulus [12], (v) particle softness-independent linear scaling of the shear modulus with concentration at ultra-high (beyond the hard sphere RCP) volume fractions [17,21], and (vi) distinctive dependences of the yield stress and other nonlinear rheological properties on volume fraction and degree of particle softness [26].

Recent computer simulation studies of the quiescent dynamics and elasticity of the soft repulsion models have observed some of the above features [17,21,27]. An interesting two-branch universality of the temperature and concentration dependences of the mean alpha relaxation time has been uncovered [27]. More generally, recent theoretical and simulation studies have also discovered a rich equilibrium phase behavior, including re-entrant phase transitions at ultra-high volume fractions due to subtle competition of energetic and entropic factors associated with soft particle overlap [22].

However, it is important to emphasize that the simple center-of-mass central force model potentials employed in simulation and theoretical studies [22] neglect a host of complexities present in polymer-based microgels (and also stars, micelles, grafted nanoparticles, emulsion droplets, liposomes [17]) which are especially relevant at ultra-high concentrations. For example, complex monomer chemistry, dangling (perhaps entangled) chains at the particle surface, residual attractions, and Coulomb repulsions (polyelectrolyte effects) can be present, along with distinctive consequences of shape deformability above random close packing such osmotic deswelling and the formation of solvent-lubricated facets [17]. These complications also render a unique experimental
quantification of volume fraction difficult. Hence, simulation and theoretical studies based on the simple interaction potentials are not generally expected to quantitatively describe suspensions of soft particles, but rather serve as a zeroth order description of many (not all) aspects at a semi-quantitative or qualitative level.

Concerning microscopic theoretical studies of soft repulsive sphere glass dynamics, there has been very little work. A micromechanical model has been developed for the elastic and flow properties beyond contact (volume fractions $\phi_{\text{RCP}} \sim 0.64$) [17, 21]. The only study of glassy dynamics has applied standard ideal MCT [28]. Ideal MCT does predict a form of dynamic scaling (over a tiny volume fraction range) based on the hypothetical ideal glass transition singularity, and a critical power law parabolic form of the effective dynamic crossover temperature, as seen in the simulations. However, several qualitative discrepancies were clearly evident: critical power law grow of relaxation times with temperature and volume fraction instead of the observed strongly activated form, and incorrect dynamic fragility trends with particle stiffness. Such failures are no doubt due to the fact MCT does not capture activated dynamics.

Hence, the intriguing experimental and simulation glassy dynamics observations are not theoretically understood in a consistent manner. We believe this reflects the fundamentally important role of activated hopping events. This motivates our present work which comprehensively applies the existing NLE theory of Schweizer and coworkers, which at the moment seems to be the only first principles no adjustable parameter theory of activated glassy dynamics and viscoelasticity at the level of forces, to the models of soft repulsive sphere fluids. Relaxation, elasticity, and some aspects of nonlinear rheology are addressed within a single framework. Given the interaction
potential uncertainties for real soft particles, we do not emphasize quantitative comparisons to experiment, but rather only qualitative comparisons.

Our goal is to apply and generalize existing statistical mechanical methods to dense fluids of soft particles to understand how particle softness affects structure and dynamics. But in order to create a predictive theory, one needs to relate structure, forces, and dynamics. We first use the model interparticle potentials between soft particles, which are controlled by chemistry, as an input to well-known equilibrium liquid state theory and predict equilibrium structure, which can be quantified via the pair correlation function and static structure factor as an input to our dynamical theories to address the following issues: (1) dynamic free energy and dynamic crossover, (2) the influence of volume fraction and particle softness on the mean relaxation time, (3) kinetic arrest diagram and dynamic fragility, (4) the quiescent shear modulus as a function of volume fraction and repulsion strength and (for microgel models) (5) nonlinear rheology. The focus of chapter 3 is on many arm stars, while chapter 4 studies crosslinked microgels.

The remainder of this chapter is structured as follows. Section 2.2 discusses the equilibrium liquid state Ornstein-Zernike theory. The single particle “naïve” MCT dynamical crossover is given in section 2.3. The quiescent NLE approach is reviewed in section 2.4. The ultralocal limit is introduced in Section 2.5. Section 2.6 briefly reviews the NLE and naïve MCT approaches employed to determine mechanical properties. Section 2.7 and 2.8 present the references and figures.

2.2 Equilibrium Liquid State Theory: Ornstein–Zernike Theory
Our interest is to use the interparticle pair potential as input to a theory for the spatial structure at the center of mass level of the soft particle fluid at nonzero concentrations. We employ the Ornstein–Zernike (OZ) approach [28] based on a single integral equation that relates the interparticle pair correlation function, \( h(r) \equiv g(r) - 1 \), to the direct correlation function, \( C(r) \), as

\[
h(r) = C(r) + \rho \int C(|\vec{r} - \vec{r}'|) h(r') d\vec{r}'
\]

where \( r \) is the CM distance between two particles and \( \rho \) is the particle number density. The Fourier space static structure factor that quantifies collective density fluctuations is given by:

\[
S(k) = 1 + \rho h(k) = \frac{1}{1 - \rho C(k)}
\]

To solve the OZ equation a closure approximation is required. For separations beyond the distance of closest approach (\( \sigma \), the particle diameter), we employ the hypernetted chain (HNC) closure for dense fluids of soft particles:

\[
C(r) = -\beta U(r) - \ln(g(r)) + h(r)
\]

where \( U(r) \) is the interparticle potential. For \( r < D \), the hard core exclusion constraint is exactly enforced, \( g(r) = 0 \). We adopt the HNC closure for multiple reasons: (1) it ensures positivity of \( g(r) \) for all separations, (2) it guarantees the correct result is obtained in the dilute limit, and (3) the HNC has proved accurate and reliable for many soft repulsive systems at the CM level (e.g. finite range Hertzian repulsive spheres [29] and carbon black fractals [30]). The OZ-HNC integral equation is solved using the KINSOL algorithm (hybrid Picard plus Newton–Raphson method) [31].
2.3 Naïve MCT Dynamical Crossover

We determine the ideal MCT glass transition, which represents a dynamic crossover to activated dynamics, using the single particle “naïve” MCT (NMCT) [6,32]. This mathematically and physically simple approach is based on computing the long time limit of the force-force correlation function, $K(t)$, given in a Fourier-resolved form by:

$$
K(t \to \infty) = \left\langle \vec{F}(0) \cdot \vec{F}(t \to \infty) \right\rangle = \frac{1}{3\beta^2} \int \frac{d^3k}{(2\pi)^3} k^2 C^2(k) \rho S(k) e^{-k^2 r_{loc}^2 \left[ 1 + S^{-1}(k) \right] / 6} \quad (2.4)
$$

where $\vec{F}(t)$ is the total force exerted on a tagged particle by the surrounding fluid at time $t$, $r_{loc}$ is the long time limit of a particle mean square displacement or “localization length”, and a Gaussian Einstein solid description of the arrested glass is adopted. If $r_{loc}$ is infinite, the system is a fluid; if it is non-zero, an ideal glass. The dynamical “vertex”, defined as $\rho k^2 C^2(k) S(k)$, describes the Fourier resolved effective mean square force on a particle. The localization length obeys a nonlinear self-consistent equation [6]:

$$
\frac{1}{r_{loc}^2} = \frac{1}{9} \int \frac{d^3k}{(2\pi)^3} \rho k^2 C^2(k) S(k) e^{-k^2 r_{loc}^2 \left[ 1 + S^{-1}(k) \right] / 6} \quad (2.5)
$$

We recall that NMCT has successfully captured many subtle dynamical arrest phenomena including: re-entrant glass melting and subsequent attractive glass formation in sticky hard spheres [33], non-monotonic variation of glass volume fraction with aspect ratio in fluids of diatomic and other uniaxial hard objects [34], and re-entrant phenomena and single versus double localization behavior in mixtures of repulsive and attractive particles [35].

2.4 Quiescent NLE Theory
To go beyond ideal MCT and treat single particle activated dynamics we employ the microscopic force-level NLE theory [6,7]. This approach is built on a locally solid-state view of highly viscous dynamics with density fluctuations the key slow variable, and a local equilibrium approximation to mathematically close the theory at the single particle motion level. NLE theory is formulated as a stochastic equation-of-motion for the instantaneous scalar displacement of a tagged particle, $r(t)$:

$$\zeta S \frac{\partial r(t)}{\partial t} = -\frac{\partial F_{\text{eff}}(r(t))}{\partial r(t)} + \delta f(t)$$  \hspace{1cm} (2.6)

$$\beta F_{\text{eff}}(r) = -3\ln(r) - \int \frac{dk}{(2\pi)^3} \rho C^2(k)S(k) e^{-\frac{k^2 r^2}{6}} \left(1 + S^{-1}(k)\right)$$  \hspace{1cm} (2.7)

Here, $\zeta_s = k_BT/D_s$ is a short time friction constant, the random thermal force satisfies $<\delta f(0)\delta f(t)> = 2k_BT\zeta S \delta(t)$, and $F_{\text{eff}}(r(t))$ is a “dynamic free energy” the derivative of which quantifies the force on a tagged particle due to its surroundings. As confining forces increase, $F_{\text{eff}}(r)$ changes from a delocalized form (decreasing function of $r$), to a transient localized form (local minimum at $r_L$ with a barrier of height $F_B$) indicating a crossover to activated dynamics. If the thermal noise in Eq. (2.6) is dropped (no hopping), or a literal dynamical Gaussian approximation is made at the ensemble-averaged level, the NMCT transition [7] is obtained which can be mathematically expressed as the first emergence of a localized solution of $\partial F_{\text{eff}}(r)/\partial r |_{r=r_L} = 0$.

Activated hopping or relaxation is quantified via the Kramers mean first passage time for barrier crossing:

$$\tau_{\text{hop}} / \tau_s = 2\pi \left(\tilde{K}_0 \tilde{K}_B\right)^{-1/2} \exp(\beta F_B)$$  \hspace{1cm} (2.8)
where $\tau_s = \beta \sigma^2 \zeta_s$ is the elementary short time scale, and $\tilde{K}_o$ and $\tilde{K}_b$ the well and barrier curvatures in units of $k_b T \sigma^{-2}$, respectively [6]. The hopping time is almost identical to the relaxation time of the experimentally measurable incoherent dynamic structure factor at the cage peak of $S(k)$ [9], a common measure of "structural relaxation".

We mention that the single particle NLE theory has very recently been generalized to treat the space-time correlated dynamics of a pair of particles [36]. Applications of this more sophisticated NLE theory to study average relaxation questions for hard sphere fluids reveals good agreement with the simpler single particle approach, thereby providing deeper theoretical support for the practical usefulness of the latter.

2.5 Ultralocal Limit

The structural input to NMCT and NLE theory that quantifies the Fourier-resolved mean square force on a tagged spherical particle is given by the "vertex" [37]:

$$V(k) = k^4 \rho C^2(k) S(k)$$  \hspace{1cm} (2.9)

When barriers are high, it is the analytically known that for interaction potentials with a hard core (hence a rigorous exclusion constraint on $g(r)$) that the large wavevector limit of Eq(6) dominates all predictions of NLE theory, from the localization length to the barrier height [38,39]. Specifically, the vertex becomes $k$-independent at large wavevectors, with an amplitude proportional to a "coupling constant", $\lambda$. Physically, the latter is a measure of the dynamical mean square force exerted on a tagged particle due to repulsive force collisions, and for spheres is:

$$\lambda = \phi g^2(\sigma)$$  \hspace{1cm} (2.10)
where \( g(\sigma) \) is the contact value. Prior work for hard core models \([34,38,39]\) has found the barrier height is proportional to this coupling constant once \( F_b \) exceeds a few \( k_B T \):

\[
F_b \approx \frac{\lambda - \lambda_c}{\lambda_c}
\]

(2.11)

where \( \lambda_c \) is the coupling constant at the ideal NMCT transition. Moreover, it has very recently been shown that for broad families of nonspherical particles with hard core repulsions, with and without attractions, Eq. (2.11) is also remarkably accurate \([40]\).

For the soft repulsive sphere systems of present interest, which do not have a hard core, the prior analytic analysis does not rigorously apply. Moreover, exact analytic exact knowledge of the relevant direct correlation function of these systems in the high \( k \) limit is not available. But, on general grounds the vertex in Eq. (2.9) is expected to behave differently at large wavevectors since there are no discontinuous jumps of \( g(r) \) to zero as for systems with a hard core repulsion. We shall empirically test in the following two chapters whether the basic ideas of the hard core based analytic limit of NLE apply to soft particles. But in stead of using the contact value \( g(\sigma) \), we use \( g_1 \), the primary peak value instead. And thus Eq. (2.10) becomes \( \lambda = \phi g_1^2 \).

2.6 Mechanical Response

The linear elastic shear modulus, \( G' \), is computed using the standard statistical mechanical formula where stress is projected onto bilinear collective density fluctuation modes and 4-point correlation functions are factorized \([41-43]\):

\[
G' = \frac{k_B T}{60 \pi^2} \left[ \int_0^\infty dk \left( k^2 \frac{d}{dk} \ln(S(k)) \right)^2 e^{-k^2 r_{loc}^2 / 3S(k)} \right]^{1/2}
\]

(2.12)
Here, $S(k)$ is the fluid static structure factor, and $r_{\text{LOC}}$ is the minimum of the dynamic free energy (transient localization length) computed from the naïve MCT self-consistency Eq.(2.6). Eq.(2.12) literally applies only in the ideal nonergodic state of MCT. We employ it here as a sensible approximation of the physically relevant intermediate time plateau of the dynamic stress relaxation function, $G(t)$, associated with the transiently localized state which exists even in the presence of activated hopping at long times.

For hard sphere fluids [44], and also fluids with an attraction plus a hard core repulsion [45], an analytic relation between the glassy shear modulus and the localization length has been derived:

$$G' = \frac{18}{5\sqrt{\pi}} \frac{\phi k_B T}{\sigma r_{\text{LOC}}^2}$$

(2.13)

where $\sigma$ is the particle diameter. As will be discussed in section 2.3, we find Eq.(2.13) describes very well our numerical calculations for the repulsive Hertzian fluids. Moreover, Eq.(2.13) has been recently shown experimentally to be remarkably accurate for both polymer-colloid depletion gels [46] and microgel suspensions [47,48].

The extension of NLE theory to nonlinear response has been achieved for spherical particle systems [49], and extensively applied to hard [49-51] and attractive [52,53] spheres, based on an applied stress and single particle microrheology perspective. Partial motivation for the theoretical approach comes from simulation findings that local dynamics is accelerated in a nearly isotropic manner despite the anisotropic nature of the macroscopic deformation, and local single particle (or segmental for polymers) dynamics is tightly coupled with bulk mechanical response [54-58]. Indeed, simulations find massive shear thinning can occur with little or no anisotropy of local structure, i.e. the system remains “effectively isotropic” on the cage scale [55,56,58]. The recent
theoretical/simulation studies of Brady and coworkers [59] also supports the assumption that bulk mechanical response can be accurately determined from single colloid dynamics (microrheology) even when the tagged and matrix particles are identical in size.

The specific ansatz underlying the nonlinear NLE approach is that a macroscopic applied stress (magnitude $\tau$) induces a constant scalar external force on a tagged segment given by: $f = c\sigma^2\tau$, where $c$ is an of order unity and weakly volume fraction dependent factor estimated from an effective particle cross-sectional area [49]. Applied deformation then modifies the dynamic free energy as [42,49,52]:

$$ F_{\text{eff}} (r;\tau) = F_{\text{eff}} (r;\tau = 0) - fr $$

(2.14)

More explicitly, using Eq.(2.7), one has

$$ \beta F_{\text{eff}} (r) = -3\ln(r) - \int \frac{dk}{(2\pi)^3} \frac{\rho C^2(k) S(k)}{1 + S^{-1}(k)} \frac{k^2}{6} e^{-\frac{k^2}{6} (1 + S^{-1}(k))} - a \beta \phi^{-2/3} \sigma^2 \tau $$

(2.15)

where here we employ $a = \pi / 6$ [49]. External stress enters ala an instantaneous dynamical variable analog of the Eyring [60] landscape tilting idea. The physical picture is stress introduces a bias which lowers activation barriers and increases localization length corresponding to a direct mechanical acceleration of relaxation and reduction of rigidity. The stress-induced force is assumed to not modify equilibrium pair correlations (which are input to the dynamic free energy) nor the fast (very local) relaxation process $\tau_s$ in the Kramers time (Eq.(2.8)). Volume-changing versus volume-conserving deformations are not distinguished in this simple approach.

Stress lowers the barrier in the dynamic free energy, and can mechanically drive a glass-to-liquid transition in a manner consistent with potential energy landscape
simulations [61]. However, the consequences of this stress-assisted speeding up of relaxation within NLE theory display multiple non-Eyring features [42,49], as observed in many simulations and experiments [54,62-64]. The localization well and barrier of the dynamic free energy are destroyed at an “absolute yield stress”, \( \tau_{\text{abs}} \). Here, cage escape no longer requires thermal activation ala an “athermal” or “granular” limit. Stress also increases the localization length, thereby reducing the elastic modulus in Eq.(2.12).

A simple constitutive equation has been constructed in the Maxwell model spirit which requires as input only the elastic modulus and mean segmental relaxation time [42,65]. Here we focus solely on the two extreme limits which do not require the full constitutive equation. The first is a step strain deformation under conditions where there are no thermally-induced activated hopping on the experimental time scale. This corresponds to an elastic solid-like rheological equation-of-state [49]:

\[
\tau = G'(\tau) \gamma
\]  
(2.16)

Eq.(2.16) implicitly defines strain, \( \gamma \), and the nonlinear shear modulus follows from Eq.(2.12) where stress enters only via an increase of the localization length. Since \( \tau_{\text{abs}} \) is the minimum stress required to destroy the activation barrier, it is equivalent to the condition that the applied force, \( f \), is equal and opposite to the maximum cage restoring force of the quiescent system computed from the dynamic free energy. The “absolute yield strain” is:

\[
\gamma_{y,\text{abs}} = \frac{\tau_{\text{abs}}}{G'(\tau_{\text{abs}})}
\]  
(2.17)

A “mixed” yield strain, employed in some experimental studies, is also defined:

\[
\gamma_{y,\text{mixed}} = \frac{\tau_{\text{abs}}}{G'(0)}
\]  
(2.18)
The second limit of interest is the long time flow regime. Based on a Maxwell model, which is useful when barriers are high and the short time (bare) contribution to the viscosity ($\eta$) is not important, one has the steady state flow relation:

$$
\tau = \dot{\gamma} \eta(\tau) = \dot{\gamma} G'(\tau) \tau_a(\tau)
$$

(2.19)

where the (shear) deformation rate is $\dot{\gamma}$, and the stress-dependent mechanical relaxation time is identified as the mean hopping time of Kramers theory [49]:

$$
\frac{\tau_a(\tau)}{\tau_s} = \frac{2\pi}{\sqrt{K_0(\tau)K_0(\tau)}} e^{\gamma_0(\tau)}
$$

(2.20)

Applied stress distorts all aspects of the dynamic free energy. The shear rate, $\dot{\gamma}$, follows from the viscous flow relation $\dot{\gamma} = \tau / \eta(\tau)$, thereby allowing calculation of the shear thinning response, i.e., $\tau_a(\dot{\gamma}), \eta(\dot{\gamma})$. We note that prior predictions of $\tau_a(\dot{\gamma})$ for a single tagged colloid in a glassy hard sphere fluid under strong shear [49] have been quantitatively tested against suspension experiments [66]. Excellent, nearly quantitative agreement with experiment was demonstrated [42]. In many other non-glassy complex fluids, perhaps most notably concentrated polymer solutions or melts not in the supercooled regime [67], shear thinning emerges when the deformation and quiescent relaxation time scales are comparable, i.e. the Peclet number is of order unity, $Pe = \dot{\gamma} \tau_a(0) \approx 1$. In contrast, the present theory predicts shear thinning begins in glassy particle fluids at extremely small values of the Peclet number, $Pe = \dot{\gamma} \tau_a(0) << 1$. The physical picture is shear thinning occurs not via destruction of the barrier, but rather by a stress-induced reduction of the barrier and corresponding massive increase of the activated hopping rate that permits flow on the experimental time scale (inverse shear
rate). It is this mechanism that leads to the onset of shear thinning at remarkably small Peclet numbers, as observed recently in computer simulation [68]. The physical picture of flow via stress-accelerated activated events is also consistent with the experimental confocal data for particle trajectories [66].

2.7. References


2.8 Figures

Above: Schematic representations of many arm star polymers and crosslinked microgels nanoparticles are shown. Below: The corresponding center of mass level interparticle potentials.

Fig. 2.1

Varying number of arms to tune particle softness

Varying single particle contact modulus $E$ - crosslink density to tune particle softness

Hertzian contact model

Finite range
CHAPTER 3

GLASSY DYNAMICS AND ELASTICITY OF DENSE FLUIDS OF MANY ARM STARS

3.1 Introduction

Many arm star polymers with tunable number and size of arms, and thus interactions, represent ideal model systems for exploring the regime of soft material behaviour that interpolates between hard spheres and polymeric coils. They can be thought of as ultrasoft colloidal spheres with a very small deformable core and a corona consisting of grafted chains (arms) (see Fig. 2.1). This regime is characterized by a rich variety of properties that reflect a combination of polymeric and colloidal features.

In this chapter, we apply the methodology in chapter 2 to perform the first theoretical study of the four colloidal characteristic features of soft particles discussed in the Introduction of Chapter 2 in the context of dense solutions of many arm stars. These nanocolloids are also a model system for other soft particles such as polymer-grafted colloids. Dramatic non-hard-sphere dynamical effects are predicted, which are understandable based on a connection between local packing structure and caging forces. Section 3.2 discusses the model, equilibrium structure, and “soft jamming” crossover. In section 3.3, we study the Naïve MCT kinetic arrest map. Section 3.4 focuses on activated barrier hopping and dynamical fragility. In section 3.5, we study the linear elastic shear modulus and experiment-theory confrontations are shown. Section 3.6 uses the ultralocal limit analysis to understand the behaviors of dynamic barrier height, mean barrier hopping time and linear elastic modulus. The chapter concludes in section 3.7 with a
summary and discussion. Section 3.8 and 3.9 present the references and figures, respectively.

3.2 Model, Equilibrium Structure and “Soft Jamming” Crossover

We adopt the well studied center-of-mass (CM) description of stars composed of f polymer arms in an athermal good solvent that interact via a pair decomposable repulsion of logarithmic (Yukawa) form at small (large) separations:

\[
18 \beta V(r) / 5 = f^{3/2} \left[ -\ln(r/\sigma) + \left(1 + \sqrt{f / 2}\right)^{-1} \right], \quad r \leq \sigma
\]

\[
= f^{3/2} \left( \sigma / r \right) \left(1 + \sqrt{f / 2}\right)^{-1} \exp[-\sqrt{f (r-\sigma) / 2 \sigma}], \quad r > \sigma
\]

(3.1)

where \( r \) is the CM separation, \( \sigma \sim 1.28 R_g \) (\( R_g \) is radius of gyration), and \( k_B T = \beta^{-1} \) is thermal energy [1-3]. The strength and spatial range of \( V(r) \) depends strongly on arm number, and hard spheres are recovered as \( f \to \infty \). Star concentration is quantified via a volume fraction \( \phi = \rho \pi \sigma^3 / 6 \), where \( \rho \) is the particle number density. Comparison of scattering experiments with the predictions of simulation and integral equation theory for the structural correlations of dense many arm star polymer fluids based on Eq.(3.1) show good agreement. Moreover, monomer level simulations of the inter-star CM potential-of-mean-force agree well with Eq.(3.1) up to high reduced concentrations (\( \phi > 1 \))[1]. We employ the Ornstein-Zernike equation with HNC closure [4] to compute the structure factor \( S(q) = \left(1 - \rho C(q)\right)^{-1} = 1 + \rho h(q) \), where \( C(q) \) and \( h(q) \) are the Fourier transform of the direct correlation function and nonrandom pair correlation function, \( h(r) = g(r) - 1 \), respectively [22].
We first consider the real space structural consequences of star interpenetrability. Fig.3.1 shows representative results for the pair correlation function of a f=128 arms star. With increasing volume fraction, the cage peak on the star size scale (r~σ) initially increases and shifts to smaller separations. However, beyond \( \phi \equiv 0.55 \equiv \phi_j \) (weakly f-dependent), qualitative changes emerge: the primary ordering peak decreases with concentration and a new peak appears at a much smaller (overlapped) CM separation, effects due to star interpenetration and increasing dominance of the logarithmic repulsion. We refer to \( \phi_j \) as a “soft jamming” threshold in analogy with a recent study of microgel suspensions [8]. This interpretation follows from the inset which shows the cage peak of \( g(r) \) goes through a maximum at \( \phi_j \). This non-monotonic behavior has been observed in experiment [8], simulation [8], and HNC integral equation theory studies [7] for repulsive microgels, and will be shown below to have dramatic consequences on the elastic and dynamic properties of dense many arm star fluids. We note that prior Rogers-Young (RY) closure based calculations of \( S(q) \) (and our own HNC-based computations) found a non-monotonic variation of the cage peak intensity with \( \phi \) [1]. This is consistent with our real space results, which to our knowledge have not previously appeared in the literature.

### 3.3 Naïve MCT Kinetic Arrest Map

Two examples of the dynamic free energy, \( F_{\text{eff}}(r) \), for many arm stars are shown in the inset of Fig.3.2. The ideal NMCT crossover is defined as when a barrier in \( F_{\text{eff}}(r) \) first emerges. One curve (black) is at a volume fraction just below the ideal NMCT crossover, the other (red) is at a high value where the barrier is \( 8k_B T \). For hard spheres no kinetic divergences are predicted at volume fractions below random close packing [9].
The NMCT ideal kinetic arrest diagram is then constructed in the main frame of Fig.3.2. Localization on the star scale is not predicted if the particles are too soft ($f < 40$), and non-monotonic behavior occurs at intermediate arm number. The NMCT boundary is compared with a more elaborate full ideal MCT calculation based on RY closure input, and also an iso-diffusivity boundary deduced from simulation [10]. Good agreement is obtained which establishes the important point that NMCT theory with HNC input reliably captures subtle ideal dynamical arrest phenomena for many arm stars.

### 3.4 Activated Barrier Hopping and Dynamical Fragility

The NLE theory is now employed to perform the study of activated barrier hopping and dynamical fragility in glassy star polymer fluids.

Fig.3.3 presents the dynamic free energy barrier height as a function of volume fraction. The barrier height increases roughly linearly with arm number below $\phi_j$. Once beyond $\phi_j$, the barrier saturates. This behavior dominates the mean hopping time trends, which is similar shown in log-linear format. Fig.3.4 shows the dimensionless mean barrier hopping time, $\tau_{\text{hop}}$, which grows strongly with both volume fraction and arm number below the soft jamming threshold. The increase is stronger than Arrhenius defined as an exponential growth, $\tau_{\text{hop}} \propto \exp(b\phi)$. The predicted supra-Arrhenius behavior can be tested via relaxation, viscosity, and/or self-diffusion experiments, which are beginning to be performed [11]. Beyond $\phi_j$, the hopping time saturates.

How tunable star softness impacts “dynamic fragility” below the jamming crossover as kinetic vitrification is approached is a fundamental issue of broad interest. This question is framed in analogy with the “Angell plot” employed for thermal glass
formers [12] where the relaxation time of different systems is normalized to a common point at the kinetic glass transition. For many arm stars, we adopt the natural fragility definition employed in recent experiment [13] and simulation [14] studies of microgel suspensions: \( m_\phi \equiv \partial (\log(\tau_{hop}/\tau_s))/\partial (\phi/\phi_s) \big|_{\phi=\phi_s} \). The glass transition volume fraction, \( \phi_s \), follows from the kinetic criterion \( \tau_{hop}/\tau_s = 10^y \). In colloid experiments and simulations [13,14] a typical \( y \sim 4 \). The dynamic fragility results using \( y=4 \) are shown in Fig.3.5. A remarkably wide range of dynamic fragilities is predicted, increasing from \( \sim 8 \) for \( f=150 \) where the relaxation is effectively Arrhenius and the soft stars behave as a “strong glass former” as observed in recent microgel experiments [13], to \( \sim 43 \) in the hard sphere limit. This roughly factor of five fragility variation is almost as large as seen in all thermal glass formers (metals, molecules, network formers) [12]. Physically, it is a dynamical consequence of the enhanced sensitivity of local structure (which determines the barrier) to \( \phi \) as individual star polymers interact via a repulsion that is spatially more rapidly varying (higher \( f \)). For experimentally relevant intermediate values of \( f \), the inset of Fig.3.6 shows \( m_\phi \) is predicted to increase logarithmically with arm number. The theoretical results are consistent with the limited experimental viscosity data available which do display a monotonic increase of fragility with increasing arm number [15,16].

The above dynamic fragility trends are not sensitive to the adopted vitrification criterion, as indicated by the \( y=9 \) results in the inset of Fig.3.5. One sees the dynamic fragility again varies by a factor of \( \sim 5-6 \) (hard sphere \( m_\phi = 83 \)). Kinetic glass formation boundaries based on the two vitrification criteria are presented in Fig.3.2. Modest shifts towards larger volume fractions relative to the NMCT ideal glass boundary are found, but the gross features of the dynamical crossover and kinetic arrest boundaries agree.
3.5 Linear Elastic Shear Modulus and Experiment-Theory Confrontations

Numerical calculations of the linear elastic modulus are shown in Fig.3.6 for an experimentally relevant range of star arm numbers. All soft colloids display a vastly weaker response to volume fraction than hard spheres ( $f \to \infty$ ). As arm number increases, the modulus monotonically grows, and a rough power law volume fraction dependence emerges with an effective exponent that increases linearly with arm number (for $f \leq 267$) as: $G' \propto \phi^n$, $n \simeq 2.4 + 0.01f$. Such power laws are, of course, approximate in that they apply only over a limited volume fraction regime, as also true in experiment. We have verified that the hard sphere result is numerically recovered beyond an experimentally impossible to achieve large value of $f > 1000$ (not shown). Above the soft jamming threshold, $G'$ fundamentally changes and exhibits a weak linear growth with volume fraction for all stars for the same physical reason that the hopping time saturates. Such a linear increase has been observed in ultra-high volume fraction microgel suspensions [17].

The theoretical results are compared in Fig.3.6 with an experiment for $f=267$ polybutadiene stars [15]. The experimental concentration variable ($c/c^*$) is converted to its theory analog as

$$\phi = \rho \pi \sigma^3 / 6 = \rho(4\pi/3)R_g^3(\sigma/2R_g)^3 = 0.26c / c^*$$ (3.2)

where $R_g$ is the radius of gyration and $R_h$ is the hydrodynamics radius and $R_g \approx R_h = 16$ nm [1,15]. The experimental shear modulus data [15] in the theory units has been shifted up by a constant factor of 42. The theory accurately predicts the apparent
power law dependence. Very recently, new experiments on $f=128$ stars have been performed at volume fractions beyond the soft jamming threshold [18]. The observed $\phi$ dependence of $G'$ becomes dramatically softer and is nearly linear.

3.6 Ultralocal Analysis

Fig.3.7 shows that $F_B$ is tightly correlated with the coupling constant, $\lambda$, consistent with prior hard sphere analysis [19], a measure of the dynamical mean square force exerted on a tagged particle due to repulsive force collisions. And for soft particles, its definition follows from the variation of Eq.(2.10): $\lambda = \phi g_i^2$. The volume fraction dependence of $\lambda$ (Fig.3.8) explains the (near) saturation of $F_B$ above $\phi_j$.

We have numerically verified that all trends in Fig.3.6 can be well understood based on the approximate analytic result derived for hard spheres within the NLE approach: $\beta \sigma^3 G' \propto \phi (\sigma / n_\ell (\phi, f))^{-2} \propto \phi \lambda^2$ [19]. The theory predicts the gas-like growth of $G'$ is a consequence of the (near) saturation of the localization length and coupling constant (Fig.3.8). Fig.3.9 further demonstrates all volume fraction and arm number dependences nearly collapse onto a single curve (for $f \leq 267$) as a function of $\lambda$ both above and below $\phi_j$. However, the effective slope is close to unity, substantively different from its hard sphere value of two [19]. Hence, the finite range of interparticle repulsions modifies the precise connection between elasticity and local structure.

Interestingly, since the barrier and modulus both grow roughly linearly with $\lambda$, an approximate proportionality between $G'$ and $F_B$ emerges, reminiscent of the “elastic shoving model” of thermal glass formers [20]. Hence, a direct and deep connection
between the barrier, which controls long time relaxation, and the glassy modulus, which controls short time elasticity, is predicted.

3.7 Summary and Discussion

In this chapter, we have presented the first theoretical study of the glassy behavior of dense fluids of many arm star polymers that addresses in a unified manner real space structure, elasticity, and relaxation via activated barrier hopping. A “thermal vestige” \[8\] of jamming is identified structurally which has massive viscoelastic consequences. Below the soft jamming crossover, the shear modulus follows a \(f\)-dependent power law concentration scaling, relaxation is non-Arrhenius, and fragility increases logarithmically with arm number. An exceptionally wide range of fragilities are predicted based on activated hopping as the dominant relaxation mechanism. It is relevant to note that a recent application of ideal MCT to fluids that interact via a tunably soft finite range harmonic repulsion (model microgel) find MCT qualitatively fails to predict the large change of fragility seen in simulations \[6\]. This reinforces a conclusion of recent theoretical \[19,21,22\], simulation \[23,24\], and experimental \[25\] work on hard spheres that activated hopping is very important at experimentally accessible high volume fractions. Above the crossover volume fraction \(\phi_c\), the shear modulus is predicted to weakly increase in a linear manner, while the relaxation time almost saturates.

One caveat involves the role of chain entanglements between arms on two interpenetrating stars at very high volume fractions \[11,15\] which is not accounted for by the present (or any other) theory. We believe this explicitly polymeric effect is not an important limitation for the highly localized physics that determines the glassy elastic
modulus. However, the slow relaxation process will be influenced, and our predicted saturation of the hopping time beyond $\phi$, likely does not occur if the star arm length exceeds the entanglement threshold. On the other hand, direct simulations of the model defined by Eq.(3.1) can test our results at ultra-high volume fractions. Moreover, it would be interesting to perform new experiments with stars of arm length below the entanglement threshold. Finally, we emphasize the generality of our NLE approach which can be employed to study other soft repulsive or attractive colloids, and to explore the role of particle softness on dynamic heterogeneity [22] and nonlinear rheology [26].

3.8 References

[5] Although the computationally more intensive Rogers-Young closure is quantitatively more accurate for many arm stars [1], we employ the HNC closure for numerical convenience and because it allows comparison with our ongoing studies (and those of others [6,7]) of model microgel suspensions based on harmonic repulsive potentials which employ this closure. As discussed in the text, and elsewhere [7], the HNC closure is reliable for the questions addressed.


3.9 Figures

Fig. 3. 1

Radial distribution function for f=128 stars at several volume fractions. Inset: Primary cage peak (upper black curve) and inner peak (lower red curve) heights as a function of volume fraction.
Fig. 3. 2

Comparison of NMCT ideal glass boundary (green) with a simulation iso-diffusivity curve (black; $D=0.017$) and full ideal MCT calculation (red) [16]. NLE theory kinetic glass boundaries for two vitrification criteria are also shown (blue: $\tau_{\text{hop}} / \tau_s = 10^4$; magenta: $\tau_{\text{hop}} / \tau_s = 10^6$). Inset: dynamic free energy for $f=128$ stars at a volume fraction just below the ideal NMCT crossover (black) and a high value where the barrier is $8 \ k_B T$ (red).
Fig. 3. 3

Dimensionless dynamic barrier height is shown as a function of volume fraction for (from bottom to top): f= 56, 64, 96, 128, 200, 267.
Fig. 3. 4

Dimensionless mean barrier hopping time is shown as a function of volume fraction for various arm numbers.
Fig. 3. 5

Fragility plot of the mean hopping time versus normalized volume fraction for a kinetic glass criterion of $\frac{\tau_{\text{hop}}}{\tau_s} = 10^4$ and arm numbers (from bottom to top): hard sphere, 1000, 500, 350, 267, 200, 150. Inset: fragility as a logarithmic function of arm number for two kinetic vitrification criteria: $\frac{\tau_{\text{hop}}}{\tau_s} = 10^4$, $\frac{\tau_{\text{hop}}}{\tau_s} = 10^9$. 
Fig. 3. 6

Dimensionless shear modulus, $G^* \equiv \beta \sigma^3 G'$, as a function of volume fraction for various star arm numbers including the hard sphere limit (black curve). Open squares are shifted [27] experimental data [7] for f=267.
Fig. 3. 7

Dynamic barrier height is shown as a function of coupling constant for $f=128$, 200, 267. HS calculation is also shown for comparison.
Fig. 3. 8

Coupling constant is shown as a function of volume fraction for $f=128, 200, 267$. 
Fig. 3. 9

$G^*/\phi$ is shown as a function of the coupling constant. The hard sphere (black squares) calculation is also shown for comparison.
CHAPTER 4

GLASSY DYNAMICS AND MECHANICAL RESPONSE IN DENSE FLUIDS OF HERTZIAN SPHERES

4.1 Introduction

This chapter presents applications of the methodology developed in Chapter 2 to dense suspensions of microgels modeled as repulsive Hertzian spheres at the center of mass level. Microgels are intramolecular crosslinked polymeric networks swollen by solvent with diameters that span the range from ~10 nm to a micron or larger. They are largely impenetrable, and have been widely studied due to their importance as advanced functional materials [1]. Microgel single particle softness or elasticity is highly variable via manipulation of solvent quality and crosslink density.

Recent computer simulation studies of the quiescent dynamics and elasticity of the Hertzian contact and closely related (so-called parabolic potential $V(r) = \varepsilon (1 - (r / \sigma))^2, r \leq \sigma$) finite range soft repulsion models have observed some of the six features discussed in the introduction of Chapter 2 [1-3]. An interesting two-branch universality of the temperature and concentration dependences of the mean alpha relaxation time has been uncovered [3]. More generally, recent theoretical and simulation studies have also discovered a rich equilibrium phase behavior, including re-entrant phase transitions at ultra-high volume fractions due to subtle competition of energetic and entropic factors associated with soft particle overlap [4].

The remainder of this chapter is structured as follows. Section 4.2 discusses interaction potential, equilibrium pair correlations and “soft jamming” crossover. Naïve
MCT calculations of the ideal glass transition are also performed of the dynamic crossover “phase diagram”. The key features of the dynamic free energy that determines activated relaxation are studied in section 4.3 as a function of volume fraction and particle softness. The influence of the latter two variables on the mean relaxation time is established in section 4.4, and the question of a master curve construction explored. Section 4.5 presents the kinetic arrest diagram, and analyzes how dynamic fragility depends on particle softness. Calculations of the quiescent shear modulus and localization length as a function of volume fraction and particle stiffness or repulsion strength are presented in section 4.6. Remarkable connections between the shear modulus and activated relaxation process are established in section 4.7, including a microscopic basis for the so-called elastic “shoving model” [5] of highly viscous liquid relaxation, and the recent experimental observation of a direct relation between elasticity and kinetic glass formation in microgel suspensions [6]. Section 4.8 studies the yield stress and strain, shear thinning of the viscosity and relaxation time, and stress-strain rate flow curves. The chapter concludes in section 4.9 with a summary and discussion. Section 4.10 and 4.11 present the references and figures, respectively.

4.2 Model, Equilibrium Structure and Dynamic Crossover

4.2.1 Hertzian model

The classic soft repulsive Herztian pair potential is:

\[
\beta V(r) = \begin{cases} 
\frac{4}{15} E (1 - r / \sigma)^{5/2}, & r \leq \sigma \\
0, & r > \sigma 
\end{cases}
\]

(4.1)
where \( r \) is interparticle separation, \( \sigma \) the particle diameter, \( k_B T = \beta^{-1} \) the thermal energy, and \( 4E/15 \) is an inverse dimensionless temperature which quantifies repulsion softness or particle stiffness [7]. For microgels, \( E^* = E k_B T \sigma^3 \) is a tunable single particle modulus controlled largely by internal polymer crosslink density. Eq.(4.1) describes as single contact, and is believed to be realistic within a pair decomposable potential energy description when particle deformation is of order 10% or less [1]. The hard sphere potential is smoothly recovered as \( E \to \infty \). Fluid volume fraction is \( \phi = \rho \pi \sigma^3 / 6 \), where \( \rho \) is the particle number density. This pair potential is an oversimplification for crosslinked polymer microgels, and cannot be expected to be reliable at very high volume fraction where Eq.(4.1) allows significant sphere overlaps, in contrast to real systems which deform, facet, and osmotically deswell [1].

4.2.2 Equilibrium structure and soft jamming crossover

Fig.4.1 shows representative results for the pair correlation function as a function of volume fraction at fixed \( E \). With increasing concentration, the primary cage peak (\( r \sim \sigma \)) initially increases and very weakly shifts to smaller separations. However, beyond a characteristic volume fraction of \( \phi \equiv 0.8 - 0.9 \equiv \phi_J \) (generally increases as \( E \) decreases), the primary ordering peak decreases with concentration, and the second peak splits. We refer to \( \phi_J \) as a soft jamming threshold in analogy with a recent experimental (simulation) study of microgel (soft repulsive) fluids [8] which found the primary peak amplitude, \( g_1 \), goes through a maximum, an effect called the “thermal vestige of jamming” [9]. We also note the OZ-HNC theory predicts a split second peak in \( g(r) \) at high volume fractions, as often seen in glasses and microgel experiments [8].
The inset of Fig.4.1 presents the corresponding static structure factors, the most obvious features of which monotonically vary with volume fraction. Hence, these soft particles present an interesting situation where the dependence on volume fraction of the two classic measures of short range order, the cage peak in g(r) and S(k), do not vary the same with concentration at high volume fractions. This reflects subtle entropic and energetic effects when particles significantly overlap.

Fig.4.2 plots the cage peak maximum of g(r), $g_1$, as a function of volume fraction for a wide range of E values spanning the range of ultra-soft to near hard sphere. Motivated by the work in [8], a differential volume fraction variable is employed: $\Delta \phi = \phi - \phi_c$, where $\phi_c$ is the hard sphere RCP value. For internal consistency, we employ our best numerical estimate of $\phi_c$ based on the HNC integral equation theory. The precise value is not analytically known, and we have extracted it (see inset) by analyzing the dimensionless isothermal compressibility, $S(0) \equiv S_0$. Numerically converged results of the OZ-HNC integral equation are obtained up to $\phi = 0.75$, the quantity $S_0^\Delta$ is then plotted versus $\phi$ in the highest volume fraction regime of (from 0.6 to 0.75) corresponding to an order of magnitude variation of $S_0$. The exponent is varied to best linearize the plot resulting in $\Delta \sim 3/4$. Modest linear extrapolation to the incompressible limit then yields an apparent jammed state at $\phi_j = 0.78$. This value is well above the correct RCP result of $\sim 0.64$, which is not surprising given the known fact that RCP for the PY closure equals unity and hence incorrect [10].

Each curve for different E values in Fig.4.2 exhibits a maximum, except those very close to hard spheres. For the latter, reliable numerical results beyond $\phi \sim 0.75$ could
not be obtained due to convergence problems of the OZ-HNC integral equation. Note that $g_1$ intensifies and shifts to higher volume fractions as particles stiffen. This feature is relevant to the rich variation of the dynamics with particle stiffness discussed later.

From Fig.4.2 one sees that $\phi_j$ is a weakly non-monotonic function of $E$ (see also Fig.4.3). However, this is a subtle point which we view as a minor quantitative effect that occurs under ultra-soft repulsion conditions where $g_1(\phi)$ is a low intensity, broad function. Hence, we only wish to emphasize that the soft jamming crossover varies very slowly as $E$ becomes small. Note that although literal “contacts” in the sense defined for hard spheres are not present, integration under the first peak of $g(r)$ yields the classic measure of number of nearest neighbors. Interestingly, we find this number is almost universal at $\phi_j$ and equal to ~12-13, which is physically sensible.

All the above structural trends appear to agree well with recent simulations [8,11,12] and experiments [8], which provides support for the zeroth order reliability of the OZ-HNC static correlations as input to dynamical theories.

**4.2.3 Naïve MCT kinetic arrest map**

Fig.4.3 shows the NMCT kinetic arrest or dynamic crossover map; the soft jamming structural crossover discussed in section 4.2.2 is also indicated. As $E \to \infty$ the hard sphere ideal glass transition of NMCT (based on HNC input) at $\phi_{\text{MCT}} = 0.445$ is recovered. No ideal localization transition is predicted if the particles are sufficiently soft, $E < 600$. A physical interpretation is that at low temperatures (high $E$, stiff particles) the dynamic caging constraints are strong and upon increasing volume fraction the system reaches the glass transition before the soft jamming crossover beyond which caging constraints weaken due to local structural disordering. However, for sufficiently
high temperatures (soft particles), the system reaches the soft jamming threshold before caging constraints become strong enough to result in localization. Interestingly, the functional form of the NMCT ideal nonergodicity boundary is well described as a parabolic critical power law: \( T_c \propto E^{-1} \propto (\phi_{MCT} - \phi)^2 \), in agreement with the recent full MCT [11] and simulation [3,11] studies.

The full ideal MCT with OZ-HNC input has very recently been applied to the Herztian contact model up to ultra-high volume fractions [13]. The effective temperature \( \sim 1/E \) of ideal kinetic arrest was found to be a non-monotonic function of volume fraction with a maximum near \( \phi \sim 1 \). This behavior was termed “anomalous”, and agrees with empirical fits of MCT formulas to the relaxation time simulation data in the crossover regime. In the inset of Fig.4.3 we present the analogous simple NMCT result. Indeed, NMCT also predicts re-entrance at extremely high volume fractions, also at \( \phi \sim 1 \), in excellent accord with the full MCT calculations [11]. The underlying physics relates to the overlapping of soft particles at very high volume fractions and the corresponding local disordering of the cage (Figs.4.1 and 4.2).

### 4.2.4 Dynamic free energy profile

An example \( F_{\text{eff}}(r) \) is shown in Fig.4.4 for a fixed value of \( E \) at three volume fractions: just below the NMCT crossover, and when the barrier is \( \sim 5 \, k_B T \) and \( 10 \, k_B T \). The hard sphere result at a volume fraction adjusted so that the barrier is \( 10 \, k_B T \) is also shown; the agreement with the analogous soft particle result is excellent. This provides empirical support that the prior analytic ultra-local analysis of NLE theory for hard spheres [14,15], which predicts when barriers are high all features of the dynamic free
energy are controlled, to leading order, by a single “coupling constant” defined by local structure in g(r), remains relevant for soft repulsive particles.

4.3 Effect of Particle Softness on Dynamic Free Energy

4.3.1 Localization and barrier lengths

Two key length scales of the dynamic free energy are the (transient) localization length (r_{loc}) and barrier location (r_B). Fig.4.5 shows results as a function of volume fraction for three values of repulsion strength (E) and the hard sphere limit. The values of E chosen are typical of estimates of single microgel rigidity of some experimental systems based on crosslinked polymer network elasticity theory \[1\]. The qualitative dependence of the two length scales on volume fraction is similar for all four systems. For soft particles, the barrier location exhibits a 2-step like growth with concentration, and then goes through a shallow maximum at a volume fraction a little beyond unity. At fixed volume fraction, r_B grows monotonically with particle stiffness (E). The corresponding localization lengths initially decrease strongly with φ, but then tend to saturate, or even very weakly increase, at ultra-high concentrations. The weak non-monotonic behavior correlates with the non-monotonic variation of local structure and the soft jamming crossover (Figs. 4.1 and 4.2). As discussed later, the localization length is the key quantity that determines the elastic shear modulus.

4.3.2 Barrier Height

Barrier heights as a function of volume fraction over a wide range of repulsive interaction strengths are shown in Fig.4.6. As expected, the barrier height grows monotonically with E at fixed volume fraction. For all soft particle systems shown, the
barrier initially increases in a nonlinear manner with \( \phi \), and more quickly for larger \( E \), reflecting the enhanced sensitivity of local structure to volume fraction for stiffer particles or equivalently, lower temperature (Fig.4.2). As the soft jamming crossover is approached, the barrier goes through a maximum, analogous to how the intensity of the local cage peak of \( g(r) \) changes. This connection is a natural one based on the ultra-local analytic analysis and Eq.(2.11). An interesting consequence of the non-monotonic behavior is that if particles are sufficiently soft, then a well-defined activated dynamical regime will not occur since the maximum barrier height never significantly exceeds thermal energy. For hard sphere limit, the barrier grows monotonically and diverges at RCP limit as:

\[
F_B \propto g_{HS}^2(\sigma) \propto \left( \phi_{RCP} - \phi \right)^{-2}
\]

(4.2)
corresponding to a double essential singularity of the mean hopping time [14,15].

4.3.3 Scaling of barrier with the coupling constant

The barrier height calculations are suggestive that the ultra-local analysis result for hard core particles that \( \lambda = \phi s_i^2 \) controls the barrier height may be accurate for Herztian repulsive particles. However, this does not mean Eq.(2.11) literally applies since the linear connection between the barrier and coupling constant emerges as a consequence of the specific hard sphere high wavevector behavior of the dynamical vertex [14]. We examine this issue in Fig.4.7, where the barrier heights for three soft particles are plotted versus the coupling constant. Over a significant range of \( F_B \), the soft particle results do roughly collapse for volume fractions below the soft jamming threshold. However, for soft particles with intermediate values of \( E \) (where results for \( \lambda > 20-30 \) cannot be attained given the soft jamming structural behavior), the slope is not
unity as in Eq.(2.11) for hard spheres (and also many arm stars [16]), but rather roughly \( F_B \propto \lambda^2 \). On the other hand, Fig.4.7 also shows that for the highest E Hertzian system, a crossover from \( F_B \propto \lambda^2 \) scaling to something approaching the linear scaling of hard spheres occurs at very large barriers (highest volume fractions). This change for stiff particles must occur given the Herztian contact model approaches the hard sphere potential as E gets very large.

The origin of the differences in the effective scaling of the barrier with the coupling constant for intermediate stiffness and very stiff (hard sphere like) systems must be related to the wavevector dependence of the dynamical vertex. Fig.4.8 presents representative vertex calculations for two soft particles and the hard sphere, where volume fraction for each system is chosen so they all have the same barrier height of 10 \( k_B T \). The hard sphere result (bottom panel) shows the expected saturation of the amplitude at large k. But, for soft repulsive particles the vertex acquires a maximum at a finite wavevector, and then decays to zero at large k. The maximum shifts to smaller k as the particles become less repulsive (lower E), even though the volume fractions have been adjusted to main the same \( F_B \). However, the maximum amplitude is not significantly dependent on E over the range studied.

We conclude that the qualitative difference of the large wavevector dependence of the dynamical vertex (very local force correlations) for soft particles of intermediate stiffness (compared to very stiff hard sphere like cases) is the origin of the different scaling of the barrier with coupling constant. However, the ability of the coupling constant to (roughly) collapse the barrier height calculations for soft particles of different intermediate levels of stiffness is maintained. This rather remarkable, but empirically-
deduced, result can perhaps be rationalized based on the near constancy of the maximum vertex amplitude.

4.4 Mean Alpha Relaxation Time

Using Eq.(2.8) the mean barrier hopping time is computed as a function of particle softness and volume fraction. All times are expressed in terms of, \( \tau_s = \sigma^2 / (k_B T) = \sigma^2 / D_s \), where \( D_s \) is the measurable “short time” diffusion constant.

4.4.1 Volume fraction and repulsion strength dependences

Fig.4.9 presents the dimensionless mean hopping times as a function of volume fraction for a wide range of particle stiffness (E). Results are shown over an exceptionally wide range of relaxation times (20 orders of magnitude) to emphasize the robust nature of the non-monotonic behavior, as expected from the barrier height calculations in Fig.4.6. In real colloidal suspensions (and often simulations too), a relaxation time range of only typically 4-6 orders of magnitude can be probed, perhaps up to \( \tau_{\text{hop}} / \tau_s \sim 10^4 - 10^6 \) which represents a practical threshold used to define kinetic vitrification. Fig.4.9 shows the relaxation times generally grow in a “non-Arrhenius” (nonexponential in \( \phi \)) manner which is stronger as E increases; such nonexponential growth has been observed in experiment [8,17]. But in all cases the dependence is weaker than the limiting hard sphere behavior. The particle stiffness (inverse temperature) of the mean relaxation time is presented in Fig.4.10, now over only a range of times typically relevant to experiments and simulations (~ five orders of magnitudes). Two qualitatively distinct behaviors are predicted: (1) asymptotic saturation at the hard sphere value as \( E \to \infty \) for the lower range of volume fractions (roughly below the hard sphere RCP), and (2) increasingly
strong growth with $E$ for the highest $\phi$ values. These trends are in qualitative accord with recent simulations [3].

We have briefly explored the possibility of interpreting the relaxation time calculations in terms of an effective hard sphere reference system. Specifically, an effective hard core diameter (or equivalently, effective volume fraction, $\phi_{\text{eff}}$) is defined by via a *dynamical mapping* criterion:

$$\tau_{\text{hop}}^{\text{HS}}(\phi_{\text{eff}}) = \tau_{\text{hop}}^{\text{soft sphere}}(\phi, E)$$ (4.3)

Using Eq.(4.3) and our hopping time calculations, we have extracted the effective volume fractions for several choices of the maximum value (kinetic glass point) of $\tau_{\text{hop}} / \tau_s$ ranging from $10^2 \rightarrow 10^7$. Results are shown in Fig.4.11 for values of the latter relevant typical colloid experiments or computer simulations, $\tau_{\text{hop}} / \tau_s = 10^2 \rightarrow 10^4$. For these cases the effective volume fractions are very well described by $(T=15/4E)$:

$$\phi_{\text{eff}}(\phi, T) \approx \phi - aT^b$$ (4.4)

where $\phi_{\text{eff}} < \phi$, $a > 0$, and $b = 0.66$.

Interestingly, our results agree rather well with the form deduced from simulations or the parabolic finite range repulsion model, and rationalized by specific physical arguments [3]. However, if the maximum value of $\tau_{\text{hop}} / \tau_s$ is the very high, e.g., $\tau_{\text{hop}} / \tau_s \rightarrow 10^7$, then we find Eq.(4.4) is again accurate but $b \sim 0.84$ (not plotted). Hence, based on our dynamical mapping the apparent exponent $b$ depends on the relaxation time range analyzed. This is perhaps not a surprising result, which may also be influenced by the accuracy of the OZ-HNC structural input which is likely not uniform as a function of volume fraction.
4.4.2 Universal collapse

Simulations of the finite range parabolic repulsion model fluid has recently discovered a collapse of the alpha relaxation time ($\tau_\alpha$) of soft repulsive spheres as a function of $T$ and $\phi$ based on two distinct scaling functions [3]. Physically-motivated (but not derived) jamming and effective hard sphere arguments which we do not repeat here suggest the form of the two master curves are:

$$\tau_\alpha \sqrt{T} \sim \exp \left\{ A |\phi - \phi|^{\mu} F \left( |\phi - \phi|^{2/\delta} / T \right) \right\}$$

(4.5)

where $A$ is a numerical constant, and $F_\pm(x)$ apply to volume fractions above/below a critical volume fraction, $\phi_0$, suggested to be the hard sphere RCP value. The exponents $\mu$ and $\delta$ were varied with best fit values of $\mu \sim 1.3$ and $\delta \sim 2.2$ obtained, which were argued to have a theoretical basis related to the specific finite range repulsive potential [3]. The crossover functions $F_\pm(x)$ are constrained by recovering the hard sphere limit and continuity at $\phi = \phi_0$: $F_- (x \to \infty) \to 1$, $F_+ (x \to \infty) \to \infty$, and $F_\pm (x \to 0) \to \phi^{\delta/2}$. All simulation data then empirically collapse onto the two distinct curves by plotting $|\phi - \phi|^{\delta} \log(\tau_\alpha \sqrt{T})$ versus $|\phi - \phi|^{2/\mu} / T$ over about 5 orders of magnitude of the ordinate. Note that in our notation, the temperature scale factor $\sqrt{T} \propto E^{1/2} / \tau_s$.

We analyze our theoretical calculations in Fig.4.9 and 4.10 in an analogous empirical manner ($T \equiv E^{-1}$) by freely floated the parameters $\phi_0$, $\mu$ and $\delta$ to achieve an optimized master plot. Our primary goal is only to check if the NLE theory is consistent with such a two master curve description based on the dominance of activated hopping dynamics. The results are shown in Fig.4.12. We note that the abscissa and ordinate values and range are quite similar (but a bit narrower) to that probed in simulation [3].
excellent collapse onto two master curves is achieved using $\mu = 1.3$, $\delta = 2.2$, and $\phi_0 = 0.78$. Remarkably, these $\delta$ and $\mu$ are identical to that deduced from simulation [27]. Moreover, the deduced value of $\phi_0 = 0.78$ agrees with our independent best estimate of RCP based on the OZ-HNC structural theory.

Now, the functional form of the lower scaling function in Fig.4.12 is very similar to that obtained in simulation [3], including saturation at large values of the abscissa. We argue this is the regime the dynamical theory should work best since the inaccurate description of jamming of the equilibrium OZ-HNC approach will have the least significance. However, the upper branch in Fig.4.12 (beyond hard sphere RCP) does not show as good a collapse, and does not appears to be a divergent form on the present scale as seen in the simulation (i.e., our results tend to “bend over”, versus the simulation which “curves up”). We do not have a deep understanding of this deviation, but suspect it is largely, or completely, due to the poor quantitative reliability of the OZ-HNC theory at very high volume fractions. This interpretation can be tested by using simulation results for the structural input in NLE theory. We also suspect that the apparent divergent form of the scaling function at ultra-high volume fractions found in the simulation is only an apparent or crossover effect, and must eventually “bend over” given the lack of a true RCP for soft particles and the finite energy cost to fully overlap particles.

Finally, we note that the full ideal MCT analysis of this system predicts very well (albeit over a tiny volume fraction range of $0.515 < \phi < 0.53$) the scaling behavior in Eq.(4.5) but based on plotting $\tau_a$, not $\log \tau_a$ as in the simulation analysis and in Fig.4.12 [11]. The latter reflects the incorrect MCT prediction of a critical power law divergence of the relaxation time, versus the correct strongly exponential (essential singularity) form.
observed in the simulation and also NLE theory. Moreover, MCT makes qualitatively incorrect predictions for the variation of dynamic fragility [11].

4.5 Kinetic Arrest Map and Dynamic Fragility

Knowledge of the mean activated relaxation time allows two additional issues of significant scientific and practical interest to be addressed: (1) the kinetic vitrification map, and (2) the dependence of a dynamic fragility on single particle stiffness.

4.5.1 Vitrification boundaries

Kinetic vitrification is defined via a maximum relaxation time criterion. Interesting questions include how it depends on the criterion adopted, and how it compares with the dynamic crossover (ideal MCT) boundary. Calculations for three experimentally-relevant criteria are shown in Fig.4.13. Modest shifts towards larger volume fractions of the kinetic vitrification volume fraction, \( \phi_v \), are predicted as the time scale for kinetic arrest grows. Hence, the threshold E (or temperature) required to clearly observe activated dynamics is significantly higher (or lower) than the MCT crossover value. However, the shape of the kinetic arrest boundaries are well described by the same parabolic form found for the NMCT analog, albeit with significantly larger apparent (empirically fit) values of \( \phi_c \). These findings are consistent with simulation [3]. Moreover, as discussed in previous contexts, they suggest a close correlation of the cage physics that enters MCT and NLE theory [18-21].

We also note that the kinetic arrest and soft jamming crossover boundaries cross when particles become soft enough (high effective temperature). This crossing, and the
lack of any deep connection between kinetic vitrification and soft jamming, is consistent with conclusions drawn from recent simulations [8].

### 4.5.2 Dynamic fragility

Given knowledge of the kinetic vitrification volume fraction (analog of \( T_g \) for thermal glass formers), one can determine how repulsion softness impacts dynamic fragility. We analyze this question below the soft jamming crossover using the results in Fig.4.9 and 4.13, and adopt a perspective analogous to the classic Angell plot employed for thermal glass formers. Specifically, fragility is defined per recent experiments as [17]:

\[
m_{\phi} \equiv \partial \left( \frac{\log(\tau_{\text{hop}} / \tau_s)}{\phi / \phi_g} \right) \bigg|_{\phi = \phi_g},
\]

where \( \phi_g \) follows from the criterion \( \tau_{\text{hop}} / \tau_s = 10^y \). In experiments [8,17,22,23] and simulations [3,22,24], a typical \( y \sim 2-5 \). A fragility plot using \( y=3 \) is shown in Fig.4.14 based on a relaxation time variation of 4 orders magnitude as is typical of colloid experiments. A wide range of dynamic fragilities is predicted. For example, \( m_{\phi} \sim 18 \) for the rather low value of \( E=6000 \) where the relaxation is effectively “Arrhenius” corresponding to “strong glass” behavior. This is qualitatively consistent with the recent experimental discovery that “soft microgels make strong glasses” [17]. With decreasing temperature, fragility monotonically grows, approaching \( m_{\phi} \sim 41 \) in the extreme fragile hard sphere limit. The growth of fragility with particle stiffness reflects the enhanced sensitivity of local structure to changes of volume fraction (Figs. 4.1 and 4.2). We also predict the dynamic fragility decreases linearly with increasing temperature (Fig.4.14 inset). Moreover, one sees that the overall trends are not very sensitive to the vitrification...
criterion although the quantitative values of $m_{\phi}$ are. Future simulation or experiments should be carried out to test these findings.

4.6 Linear Shear Modulus

Fig.4.15 presents calculations of the linear shear modulus, in units of $k_B T \sigma^{-3}$, as a function of volume fraction over a wide range of dimensionless repulsion strength, $E$, that quantifies the Hertzian repulsion. All soft particle systems display a much weaker response to volume fraction than hard spheres. The present theory quite accurately accounts for the volume fraction dependence of the glassy shear modulus of hard sphere suspensions [25,26]. Quantitatively, a dimensionless shear modulus of $\sim 10^{-10^4}$ corresponds to $\sim 40$-40,000 Pa for a $\sigma=100$ nm diameter particle at room temperature. The growth of $G'$ with volume fraction does not display any simple functional form over a wide range. Over a narrow intermediate range of volume fractions, apparent power law growth, $G' \sim \phi^n$, is present for sufficiently stiff particles, where $n \sim 7$-9. At high concentrations, the modulus decreases because of the reduction of local packing order associated with the soft jamming crossover.

We have numerically verified that Eq.(2.12) relating $G'$, $\phi$, and the localization length is well obeyed. The inset of Fig.4.16 presents some representative evidence for this statement; ones sees that over a range where the dimensionless modulus grows by a factor of $\sim 30$-40, deviations from Eq.(2.12) are a factor of $\sim 1.1$-1.5. This theoretical result agrees with combined confocal and mechanical measurements on microgel suspensions which reveal “perfect agreement” between the low frequency macroscopic
glassy shear modulus and the local “cage modulus” estimated from a relation like Eq.(2.12) [27,28].

To make qualitative contact with microgel experiments, and choose model parameters of practical relevance, we note that three samples in a recent study [29] were characterized by an average number of monomers between two crosslinks of $N_x = 140, 70$ and $28$. Adopting ideal polymer network theory [30], the corresponding dimensionless Hertzian stiffness parameters at room temperature is estimated to be: $E = 4259, 5832$ and $11718$. For these systems, the theory predicts apparent shear modulus power law exponents of $n \sim 8-9$, while experiments [29] find exponents of $n \sim 6-7$. Creep measurements on dense hard spheres with an attached microgel coating [31] also find the shear modulus grows with volume fraction far weaker than in hard sphere suspensions, and displays an apparent power law behavior with an exponent of $n \sim 5-7$.

However, in real microgel systems beyond a threshold volume fraction (analog of RCP) the particles generally deswell and facet [1], and a generic linear growth with concentration of the shear modulus emerges [1,7]. This behavior is not captured by our present approach. We believe the reason is because the soft repulsive sphere model must have limitations when particles are forced to significantly overlap. Future computer simulations that compute $G'$ of the Hertzian model in the equilibrated (glassy) fluid state can test our results, especially the non-monotonic behavior in Fig.4.15.

The main frame of Fig.4.16 tests the analytic prediction that the dimensionless shear modulus divided by the volume fraction scales as the square of the “coupling constant”, $\lambda \equiv \phi g_1^2$. Recall the latter quantifies the magnitude of caging constraints under high barrier conditions, where $g_1$ is the primary peak height of the pair correlation
function [14]. It appears this connection is reasonably well obeyed, in terms of both the quadratic power law scaling and as a tool to collapse the modulus data for particles of different repulsion strengths, at least for the intermediate E values studied in Fig.4.16.

4.7 Connections between the Elastic Modulus, Alpha Relaxation and Kinetic Arrest

Puzzling connections between short length and time dynamical or elastic properties, and the slow and longer length scale alpha relaxation process, have repeatedly been found experimentally for diverse highly viscous liquids [5]. For example, the phenomenological shoving model [5] asserts that the activation barrier and temperature-dependent glassy elastic shear modulus are linearly correlated [32]:

\[ F_b(T) = G'(T)V_c \]  

(4.7)

where \( V_c \) is a material-specific, but weakly thermodynamic state dependent, volume. There is no first principles theory for this quantity, but fitting of Eq.(4.7) to experiments on thermal liquids typically yields a value much smaller than the elementary atomic or molecular volume (\( V_m \)); for example, for orthoterphephenyl (OTP), \( V_c \sim V_m /30 \) based on modeling OTP as a sphere of diameter 0.7 nm [39]. Eq.(4.7) implies local elastic physics controls the alpha relaxation process and hence dynamic fragility. Remarkably, such a relation also appears to be valid for dense suspensions of soft repulsive microgels [17], where \( V_c/V_m \) depends on particle stiffness. In this section we test whether NLE theory predicts a connection between the shear modulus, alpha relaxation time, and kinetic vitrification volume fraction for dense fluids of soft repulsive spheres.

4.7.1 Barrier-modulus correlation
Fig.4.17 cross plots the theoretical dimensionless barrier computed in section 4.3.2 versus the dimensionless fluid modulus per particle. A reasonably good, but clearly only approximate, linear relation is predicted for soft particles of significantly different repulsion strengths:

\[ F_B \propto G' \sigma^3 \phi^{-1} \propto k_B T \left( \frac{\sigma}{r_{LOC}} \right)^2 \]  
(4.8)

The inset shows linearity holds quite well for different repulsion strengths up to barrier heights of \(~10\) \(k_B T\); significantly, the latter range is relevant to the recent microgel experiments where barriers were deduced to be \(~7\) \(k_B T\) or smaller for intermediate and soft particles [17]. Quantitatively, the inset of Fig.4.17 implies: \(F_B = G'(\pi \sigma^3/6)b\), where \(b \approx 0.02 - 0.08\) for the three soft repulsive particles and \(\phi \sim 0.5-1\). Hence, in the language of the shoving model the theoretical \(V_c/V_m\) ratio lies in the range of 2-8\%, reasonable values in comparison with the microgel experiments [17]. Eq.(4.8) is understandable within the context of our approach from the demonstration in section IIIB that \(F_B \propto \lambda^2\) and the results in Fig.4.16. A corollary is the proportionality of the barrier with the inverse transient localization length.

The above behavior for thermal soft repulsive particles stands in contrast with hard spheres (as shown in Fig.4.17) where numerical studies and analytic analysis have established [33]: \((r_L/\sigma)^{-1} \propto F_B \propto \sqrt{\beta \sigma^3 G'} \phi \propto \lambda\). This difference is no doubt related to the singular nature of the hard core repulsion and associated discontinuity of the radial distribution function at contact which results in a qualitatively different high wavevector scaling of the dynamical vertex (see Fig.4.8). Interestingly, our recent NLE study of many arm star colloids found [16]: \(F_B \propto G' \phi \propto \lambda\). That is, the barrier and shear modulus
are proportional, but both follow a linear, not quadratic, scaling with coupling constant. Hence, we conclude that the behavior of spherical particles which interact via the finite range Hertzian repulsion, Yukawa plus logarithmic repulsion for stars, and hard core repulsion can be all different with regards to the absolute and relative dependence of the activation barrier and shear modulus on coupling constant.

4.7.2 Modulus-vitrification correlation

If the activation barrier scales linearly with \( G' \), then it is natural to expect the kinetically-defined vitrification volume fraction will also be linearly related to \( \phi \). Indeed, such a correlation has been empirically noted, in a model independent manner, in microgel experiments [6]. In Fig.4.18, we cross plot our kinetic volume fraction (\( \phi_g \)) results versus the dimensionless shear modulus at \( \phi_g \). A good linear relation is obtained. The inset shows the analogous plot but based on the single particle repulsive potential strength parameter, \( E \), but now in a log-linear format. The latter is adopted to display the trend over a wide range of single particle stiffness parameters. If the results are re-plotted in a linear-linear fashion, then over the modest range of modulus values examined in the main frame the plot is highly nonlinear (not shown). This difference is not unexpected since the macroscopic modulus, \( G' \), depends on fluid volume fraction in contrast to the 2-particle pair potential property, \( E \).

4.8 Nonlinear Rheology

Many experiments on high volume fraction microgel suspensions or pastes find solid-like behavior under quiescent conditions [1]. However, measurements of the frequency-dependent loss modulus sometimes reveal a rise at the lowest frequencies
probed, suggesting the presence of an ultra-slow structural relaxation process at frequencies (times) too low (too large) to measure with typical rheometers. Practical engineering motivations have also led to many nonlinear rheological measurements being performed on microgel suspensions [1,34-36]. Key questions are yielding (stress and strain), shear thinning of the viscosity, and the flow curve. In this section we study such questions under the assumption that homogeneous flow is achieved. We again emphasize our results are based on the soft sphere model which must have limitations with regards to microgel pastes at very high (jammed) volume fractions due to osmotic deswelling, facet formation, and other effects [1]. Hence, our theoretical results are most unambiguously tested via comparison with Brownian dynamics simulations of Hertzian spheres under large deformations.

4.8.1 Stress dependence of barrier and absolute yielding

Fig.4.19(A) presents representative calculations of the effect of stress on the dynamical barrier height. A doubly normalized format is adopted to emphasize the generic behavior for different repulsion strengths and volume fractions. The barrier decreases with stress in a nonlinear manner, in contrast to the simple Eyring model linear decrease [37]. Nondimensionalization of stress by its absolute yield value leads to a good, but not perfect, collapse. The corresponding absolute yield stresses are shown in Fig.4.19(B), in both linear (main frame) and logarithmic (inset) formats. As true of the quiescent shear modulus, the functional dependence on volume fraction is not simple, though narrow regimes of apparent power law variation at intermediate volume fractions can be seen. Stress also increases the localization length of the dynamic free energy, and
hence decreases the shear modulus (not shown), as discussed previously for hard and sticky spheres [38,39].

Fig.4.20 presents calculations of the absolute and mixed yield strains (see Eq.(2.17) and Eq.(2.18)) as a function of volume fraction for the same systems studied in Fig.4.19. We note that the precise numerical value of the yield strain is sensitive to the numerical prefactor “a” in Eq.(2.14); the yield strain calculations in Fig.4.20 (based on a= π/6) change in a linear manner with this parameter. The computed yield strains display a relatively weak dependence on volume fraction and repulsion strength compared to the many orders of magnitude variation in the yield stress and modulus. This reflects their similar dependences on volume fraction. The absolute yield strains initially grow rapidly (low barrier regime), and then nearly saturate or weakly decrease at very high concentrations. The mixed yield strain analogs behave similarly, but weakly increase at high volume fractions. The differences between these two yield strains reflects the fact that the shear modulus at the absolute yield stress is ~2-3 times smaller than its quiescent value (a “strain softening” effect, not shown). We have also computed a “perturbative” yield strain, defined as when the quiescent shear modulus is reduced by 10%; we find it is ~ 5-9 % for all volume fractions and E values studied in Fig.4.20 (not shown).

With regards to microgel experiments, yield strains (often defined as our “mixed” quantity) are typically 5-10%, and weakly dependent on volume fraction and particle stiffness [1,28,29]. The elastic-solid-like relation in Eq.(2.16), \( \tau_y = G^* \gamma_y \), that our calculations are based on appears to be well obeyed experimentally [1]. For the microgel-like system studied via creep and creep recovery measurements [31], the yield strain is a
non-monotonic function of volume fraction: ~10% at an effective $\phi \sim 0.58$, then passes through a shallow minimum at $\phi \sim 0.62$, followed by a gentle rise to ~18% at $\phi \sim 1.05$. Quantitative comparison of our calculations with these experiments is difficult due to both the complexities of microgels not captured by the soft sphere model and the difficulty of precisely knowing the volume fraction.

4.8.2 Shear Thinning and Flow Curves

We now apply Eqs. (2.19) and (2.20) to study the long time dynamical behavior under constant stress or steady shear conditions. Fig.4.21 presents representative calculations of the mean barrier hopping time for three repulsion strengths, and the corresponding hard sphere behavior, as a function of dimensionless stress; the inset shows the dimensionless hopping times. The quiescent relaxation times vary over 10 orders of magnitude, and all exhibit stress-thinning commencing at a system specific stress. The main frame nondimensionalizes the hopping time by its quiescent value in order to probe whether the functional form of the stress-thinning is generic. A reduction of the relaxation time by an order of magnitude requires a dimensionless stress of ~3–5. To zeroth order, quite good collapse of the different curves is obtained, although the curves do “splay apart” at high stresses, as expected.

Calculations of the stress versus shear rate (both nondimensionalized) flow curves are shown in Fig.4.22. With increasing single particle stiffness (E) and/or volume fraction, the flow curves are shifted to lower shear rates. For intermediate reduced shear rates, a power law like regime emerges, $\tau \propto (\dot{\gamma} \tau_s)^\nu$, the breadth of which grows with increasing volume fraction or particle stiffness. The apparent exponent, $\nu$, decreases with increasing volume fraction and/or repulsion strength, varying over the range ~0.08 to 0.38 for the
first 7 curves (from left to right) in Fig.4.22. Since experiments or simulations often only probe a limited shear rate range, such apparent power laws could dominate the observation window. Also, recall our calculations do not take into account the “bare” or short time viscoelastic response. This would lead to an upturn of the flow curves at high shear rates, which may often be the range observed experimentally [1].

The calculations in Fig.4.22 for fixed $E =11718$ are re-plotted in Fig.4.23 in a manner motivated by recent experiments that have searched for universal behavior [1, 28,29]. In the experiments the stress is reduced by an absolute yield value, and shear rate by a time scale formed from the bare relaxation process (“beta” process associated with the onset of transient localization) and the locally determined glassy shear modulus [29], $\dot{\gamma} \eta_s /G'$, where $\eta_s$ is the solvent viscosity. Values of $\dot{\gamma} \eta_s /G'$ have been reported to span the wide range of $10^{-11}$ to 100. As a reasonable surrogate of this dimensionless shear rate we employ: $\dot{\gamma} \tau / G' \equiv \dot{\gamma} \tau / G^*$. Then, based on a typical value of $\tau_s /\tau_0 \sim 10$, we estimate $\dot{\gamma} \tau_s / G^* \sim 100 \dot{\gamma} \eta_s /G'$.  

Fig.4.23 demonstrates that there is a near collapse of the flow curves in this representation under high (beyond soft jamming) volume fraction conditions. Moreover, at intermediate reduced shear rates an apparent power law applies over many orders of magnitude with a very small slope. We note that the experimental flow curves [1] for “jammed” microgel pastes can sometimes be characterized as an apparent power law over roughly 4 orders of magnitude of (low) shear rates with $\nu \sim 0.04$-0.08. Such experimental behavior is more often described [1] as indicating a stress plateau, or “yield stress”, of the empirical Hershel-Buckley form: $\tau = \tau_s + a \dot{\gamma}^m$. The latter form has been observed in jammed microgel pastes, with an exponent $m \sim 0.5$, and a universal collapse of [1,29]:
\[
\frac{\tau}{\tau_s} = 1 + K \left( \frac{\eta_s \dot{\gamma}}{G} \right)^{1/2}
\] (4.9)

We believe the physics underlying the power law in shear rate response in Eq.(4.9) does not reflect the alpha relaxation process (which the apparent power law in Fig.4.23 does), but rather a smaller length scale process likely related to elasto-hydrodynamic physics [1,36] for deformable particles that is absent in our theoretical model. We suspect our apparent power law prediction with a tiny exponent is more relevant to the small deviations of experimental flow curves from a flat response at low shear rates, reflecting the existence of a very slow alpha relaxation.

The theoretical flow curves for different repulsion strengths at high volume fractions also do not collapse in the representation of Fig.4.23 (not shown), in contrast to experiment [1,35]. The origin of this disagreement is unclear, but could be a consequence of real world complexities of microgel particles, our neglect of all dynamical processes except the slowest alpha relaxation, inaccuracies of the OZ-HNC input to the dynamical theory at very high volume fractions, and/or nonlocal mechanical effects not present in the NLE theory which is based on single particle hopping.

Finally, Fig.4.24 presents the shear viscosity normalized by its quiescent value as a function of the dimensionless Peclet number \( Pe \equiv \frac{\dot{\gamma} \tau_{\text{hop}}(\tau = 0)}{G} \) for a fixed particle repulsion strength and six volume fractions. At the higher volume fractions beyond the soft jamming crossover, a good collapse occurs. In all cases, shear thinning begins at remarkably small values of \( Pe \approx 0.001-0.01 \ll 1 \), as also predicted by NLE theory for polymer glasses [27]. This behavior reflects the physical idea that flow under strong shear proceeds via stress-assisted activated barrier hopping, not a literal complete destruction of
the barrier. Power law thinning of the viscosity over many orders of magnitude is generically predicted but with an apparent exponent smaller than unity, roughly $\eta \propto \dot{\gamma}^{-0.8}$. Interestingly, this apparent exponent is very similar to the predictions of NLE theory [13,40], and the corresponding single particle relaxation experimental observations [41], for hard sphere colloid suspensions.

4.9 Summary and Discussion

In this chapter, we have presented the first microscopic theoretical study of activated glassy dynamics in dense fluids of finite range soft repulsive particles. Our results provide a physical basis for several of the striking characteristic phenomena described in the Introduction. The alpha relaxation time in the activated hopping regime is a rich function of volume fraction and temperature, including exhibiting a maximum value at ultra-high volume fraction due to a soft jamming crossover that signals local packing disorder due to particle overlap. A kinetic arrest diagram is constructed, and its qualitative features agree with the dynamic crossover (MCT) analog. The isothermal dynamic fragility varies over a wide range, and soft particles are predicted to behave as strong glasses. The highly variable dependences of the relaxation time on temperature and volume fraction are approximately collapsed onto two distinct master curves.

The present work serves as a starting point for the development of a predictive theory of multiple phenomena in real microgel suspensions such as the linear variation of the shear modulus with volume fraction above RCP, distinctive nonlinear rheology, and dynamic heterogeneity effects where real world complications, such as osmotic deswelling and faceting, are important. The present work also motivates further
generalization of NLE theory to treat block copolymer micelles and the role of attractive forces for soft colloids.

We have applied NLE theory to study how particle softness influences the elastic shear modulus, the connections between the modulus (a short time property) and activated relaxation (a long time property), and the nonlinear rheological effects of stress-induced yielding, shear thinning of the relaxation time and viscosity, and stress versus shear rate flow curves of the repulsive Hertzian contact model of soft sphere fluids. Below the soft jamming threshold, the shear modulus roughly follows a power law dependence on volume fraction over a narrow interval for stiff enough particles with an apparent exponent that grows with repulsion strength. The shear modulus varies inversely with the transient localization length under all conditions studied. For the barrier and alpha relaxation time, to a first approximation these local properties are controlled by a single coupling constant determined by local fluid structure which quantifies the effective mean square force on a tagged particle.

In contrast to the behavior of hard spheres, the NLE theory for Hertzian spheres predicts an approximately linear relation between the elastic modulus and activation barrier. This suggests a microscopic foundation for the often observed, in both thermal liquids [5] and soft microgel suspensions [17], connections between a (relatively) short time/distance property and the long time/length scale relaxation process. Moreover, the predicted proportionality is qualitatively of the elastic shoving model form [5]. A consequence of this connection is a linear relation between the kinetic volume fraction and shear modulus, consistent with a recent experiment on microgel suspensions [6].
Yielding, shear and stress thinning of the alpha relaxation time and viscosity, and flow curves were studied as a function of volume fraction and particle stiffness. Yield strains were found to be relatively weakly dependent on volume fraction and single particle stiffness for parameters relevant to typical microgel suspensions. Shear thinning is predicted to commence at Peclet numbers far less than unity, a signature of relaxation via stress-assisted activated barrier hopping. Power law thinning of the viscosity over many orders of magnitude of shear rate is generically predicted but with an apparent exponent smaller than unity. Approaching the soft jamming threshold, a nearly universal master flow curve can be constructed at fixed repulsion strength which exhibits a power law form over many intermediate orders of magnitude of reduced shear rate. The breadth and apparent exponent in this regime systematically increases and decreases, respectively, as repulsion strength and/or volume fraction grows. Some of the theoretical results are consistent with microgel experiments, some are not. To achieve a better understanding in the absence of real world complications, we suggest new computer simulations be performed for the repulsive Hertzian spheres under strong flow conditions.

4.10 References


Fig. 4. 1

Radial distribution functions for $E = 11718$ at volume fractions (bottom to top): 0.3, 0.5, 0.7, 0.9 and 1.1. Inset: Structure factor for $E = 11718$ at volume fractions 0.3, 0.5, 0.7, 0.9 and 1.1 (first peak position from left to right).
Fig. 4.2

Cage peak amplitude, $g_1$, versus differential volume fraction $\phi - \phi_c$ for (bottom to top): $E = 100$ (squares), 1000 (circles), 5832 (up triangles), 11718 (down triangles), $10^5$ (diamonds), $10^6$ (left triangles), $10^7$ (stars). Inset: Zero wavevector value of the structure factor plotted as $S_0^{0.75}$ versus volume fraction; the linearly extrapolated value indicates the RCP state based on the HNC closure.
Fig. 4. 3

NMCT ideal glass transition boundary (solid squares) and soft jamming boundary (solid star) in the format of inverse dimensionless repulsion strength (reduced temperature) versus volume fraction. The curve through the NMCT points is a parabolic critical power law fit. Inset: Analogous NMCT ideal glass transition boundary extended to very high volume fractions where re-entrant behavior is predicted.
Fig. 4. 4

Dynamic free energy as a function of particle displacement for $E=11718$ at volume fractions (from top to bottom) just below the NMCT crossover and when the barrier is $\approx 5\ k_B T$ and $10\ k_B T$. The hard sphere result is the dashed (black) curve for a $10\ k_B T$ barrier.
Fig. 4. 5

Localization lengths (filled symbols) and barrier locations (open symbols) as a function of volume fraction for three repulsion strengths: $E=4259$ (black squares), 5832 (red circles) and 11718 (green up triangles). Hard sphere results are also shown: localization length (solid black) and barrier location (dashed red).
Fig. 4. 6

Dynamic free energy barrier height (in units of the thermal energy) as a function of volume fraction for various repulsion strengths (from top to bottom): hard sphere, \( E=30000, 20000, 10000, 8000, 5000, \) and 3000.
Fig. 4. 7

Dynamic barrier as a function of the dimensionless coupling constant for three values of $E$ of 4259 (red, open circles), 5832 (green, open triangles) and 11718 (blue, open diamonds). The hard sphere result (black, filled squares) is also shown.
Fig. 4. 8

Dynamical vertex (Eq.(2.9)) at a fixed barrier height of $10 \, k_B T$ for (from bottom to top) the hard sphere and two soft spheres ($E=11718$ and 5832).
Fig. 4. 9

Dimensionless mean barrier hopping (relaxation) time as a function of volume fraction for repulsion strengths (from top to bottom): hard sphere, $E=30000$, 20000, 10000, 8000, 5000, and 3000.
Fig. 4. 10

Dimensionless mean relaxation time versus repulsion strength for (from bottom to top at high E): $\phi = 0.55, 0.6, 0.65, 0.7, 0.75, 0.8, 0.85, 0.9$. 
Fig. 4. 11

Determination of the exponent of the effective hard sphere mapping in Eq(10) for soft repulsive particles based on two vitrification criteria: $\tau_{\text{hop}} / \tau_s = 10^2$ (black squares) and $\tau_{\text{hop}} / \tau_s = 10^4$ (red circles).
Fig. 4.12

Collapse onto two master curves of the theoretical relaxation time calculations of Fig. 4.11 based on Eq. (4.5). The dashed line has unit slope.
Fig. 4. 13

NMCT ideal glass transition boundary (solid squares), and kinetic arrest curves based on vitrification criteria of $\tau_{\text{hop}} / \tau_s = 10^2$ (open square), $10^3$ (open triangle), $10^5$ (open diamond), in the format of dimensionless temperature versus volume fraction. Curves through the NMCT and kinetic vitrification points are parabolic critical power law fits.
Fig. 4. 14

Fragility plot for a kinetic vitrification criterion of $\frac{\tau_{\text{hop}}}{\tau_s} = 10^X$ and (from bottom to top) repulsion strength (E) values of: infinity (hard sphere), 30000, 16000, 8000, 6000. Inset: Fragility as a function of scaled temperature for the three indicated kinetic arrest criteria.
Fig. 4.15

Log-log plot of the dimensionless shear modulus (units of $k_B T/\sigma^2$) as a function of volume fraction for various Hertzian potential dimensionless strengths of (from top to bottom): hard sphere, $E=30000$, 20000, 10000, 8000, 5000, 3000, 2000, 1000, 800.
Fig. 4. 16

Dimensionless shear modulus divided by volume fraction versus the coupling constant \( \langle \phi g_1^2 \rangle \), where \( g_1 \) is the cage peak amplitude of the pair correlation function) for \( E = 4259 \) (red, open circles), 5832 (green, open up triangles) and 11718 (blue, open diamonds). Hard sphere results are shown as solid squares. Inset: \( G^* \phi^{-1} (r_{\text{LOC}} / \sigma)^2 \) as a function of volume fraction for the same three soft particles examined in the main frame.
Log-log plot of the dynamic free energy barrier (units of thermal energy) as a function of dimensionless shear modulus divided by volume fraction for the same three soft particle systems as in Figure 2 (E = 4259 (red, dashed lines), 5832 (green, dotted lines) and 11718 (blue, dash-dot lines). Hard sphere results are also shown as black, solid lines. Inset: analogous linear-linear plot.
Kinetic glass transition volume fraction, $\phi_g$, versus the dimensionless shear modulus based on the hopping time vitrification criterion $\tau_{hop}/\tau_s = 10^3$. Inset: $\phi_g$ as a function of the corresponding single particle dimensionless repulsion strength, E.
Fig. 4. 19 (A)

Barrier height divided by its zero stress value as a function of applied stress nondimensionalized by the absolute yield stress for three $E$ values and two volume fractions (solid, 0.7; dashed, 0.9). The hard sphere result is also shown.
Fig. 4. 19 (B)

Linear plot of the dimensionless absolute yield stress as a function of volume fraction (From top to bottom: hard sphere, E=11718, E=5832, E=4259). The inset shows the same results in a log-log format.
Fig. 4. 20

Two measures of yield strain: absolute (solid curves) and mixed (dashed curves) as a function of volume fraction for $E = 4259, 5832, 11718$, from top to bottom at large $\phi$. 
Mean barrier hopping time normalized by its zero stress quiescent value as a function of dimensionless applied stress for $E=4259$, $5832$, $11718$ (from top to bottom) and two volume fractions (solid, 0.7; dash, 0.9). Inset: Same results but the dimensionless hopping time is expressed in units of the short relaxation time for $E=4259$, $5832$, $11718$ (from bottom to top) and two volume fractions (solid, 0.7; dash, 0.9).
Fig. 4. 22

Dimensionless shear stress as a function of shear rate nondimensionalized by the short relaxation time for various volume fractions: 0.6 (solid), 0.7 (dash), 0.8 (dot), 0.9 (dash-dot), and E=4259 (black square), 5832 (red circle), 11718 (green triangle).
Flow curve in the representation of stress reduced by the corresponding absolute yield value versus shear rate reduced by a time scale involving the short time relaxation process and the dimensionless glassy shear modulus. Results are shown for a single $E=11718$ at six volume fractions. Note the near collapse in the high volume fraction soft jammed regime ($\phi > \phi_J$), and the lack of collapse below this crossover volume fraction.
Shear viscosity reduced by its quiescent value as a function of shear rate reduced by the quiescent relaxation time (i.e., Peclet number). Results are shown for $E=11718$ and six volume fractions.
CHAPTER 5

THEORY OF THE STRUCTURE AND MISCIBILITY OF SOFT FILLER POLYMER NANOCOMPOSITES: METHODOLOGY

5.1 Introduction

The addition of nanoparticles or fillers to dense polymer melts can profoundly modify the mechanical, thermal, optical and/or other material properties of the resulting polymer nanocomposite (PNCS) because the large surface to volume ratio of those nanoparticles. Nanoparticles can be of very different shapes, the simplest and most widely studied are spheres. However, in order to effectively tune the materials properties often requires nanoparticle dispersion, which is a challenging topic of intensive studies. [1] The major physical reasons for the aggregation of nanoparticles lies on the facts that the large entropy penalty to have polymers packing around nanoparticle, which generate strong depletion attractions among nanoparticles [2-5], and direct Van der Waals attractions if the dielectric constants are mismatched. There are multiple potential ways to avoid particle aggregation, such as adding surfactant or polymer brushes to add interfacial repulsions between nanoparticles to counteract depletion attraction, or engineer polymer-particle attraction of appropriate strength. Recently, the consequence of surface morphology of spherical fillers has been studied experimentally [6]. It is possible to disperse soft spherical nanoparticles, which have a rough, fluctuating surface, in chemically matched homopolymer melt, which is not true if the filler is a smooth hard sphere with no polymer-particle attraction [7]. A generic key fundamental issue here is
how the nanoparticle surface corrugation and fluctuation modify the statistical spatial organization of the nanoparticles in a dense polymer matrix.

From a theoretical point of view, computer simulations of nanoparticles dissolved in a dense polymer melt are an attractive option. However, they are computationally very expensive and difficult to equilibrate due to the relevant high total packing fraction, large size asymmetry between monomers and fillers, and chain connectivity constraints. Significant progress has been made in the development of approximate statistical mechanical theories for polymer nanocomposites during the last decade based on the microscopic integral equation approach known as the Polymer Reference Interaction Site Model (PRISM) theory [8], which accounts for packing effects on the monomer and beyond scale, and the strength and range of material-specific attractive and repulsive interactions. PRISM theory has been extensively applied to the problem of spherical fillers in polymer melts and dense solutions [7,9,10].

Our present work is partially inspired by recent experiments on the dispersion of crosslinked polystyrene nanogels in chemically matched dense polymer matrix of linear chain-like polystyrene (monomer size~1 nm) [6]. These nanoparticles are intramolecular crosslinked polymeric networks with diameters that range from ~5 nm to 7 nm or larger depending on the pre-polymer molecular weight (before crosslinking process) and the degree of intramolecular crosslinking [6]. The Kratky plots obtained from neutron scattering data in solution show a shift toward particle-like nature for heavily crosslinked nanogels (20 mol % crosslinker) [11]. Based on viewing the nanogel as a hard sphere, it has been speculated that this entropically unfavorable dispersion is offset by an enthalpy gain due to an increase in molecular contacts at dispersed nanoparticle surfaces as
compared with the surfaces of phase-separated nanoparticles [6]. No direct evidence of any kind exists for this explanation. The nanoparticles are largely, but not entirely, impenetrable, and have been widely studied due to their importance as advanced functional materials, e.g. the nanoparticles alone can form liquids and gels under various conditions and undergo surface segregation in thin films [12]. Single nanogel softness or elasticity is highly variable via manipulation of solvent quality and crosslink density. This feature makes the nanogels distinctive from its counterpart like rough and rigid hard sphere fractals [13]. By definition, the surface of such soft nanoparticles must be fuzzy and fluctuating. These facts serve as our major motivation, but we can investigate much broader classes of surface rough nanoparticle schemes, e.g. rigid but rough carbon black nanoparticles [13], nanoparticle coated liposome (Pickering emulsion) [14], and repulsive polymer-tethered colloids [15], using the following methodology.

Our goal is to develop a new hybrid small scale Monte Carlo (MC) simulation plus Polymer Reference Interaction Site Model (PRISM) theory. We first construct a minimalist multi-scale model, which explicitly studies the role of surface corrugation and fluctuation by introducing the dimensionless length scales for particle-monomer size asymmetry, surface corrugation and fluctuation magnitude. Then we perform small-scale MC simulation to correctly capture the effective interactions among particles and monomers. We then employ PRISM theory to study the spatial statistical correlation functions of the mixture to understand how the surface morphology affects depletion attraction and bridging and whether it will stabilize dispersion. The following studies are done in two major categories: (1) the athermal limit, i.e. all local interactions are hard-
core interactions, and (2) when interfacial polymer particle attractions exist. For both categories, we study systems that have either a frozen surface or a fluctuating surface.

It is important to realize that every surface has corrugation. Even for a silica particle, it may not be smooth at atomic scale, but it is very likely to be smooth at the monomer (~nm) length scale. Another example is carbon black widely used in tire industry. They are rigid and rough nanoparticles crucial to tune the mechanical responses of tires. It is hard to know at what level of description the modeling of surface roughness matters most. We do not aim to address every aspect of the problem but to offer one new computational approach that accounts for effect of the surface corrugation and fluctuation in a unified way.

The remainder of this chapter is structured as follows. Section 5.2 discusses the new minimalist multi-scale model of soft nanoparticles and the setup of small-scale Monte Carlo simulations: bead-core model, the Gaussian distribution of bead position fluctuation, effective interaction between two nanoparticles in a vacuum, and the effective interaction between one nanoparticle and one monomer in a vacuum. A review of PRISM theory is given in section 5.3. The theoretical details of the extension of PRISM theory to treat soft, interfacially rough filler PNCS and three-step approach are presented in section 5.4. Section 5.5 and 5.6 present the references and figures, respectively.
5.2 Minimalist Model of Soft Nanoparticles and Effective Interactions based on Small Scale Monte Carlo Simulation

Our goal is not to describe exactly the morphology of any particular real soft nanoparticles in a particular polymer melt or solvent. Rather, we aim to construct representative but minimalist models that encode the most basic aspects of surface corrugation and fluctuation and extreme limiting cases of dynamic surface fluctuation. Crosslinked nanogels of size ranges from 5 nm to 10 nm serve as motivation for model construction. These soft particles have many features, including characteristic length scales like surface corrugation size and fluctuation magnitude, related to well controlled crosslink densities.

5.2.1 Bead-core model of spherical nanoparticle with static corrugation

We characterize the nanoparticle surface roughness by constructing a core-bead model. The particle has a hard core of diameter D, and there are N spherical beads centered at the surface of the core and covering the surface (see Fig.5.1). The bead diameter is σ. The relative ratio of core size and bead size, \( D/\sigma \), characterizes the static corrugation. For geometry reasons, there are only a limited set of options of ratio to choose so that the surface is densely covered by the beads [16]. In our studies, unless stated otherwise, we use 72 because this number of beads is needed to achieve \( D/\sigma = 5 \), which gives a ratio relevant for real world nanogels (particle size~ 5nm and monomer size ~1 nm). Other cases studied are 162 and 282, which gives relative ratio of \( D/\sigma = 7.8 \) and \( D/\sigma = 10 \), respectively.

Instead of a full site level description of the soft filler that includes both the surface corrugation length scale as well as all the internal degree of length scales, here we
use a hard core to model all internal buried site level information. As a result, we assume all the internal sites avoid particle or monomer penetration beyond the surface corrugation level. This approximation can help us to avoid conceptual and computation problems while keeping the most important feature for describing depletion phenomena that is largely dependent on length scales of order one half a monomer diameter.

5.2.2 Gaussian distribution of bead position fluctuation

We introduce surface fluctuation by allowing the beads to fluctuate radially (no transverse motion allowed) and incoherently (beads positions are fluctuating randomly and not in the same phase), obeying a Gaussian distribution function:

\[
p(r, u) \propto e^{-\frac{(r-R)^2}{u^2}}, 0 < r < \infty
\]  

(5.1)

where \( p(r, u) \) is the probability to find a bead at distance \( r \) from the origin of the core of radius \( R=0.5D \). The parameter \( u \) quantifies the magnitude of radial position fluctuation, which has a dimension of length and is related to a statistically sensible mean squared fluctuation magnitude, which we take to be small and less than \( \sigma/2 \). The latter length is of order the range of the polymer mediated entropic depletion attraction. Moreover, we desire to maintain particle shape stability. The assumption of incoherent fluctuation generates maximal dynamic disorder in surface roughness. The relation between the statistical mean squared fluctuation magnitude and \( u \) is:

\[
\sqrt{\langle (r-R)^2 \rangle} = \int_0^\infty (r-R)^2 p(r, u)dr
\]  

(5.2)

Some representative numbers used in our calculation are shown below:
We also study another limiting model: the beads can fluctuate in a coherent manner (polar opposite), which we believe is less realistic compared with the incoherent fluctuation model. Unless otherwise indicated in our following discussions, the incoherent fluctuation model is employed.

5.2.3 Small-scale Monte Carlo simulations and effective interactions

The center-of-mass (CM) level effective interaction description within an effective one-component fluid model has been extensively utilized for “soft colloids” such as many arm stars, crosslinked microgels and block copolymer micelles [17-21], and also charged colloidal stars, branched polyelectrolytes and carbon black fractals [22,23]. CM-level coarse-grained models of water have also been constructed and studied [24,25]. The idea is to average over the internal degrees of freedom at the two “particle” level to obtain a CM effective interaction. The nanoparticles of present interest are interfacially rough, spherical particles, with/without surface fluctuation/interfacial cohesion. These features, in conjunction with surface roughness, result in an effective interaction that displays soft repulsions or attractions. Our current research makes one-step forward compared to typical one-component fluid models by utilizing these CM level interactions in an effective two-component mixture calculation.

We now discuss details of the dilute two-particle effective potential calculation at the center-of-mass level, $U_{nn}^{\text{eff}}(r)$. The cross potential $U_{mn}^{\text{eff}}(r)$, of the dilute one particle one monomer effective potential calculation is similarly treated. The nanoparticles can
rotate and adopt different orientations characterized by two angles $\theta, \phi$. The conditional configurational partition function for two particles at fixed CM separation, $r$, is written as an integral over the two angles of rotations of each aggregate, $(\theta, \phi)$, where, in general, it is a function of these angles:

$$Z(r) = \frac{1}{4\pi^2} \int \sin \theta_1 \sin \theta_2 d\theta_1 d\phi_1 d\theta_2 d\phi_2 e^{-\beta E(r, \theta_1, \theta_2, \phi_1, \phi_2)}$$  \hspace{1cm} (5.3)$$

is computed using standard multi-dimensional integration methods akin to an elementary Monte Carlo integration:

$$Z(r) = \frac{1}{(4\pi)^2} \prod_{i=1}^{2} (\theta_{i,\text{max}} - \theta_{i,\text{min}})(\phi_{i,\text{max}} - \phi_{i,\text{min}}) \frac{1}{N} \sum_{n=1}^{N} \sin \theta_{1,n} \sin \theta_{2,n} e^{-\beta E(r, \theta_{1,n}, \theta_{2,n}, \phi_{1,n}, \phi_{2,n})}$$  \hspace{1cm} (5.4)$$

where $(\theta_{1,n}, \theta_{2,n}, \phi_{1,n}, \phi_{2,n})$ are four uniform random numbers falls in the range within integration limits. Consider the athermal limit as an example, which means that all local interactions are hard-core at the elementary site level. To calculate the effective potentials for particles with fluctuating surfaces, we need to average out the fluctuation degrees of freedom in addition to the above rotational degrees of freedom.

$$Z(r) = \frac{\pi^2}{4} \frac{1}{N} \sum_{n=1}^{N} \sin \theta_{1,n} \sin \theta_{2,n} e^{-\beta E(r, \theta_{1,n}, \theta_{2,n}, \phi_{1,n}, \phi_{2,n})}$$  \hspace{1cm} (5.5)$$

where the average is done with respect to the bead position probability distribution function $p(r_1^1, r_1^2, ..., r_2^1, r_2^2, ..., r_{2,2}, u)$. This is computed using standard multi-dimensional integration methods akin to an elementary Monte Carlo integration:

$$Z(r) = \frac{1}{M} \sum_{m=1}^{M} \left\{ \frac{\pi^2}{4} \frac{1}{N} \sum_{n=1}^{N} \sin \theta_{1,n} \sin \theta_{2,n} e^{-\beta E(r, \theta_{1,n}, \theta_{2,n}, \phi_{1,n}, \phi_{2,n})[r_{1,n}]} \right\}$$  \hspace{1cm} (5.6)$$
where \( \{r^i_p\} = \{r^1_p,\ldots,r^7_p,\ldots,r^1_i,\ldots,r^2_i,\ldots,r^2_i,\ldots\} \) are independent Gaussian random numbers indicating the distance between the bead \( i \) (or \( j \)) on particle 1(or 2) and its core origin. The probability to find two particles separated by a distance in the interval \( r \) and \( r + dr \) is \( P(r)dr \propto 4\pi r^2 dr e^{-\beta U_{eff}(r)} \propto 4\pi r^2 dr Z(r) \), where \( U_{eff}^{mn}(r) \) is the desired effective potential. By exploiting spherical symmetry, one can then write the potential as:

\[
U_{mn}^{eff}(r) = -k_B T \ln[Z(r)] \equiv -k_B T \ln\left\{ \frac{1}{M} \sum_{m=1}^{M} \left[ \frac{\pi^2}{4} \sum_{n=1}^{N} \sin \theta_1 \sin \theta_2 e^{-\beta E(r,\theta_1,\theta_2,\phi_1,\phi_2,\{r^i_p\})} \right] \right\}
\]

\[
U_{nn}^{eff}(r) = -k_B T \ln\left\{ \frac{1}{M_{noc}} \sum_{m=1}^{M_{noc}} \left[ \frac{\pi^2}{4} \sum_{n=1}^{N_{noc}} \sin \theta_1 \sin \theta_2 \right] \right\}
\]

(5.7)

where “noc” stands for “non-overlapping configurations”. We use the following rule to define overlapping configurations: any part of particle 1 (core or bead) overlaps with any part of particle 2 (core or bead). Here the summation is equivalent to counting noc because:

\[
E = 0, \text{noc} \quad E = +\infty, \text{otherwise}
\]

(5.8)

To calculate \( U_{mn}^{eff}(r) \), one needs two uniform random numbers \( (\theta, \phi) \) and 72 independent Gaussian random numbers, and the same procedure as described above is followed. An example of the number of configurations we used to get accurate results is \( M=1000, N=1000 \). Therefore, the total number of configuration is \( 10^6 \).

5.2.4 Interfacial attraction at surface corrugation level \( U_{mm}^{eff}(r) \)

The chemical nature of the polymer and nanoparticle is encoded partially in size asymmetry (\( D/d \) and/or \( d/\sigma \) if the particle surface is rough) and partially in effective pair potentials: \( U_{mm}^{eff}(r) \), \( U_{mn}^{eff}(r) \), \( U_{nm}^{eff}(r) \), where \( m \) stands for monomer and \( n \) stands for (CM) nanoparticle. If all these interactions are hard core, then the polymer
nanocomposite is effectively an athermal system. However, a more common situation is when $U_{mn}^{\text{eff}}(r)$ and $U_{mm}^{\text{eff}}(r)$ are effectively hard core interactions and $U_{mn}^{\text{eff}}(r)$ is composed of a repulsive branch (often hard core) and longer-range effective attractive interactions:

$$
U_{mn}^{\text{eff}} = \infty, r < \sigma_{mn} \\
U_{mn}^{\text{eff}} = -\varepsilon \exp[-\frac{r - \sigma_{mn}}{\alpha}], r > \sigma_{mn}
$$

where $\varepsilon$ is the contact cohesion strength, $\alpha$ is the attraction range and $\sigma_{mn} = (D + d)/2$.

Based on prior PRISM theory studies of such a nanocomposite with smooth hard sphere fillers [26], in this enthalpic mixture where $\beta\varepsilon \gg 1$, strong enough attractive interactions between the filler and monomers can result in thin layers of polymer strongly associating with, or adsorbing onto, the particles. This results in a particle-particle potential of mean force which favors well-defined, small interparticle separations, i.e., local “bridging”. For $\beta\varepsilon << 1$, the entropic depletion attraction is dominant and nanoparticles contact aggregate, leading to classic macrophase separation. Between these two extremes is a third behavior, in which a polymer gains enough cohesive interaction energy to associate with a single filler, but not enough to give up the additional entropy required for association with multiple particles. In this case, a nanoparticle is surrounded by a thermodynamically stable “adsorbed” polymer layer, typically on the order a few monomer diameters thick, which sterically stabilizes the particles in the polymer matrix. For all situations, polymer degree of polymerization is a second order effect due to the high total packing fraction of a dense PNCs.

In our multi-scale modeling where particles have two length scales $(D, \sigma)$ instead of one, in $U_{mn}^{\text{eff}}(r)$ the nature of the interfacial attraction is related with the surface
corrugation and bead size. This is more realistic in the sense that the interfacial cohesion has to be related to the interface which is mimicked by corrugated beads. As a result, we define the bare interaction at bead-monomer level as:

\[ E_{mb} = \infty, r < \sigma_{mb} \]
\[ E_{mb} = -\varepsilon_{mb} \exp\left(-\frac{r - \sigma_{mb}}{\alpha_{mb}}\right), r > \sigma_{mb} \] (5.10)

where \( \varepsilon_{mb} \) and \( \alpha_{mb} \) are the attraction strength and attraction range between the polymer monomer and surface bead, and \( \sigma_{mb} = (\sigma + d)/2 \). Thus, the effective interaction between one nanoparticle and one monomer is modified as: for frozen surface,

\[ U_{mn}^{eff}(r) \equiv -k_B T \ln\left[ \frac{\pi^2}{4N} \sum_{n=1}^{N} \sin \theta e^{-\beta E_{mb}(r,\theta,\phi)} \right] \] (5.11)

for fluctuating surface,

\[ U_{mn}^{eff}(r) \equiv -k_B T \ln\left\{ \frac{1}{M} \sum_{m=1}^{M} \left[ \frac{\pi^2}{4N} \sum_{n=1}^{N} \sin \theta e^{-\beta E_{mb}(r,\theta,\phi,\phi')} \right] \right\} \] (5.12)

**5.3 Equilibrium Theory of Polymer Nanocomposites**

The Polymer Reference Interaction Site Model (PRISM) integral equation approach [8] has been recently extended to treat the structure, thermodynamics and phase behavior of mixtures of hard particles and homopolymers in solutions [9] and nanocomposite melts [10]. Objects of arbitrary shapes are represented as bonded sites that interact via pair decomposable site–site potentials. If a species is rigid, then computation of the corresponding intramolecular pair correlation function is a simple exercise in geometry. For flexible polymers, the intra-chain structure is described statistically. It is either approximated by an ideal (in the global Flory sense) coil at
various levels of chemical realism (e.g., Gaussian, freely-jointed, semiflexible, or rotational isomeric chain), or determined in a fully self-consistent manner with intermolecular packing correlations based on a medium-induced solvation potential and single chain Monte Carlo simulation [8,27]. The chemical nature of the polymer and nanoparticle is encoded in pair potentials, \( U_{ij}(r) \), composed of a repulsive branch (often hard core) and longer-range attractive interactions (if there is interfacial cohesion). The theory is defined by a set of coupled nonlinear matrix integral equations

\[
H(r) = \int \frac{dr}{r} \int \frac{dr}{r} \Omega(|r-r^-|)\zeta(|r^- - r^+|)\Omega(r^+) + \int \frac{dr}{r} \int \frac{dr}{r} \Omega(|r^- - r^+|)\zeta(|r^+ - r^-|)H(r^-)
\]

(5.13)

Here, \( H(r) \) contains elements \( \rho_i, \rho_j, (g_{ij}(r) - 1) \), \( \rho_j \) is the corresponding site number density, \( g_{ij}(r) \) is the intermolecular site-site radial distribution function, which describes how the density varies as a function of the distance \( r \) from a reference site. \( \zeta(r) \) contains elements \( C_{ij}(r) \), which are renormalized site–site intermolecular potentials or "direct correlation" functions. \( \Omega(r) \) contains elements \( \omega_{ij}(r) \), which defines the intramolecular pair correlations (species statistical shape) and is linear in site number densities. The intramolecular correlation function obeys:

\[
\omega_{\alpha\gamma}(r) = N_{\alpha}^{-1} \sum_{i=1}^{N_{\alpha}} \delta(r - |r_i|), \alpha = \gamma
\]

\[
\omega_{\alpha\gamma}(r) = (N_{\alpha} + N_{\gamma})^{-1} \sum_{i=1, j=1}^{N_{\alpha} + N_{\gamma}} \delta(r - |r_i|), \alpha \neq \gamma
\]

(5.14)

where \( \alpha, \gamma \) correspond to different components, i.e. monomer or nanoparticle. The first term on the right hand side of equation (5.13) describes all intermolecular correlations in the dilute limit, and the second term quantifies many body effects.
To render the number of integral equations tractable, polymer chain end effects are pre-averaged [8]. For example, for a mixture of hard spheres (A) and single site (B) homopolymers, there are three intermolecular pair correlation functions: \( g_{AA}(r) \), \( g_{AB}(r) \), and \( g_{BB}(r) \). Even if the intramolecular correlations are known, one requires an approximate closure which provides a second set of relations between the pair and direct correlation functions and bare potentials. Reliable closures for polymer–particle systems are not obvious due to the large structural and packing asymmetry between flexible chains and hard particles. The classic site–site Percus–Yevick (PY) closure [28] is employed for polymer–polymer (p–p) and polymer–nanoparticle (p–n) correlations,

\[
C_{ij}(r) = (1 - e^{\beta U_{ij}(r)}) g_{ij}(r)
\]  

(5.15)

and the hypernetted chain (HNC) closure is adopted for nanoparticle–nanoparticle (n–n) correlations:

\[
C_{nn}(r) = -\beta U_{nn}(r) + h_{nn}(r) - \ln g_{nn}(r)
\]  

(5.16)

Numerical solution of above equations yields \( g_{ij}(r) \), and collective concentration-concentration fluctuation partial scattering structure factors in Fourier space, \( S_{ij}(k) \), describing correlated concentration fluctuations over all length scales. Of special interest is the dilute two particle potential of mean force (PMF):

\[
\beta W_{nn}(r) = -\ln(g_{nn}(r))
\]  

(5.17)

from which second virial coefficients can be deduced. The number of coupled equations increases as number of components increases, which results in great numerical challenges to solve these coupled nonlinear integral equations. [8] We note that PRISM theory is not a mean field theory since it predicts correlations over all lengths scales (which are
coupled) within a compressible fluid framework. The intermolecular structure is functionally related to the intramolecular structure and bare interparticle interactions. However, PRISM theory only treats spatially homogeneous states. For dense PNCs, most PRISM studies to date have employed a freely-jointed chain (FJC) homopolymer model (degree of polymerization, N) composed of sites of diameter d, and hard spherical particles (diameter D), under fixed melt-like total packing fraction conditions.

The packing fraction or volume fraction of a particular species is defined as:

\[ \phi_i = \frac{\pi}{6} \rho_i D_i^3, i = m, n \]  \hspace{1cm} (5.18)

where \( D_i \) is the size for species i. The total packing fraction or volume fraction:

\[ \eta = \sum_i \phi_i, i = m, n \]  \hspace{1cm} (5.19)

5.4 Combining Small Scale Monte Carlo Simulation with PRISM Theory: Three-Step Approach

5.4.1 PNCs: Multi-scale modeling and model parameters setup

Fig.5.2 shows a representation of the proposed multi-scale modeling approach for soft, interfacially rough filler PNCs. Polymers are treated as athermal chains of N spherical interaction sites, or monomers, of diameter d that interact via pair-decomposable hard-core potentials. A freely jointed chain (FJC) model is adopted with a rigid bond length \( l = 4d / 3 \) (corresponding to a persistence length of 4/3), and d is the polymer segment i.e. monomer diameter. The FJC structure factor is:

\[ \omega_p(k) = [1 - f^2 - 2N^{-1} f + 2N^{-1} f^{N+1} ]/(1 - f)^2 \]  \hspace{1cm} (5.20)
where \( f = \sin(kl)/kl \). The FJC chain model ignores nonideal conformational effects, which are expected to be minor for the melt conditions of interest [29,30]. In principle, filler perturbation of polymer conformation at nonzero volume fractions could be treated based on the fully self-consistent version of PRISM theory, which involves the construction of a medium-induced solvation potential and solution of an effective single-chain problem with Monte Carlo simulation. [8,27] The accuracy of this approach for polymer nanocomposites, particularly when the monomers are strongly attracted to the fillers, is not fully known. However, the few existing experiments and simulations for dense polymer nanocomposites at finite filler loadings suggest that conformational perturbations are small or negligible. [29,30] Most importantly for the present work is that, because our focus is the dilute filler limit, within the liquid-state theory approach the statistical conformations are not perturbed. We consider the dilute particle limit \((\phi_n \to 0)\) and polymer melt condition \((\eta = 0.4)\).

Nanoparticle fillers are treated as spheres with the surface corrugation beads as discussed in section 5.2. A. We study core bead size ratios of \( D/\sigma = 5 \) (72 beads), 7.8 (162 beads), and 10 (282 beads).

5.4.2 PRISM theory sequentially solving strategy and closures

Using the two effective potentials obtained from the small scale MC simulations, we erase all beads from the nanoparticles and perform an effective two-component PRISM calculation in the dilute particle limit. There, the 3 coupled integral equations, written here in Fourier space, can be sequentially solved:

\[
\begin{align*}
  h_{pp}(k) &= \omega_p(k)C_{pp}(k)S_{pp}(k) \\
  h_{pn}(k) &= C_{pn}(k)S_{pp}(k) \\
  h_{nn}(k) &= C_{nn}(k) + \rho_p C_{nm}^2(k) S_{pp}(k) \equiv C_{nn}(k) + W(k)
\end{align*}
\]  

\[ (5.21) \]
By using PY closure for monomer-monomer and particle-monomer, we can solve the first two equations and then we perform a Fourier Transform of the last equation and get

\[ g_{nn}(r) = C_{nn}(r) + 1 + W(r) \]  \hspace{1cm} (5.22)

The closure for the particle-particle correlation is the HNC. However, numerical solutions based on using the PY closure is more easily obtained and can be related (when \( \phi_n \to 0 \)) to the solution based on HNC through the following procedure: For soft fillers, \( g_{nn}(r) = 0, r < D^* \), where \( D^* \geq D \) (\( D^* \) > \( D \) representing the CM separation distance, at which no configuration exists that avoids overlaps. ). By using PY closure for particle-particle direct correlation function, one has

\[ C_{nn}^{PY}(r) = (1 - e^{\beta U_{nm}^{eff}(r)}) g_{nm}^{PY}(r), r > D^* \]. Thus,

\[ g_{nm}^{PY}(r) = e^{-\beta U_{nm}^{eff}(r)} (1 + W(r)), r > D^* \]. Then the HNC closure for particle-particle correlations are:

\[ g_{nn}^{HNC}(r) = g_{nn}^{HNC}(r) - 1 - \ln g_{nn}^{HNC}(r), r > D^* \]. Thus,

\[ g_{nn}^{HNC}(r) = e^{-\beta U_{nm}^{eff}(r)} e^{W(r)}, r > D^* \]. We also have

\[ g_{nn}^{HNC}(r) = \exp[-\beta U_{nm}^{eff}(r) + e^{\beta U_{nm}^{eff}(r)} g_{nm}^{PY}(r) - 1], r > D^* \] \hspace{1cm} (5.23)

Based on the equation above, one can also write the polymer mediated potential of mean force as

\[ W_{polymcr}^{polymer}(r) = -k_B T \ln g_{nn}^{HNC}(r) = U_{nm}^{eff}(r) + k_B T [e^{\beta U_{nm}^{eff}(r)} g_{nm}^{PY}(r) - 1] - U_{nm}^{eff}(r) - k_B T W(r) \] \hspace{1cm} (5.24)

5.4.3 Three-step approach

Fig.5.3 presents the conceptual idea of the three-step approach: On step one and two, we carry out small scale MC simulations to construct the effective pair interactions. Then on step three, all beads from particles are erased and we use effective interactions to mimic their effects. Monomers are connected into chains and the “Center of Mass” level
nanoparticle (dilute) in homopolymer melt mixtures problem is solved via a standard two-component PRISM theory methods described above.

A natural question might is why we avoid doing calculations directly targeted on dealing with three components (core, bead, and monomer) at the same time? The answer lies in two facts. First, dealing with multiple length scales at the same time involves solving coupled nonlinear integral equations, which is not a trivial computational problem and generally is very difficult [31]. Considering the fact that our system has large size asymmetry (i.e. nanoparticle vs. monomer/bead/fluctuation magnitude) and four length scales, this problem becomes even more difficult. More importantly, the three-step approach can be considered as a general solution to treat multi-scale systems, because of the conceptual reduction of dimensions to treat two length scales at the each time, we are free to extend our studies to much more complicated systems easily, i.e. changing the fluctuation manner, local interaction, introducing randomness in corrugation and etc.

5.5 References


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[31] There are 6 coupled nonlinear integral equations to solve for a 3-component PRISM calculation.
5.6 Figures

Fig. 5. 1

Schematic representation of a bead-core model of rigid structured nanoparticles (Number of beads=72) is shown. There are two length scales: the core size $D$ and the surface bead size $\sigma$. If the beads fluctuate, a third length, the amplitude of vibration enters.
Fig. 5. 2

Representation of the multi-scale modeling of soft, interfacially rough polymer nanocomposites. The chain length, N, is fixed to be 100. There are five length scales: Particle size (D), surface bead (corrugation) size (σ), monomer size (d), u in unit of length, related to surface fluctuation magnitude and polymer radius of gyration

\[ R_g = \sqrt{N/6} \cdot d \]. From previous PRISM studies, the radius of gyration is a secondary effect, so there are three important dimensionless length scale ratios: \( D/d \), \( D/\sigma \) and \( u/\sigma \).
Fig. 5. 3

Representation of 3-step approach: Step 1 & 2, we conduct small scale MC simulations to obtain effective interactions; on step 3, we erase beads on the surface and use effective interactions to mimic their effects and do an effective two-component PRISM calculation.
CHAPTER 6

THEORY OF THE STRUCTURE AND MISCIBILITY OF SOFT FILLER POLYMER NANOCOMPOSITES:
RESULTS AND DISCUSSION

6.1 Introduction

This chapter presents applications of the methodology developed in the previous chapter. We start with the smooth hard sphere filler, then add surface beads to mimic static surface corrugation and vary it by changing the number of beads on the surface. Surface fluctuation is then added by allowing beads to fluctuate radially either in an incoherent or coherent manner to vary the “dynamic” surface corrugation. Fig. 6.1 illustrates the types of systems studied. All these initial studies are for the athermal mixture, which is the chemically matched mixture of high interest for experimentalists, e.g. crosslinked polystyrene and linear polystyrene chain mixture [1]. Finally, interfacial cohesion is added and its consequences are studied. All calculations are for the incoherent surface fluctuation model unless otherwise noted.

Section 6.2 presents the effective interaction between two nanoparticles, and the effective interaction between one nanoparticle and one monomer, in a vacuum, for both conditions in the athermal limit and with interfacial cohesion. In section 6.3, we study the athermal limit and focus on the following issues: (1) The influence of static surface corrugation of rough hard sphere (HS) fillers on their statistical spatial organization in a dense polymer melt matrix. (2) The consequences of a fluctuating surface at a given static surface corrugation. (3) The variation of static surface corrugation. (4) Comparison between the incoherent fluctuation model and the coherent fluctuation model. Section 6.4
studies the role of interfacial cohesion and answers the following questions: (1) How does surface fluctuation modify “bridging” phenomena given the same static corrugation? (2) How does the filler PMF vary with particle size? (3) How can we make connections with prior studies of smooth HS fillers? The chapter concludes in section 6.5 with a summary and discussion. Section 6.6 and 6.7 present the references and figures, respectively.

6.2 Effective Interactions

6.2.1 Nanoparticle-nanoparticle, $U_{nn}^{\text{eff}}(r)$

Under purely hard core conditions, we first examine the effective potential for the frozen corrugated surface case, i.e. all beads are fixed at the particle surface. The resulting interaction is a soft repulsion. When there is surface fluctuation, $U_{nn}^{\text{eff}}(r)$ is softer. Let us first examine its functional forms (See Fig.6.2 and 6.3), which is qualitatively the same for all athermal cases. The softer the particles are (the larger the surface fluctuation magnitude is), the softer the repulsive potential is, regardless of the particle-monomer size ratio (only $d = \sigma$ case is shown here.). The effective interaction (Fig.6.2) starts from zero when the two outer shells (one can draw a circle that can envelope the bumpiness formed by the surface beads) first touch each other. Then as the two particles approach closer, the beads on one particle fit into the crevices of the other particle’s surface, and a soft repulsion grows in. When particles can effectively feel the full excluded volume geometric constraint, no smaller CM separation distance exists that avoids overlaps, and $U_{nn}^{\text{eff}}(r)$ diverges.

6.2.2 Nanoparticle-monomer, $U_{nm}^{\text{eff}}(r)$
We first show the athermal condition case. The effective interaction between one particle and one monomer $U_{mn}^{\text{eff}}(r)$ (see Fig.6.3) is qualitatively similar to $U_{mn}^{\text{eff}}(r)$. Since it depends on monomer size, the repulsion result shifts to larger separations as monomer size increases. The potential shape approaches the bare hard-core interaction as the monomer size increases because the surface corrugation becomes less important if monomer averages out the surface roughness (see Fig.6.4).

Then we show the case with interfacial cohesion. Let us look at the function form of the effective interaction (see Fig.6.5). We denote the magnitude of the minimum of the interaction as $\varepsilon_{mn}$, and the separation distance as $\sigma_{mn}$, “first contact distance”, which is the smallest distance that a monomer can touch one surface bead along the radial direction under frozen surface condition. We find the following features. For frozen surfaces, $\varepsilon_{mn} = S\varepsilon_{mb}$, where $S$ is a constant depending on size asymmetry $D/d$. $\varepsilon_{mn}$ scales linearly with $\varepsilon_{mb}$, and the prefactor is a function of particle size asymmetry, i.e. $S(D/d = 5) = 3.09$, $S(D/d = 7.8) = 3.14$ and $S(D/d = 10) = 9.44$. The increase of this prefactor is due to the change of particle surface curvature which induces more contacts between surface beads and monomer. The length $\sigma_{mn}$ remains the same for different attraction strengths, $\sigma_{mn} = (D + \sigma + d)/2$. Using $\sigma_{mn}$ as a characteristic separation distance, the right branch of the potentials collapses for different attraction strengths. This means that at large separation distance, the particle level attraction range remains the same for different attraction strength given the same local (bead level) attraction range, surface corrugation does not matter. The left branch of the potentials splays apart because of particle surface corrugation. For fluctuating surfaces, $\varepsilon_{mn}$ does not scale linearly with
\( \varepsilon_{mb} \), and there is only a minor increase as particle size increases (i.e. \( D/d \) increases from 5 to 10). The first contact distance, \( \sigma_{mn} \), ranges from above \( (D + \sigma + d)/2 \) to below this value as \( \varepsilon_{mb} \) increases. The right branch of the potentials collapses for different attraction strengths while the left branch splays apart.

6.3 Athermal Systems: Pair Correlations & Thermodynamics

6.3.1 Frozen surface: Influence of static surface corrugation

In this case, the positions of the beads on the surface of nanoparticles are fixed, thereby allowing study of the pure effect of having surface corrugation on hard fillers. Fig.6.6 presents the particle-monomer pair correlation function. Since the particles now have a rough surface, it is impossible for monomers to be in direct contact with the core, thus it goes to zero strictly before close contact. (For MC, due to the particle geometry, there will be a closest approaching distance \( \sigma_{pm} \) that is larger than close contact distance \( (D + d)/2 \). Technically, this is determined when \( g_{pm}(r) \) goes to zero.) The position of the primary ordering peak is shifted to larger separation accordingly.

The primary ordering peak is generally more pronounced for smooth HS fillers than rough HS fillers. This is understandable because in the rough case, the monomer can no longer touch the core directly. Instead, there is extra disorder when monomers explore crevices, driven by the desire to maximize entropy. Thus, the primary ordering peak gets broader, and the magnitude gets smaller. As one increases monomer size with particle size fixed, the magnitude of primary peak for smooth HS decreases monotonically. However, for rough HS cases, it increases monotonically. This is understandable since
when monomer size increases, the surface corrugation appears “smoother”, i.e. the surface corrugation is averaged out. Thus, the larger the monomer is, the smaller the difference in the magnitude of primary peak for the smooth and rough cases.

Fig. 6.7 presents the PMF between nanoparticles, which in general has two origins. One comes from the direct interaction, the other comes from the polymer-mediated interaction. Thus

\[
W_{nn}(r) = U_{nn}^{\text{eff}}(r) + W_{nn}^{\text{polymer}}(r)
\]  

(6.1)

The potential of mean force diverges at a larger interparticle separation for rough HS cases because the surface corrugation introduces geometric constraint. The entropic polymer mediated depletion attraction is weakened generally with surface corrugation. This is understandable as the entropic penalty for polymers to pack around the surface of nanoparticles is reduced as the monomers can now fit into the crevices of the surface beads. As monomer size increases with particle size fixed, for smooth HS systems the depletion attraction becomes smaller. For rough HS cases, the weakest depletion attraction occurs for the largest monomer size, but the magnitude of depletion attraction is similar for the other two cases while larger monomer case can feel the geometric constraint at a larger particle separation.

The particle second virial coefficient, \( B_2 \), characterizes the total thermodynamic pair interaction between two nanoparticles and consists of both a “direct” and an “indirect” (polymer-mediated) contributions.

\[
B_{2,nn} = -\frac{1}{2} \int dr (e^{-\beta W_{nn}(r)} - 1)
\]  

(6.2)
To obtain the spinodal demixing condition for a dilute effective one-component (E1C) system, one needs $\bar{B}_2 = B_{2,\text{ref}} / B_{2,\text{ref}}$, where $B_{2,\text{ref}} = B_{2,\text{smHS}} = 2\pi D^3 / 3$ for smooth HS fillers. However, this reference state is varying for rough hard spheres as the static surface corrugation weakly changes, $B_{2,\text{RoughHS}} = aB_{2,\text{smHS}}$. The prefactor “$a$” is calculated based on the rough HS pair potential between two nanoparticles. 

$$a = -\int d\mathbf{r} \left( e^{-\mathbf{R} \cdot \mathbf{d}} - 1 \right) / 2.$$ 

As a result, the normalized $\bar{B}_2$ has taken into account of the direct geometry difference due to surface corrugation.

We then analyze the $\bar{B}_2$ for frozen surface fillers. It is always negative for all cases implying significant depletion attraction. The absolute value of $\bar{B}_2$ is always larger for smooth HS than rough HS fillers, meaning that the surface corrugation reduces depletion attraction. For smooth HS cases, as one increases monomer size with particle size fixed, the absolute value of $\bar{B}_2$ monotonically decays while for rough HS cases the change is non-monotonic. This is understandable because the smaller the monomers are, the bigger influence the surface corrugation has on $\bar{B}_2$. The crevices that monomers can fit into reduce depletion attraction.

The spinodal solubility limit volume fraction, which is often used as a rough indicator for particle dispersion, is given by [2]:

$$\phi_s = -(8\bar{B}_2 \eta_s)^{-1}$$

(6.3)

Surface roughness enhances dispersion by a factor ranges from 1 ($d = 2\sigma$) to 1000 ($d = 0.5\sigma$) compared with its smooth hard sphere filler counterpart depending on size asymmetry $D/d$ (see below).
The experiment [1] which serves as one of our motivation found that it is possible to disperse crosslinked polystyrene nanoparticles in linear polystyrene chain matrix. This fact is determined from Small Angle Neutron Scattering (SANS) experiments via presence or absence of fractal-like scattering at small wave vector and at nanoparticle concentrations of 2 wt %. The fractal-like behavior is indicative of contact clustering aggregates. Our theoretical calculation provides a possible explanation via the existence of crevices formed by surface corrugation which can “mute” depletion attraction and enhance dispersion.

6.3.2 Fluctuating surface: Influence of surface corrugation and fluctuation

Fig.6.8 shows the particle-monomer pair correlation function. Since the particles now have a rough surface, it is impossible for monomers to be in direct contact with the core, thus it goes to zero equal or larger than close contact distance \((D+d)/2=0.6D\) for \(d=\sigma=0.2D\). The primary ordering peak is most pronounced for the frozen surface case. The larger fluctuation magnitude is, the less ordering is found as the primary ordering peak is less pronounced. This is understandable because the monomer can explore more space around the nanoparticle as the surface is soft and the corrugation is not frozen. Also, for fluctuating surface cases, it goes to zero at smaller separation distances approaching close contact distance.
Fig. 6.9 presents the PMF between nanoparticles. When the surface “looks rough” on the monomer size scale, i.e. $d < \sigma$ (see Fig. 6.9(A)), the depletion attraction gets stronger both in terms of the attraction strength (the minimum) and spatial range, compared to the frozen limit, with growing surface fluctuation. This can be understood in the sense that surface fluctuation tends to average out surface corrugation, which is the key factor to reduce the entropic penalty for polymers to pack around the nanoparticles. However, when surface “looks smooth” on the monomer size scale, i.e. $d \geq \sigma$ (see Fig. 6.9(B)), this effect becomes significantly less pronounced. For $d = 2\sigma$, the minimum of the potential goes up with increasing surface fluctuation magnitude.

For $N=72$ particles (see Fig. 6.10), the $\bar{B}_2$ are negative for all surface fluctuation amplitudes. In addition, increasing surface fluctuation magnitude leads to more negative $\bar{B}_2$, which is an indication of strong depletion aggregation. This conclusion is most valid when the monomer size is equal or smaller than the corrugation size. When the monomer size is larger than the corrugation scale, the effect can be reduced and the trend can even be reversed. The spinodal solubility limit filler volume fraction, $\phi_s$, follows directly from $\bar{B}_2$ (see Fig. 6.11(A) & (B)). Systems become less miscible as surface fluctuation increases (see Fig. 6.11(C)). Similarly, solubility is not sensitive to surface fluctuation if the monomer size is larger than corrugation size. The system can even be slightly more miscible as fluctuations get large. Compared with smooth HS fillers, there will be a critical fluctuation magnitude, below and above which miscibility can change several orders of magnitudes. In summary, the existence of surface corrugation enhances dispersion, while for $N=72$ case, surface fluctuation suppresses
dispersion when the surface “looks rough” to the polymer monomers. However, is this conclusion generally true?

6.3.3 Variation of static surface corrugation: Changing \( D/\sigma \)

The relevant surface corrugation that serves as an extra source of disorder by creating crevices and weakens depletion attraction can be varied in several ways: (1) Fix \( d/\sigma \) and change \( D/\sigma \), i.e. change the particle size given the fixed local surface corrugation size, or (2) fix \( D/d \) and change \( D/\sigma \), i.e. change the static surface corrugation size given the same particle size. The following studies of the particle second virial coefficient and miscibility are carried out accordingly.

The matched bead-monomer size \( \sigma = d \) condition is perhaps most relevant to the matched chemistry crosslinked polystyrene nanogels in linear polystyrene systems [1]. However, why one might consider the monomer size to be the relevant corrugation size is not straightforward to answer based on our coarse-grained models. The bead on the filler surface is meant to mimic the most relevant length scale to discuss the effect of surface corrugation on the depletion effect. As a result, although groups on the surface larger than the monomer size scale do exist and contribute to surface corrugation, it is the monomer length scale that matters for depletion effect and dispersion properties.

We now study multiple particle sizes ranging from \( D/\sigma = 5, 7.8 \) to 10 (the corresponding numbers of beads are 72, 162, 282) for the same monomer size (bead size). The trend is straightforward. (1) At zero fluctuation (see Fig.6.12), the larger the particle is, the stronger the depletion attraction is. (2) For all particle sizes, as the fluctuation magnitude increases, the depletion attraction also gets stronger. For smaller particles, the attraction range increases while the attraction strength (the minimum of the PMF)
remains almost the same magnitude. In contrast, for large particles, both the range and strength increase. Surface fluctuation suppresses dispersion despite the size differences (see Fig.6.13). (3) However, for all cases studied, the rough fillers are more miscible than their smooth HS counterparts. The dependence of the filler spinodal solubility limit volume fraction on fluctuation magnitude follows roughly an exponential law. Our physical understanding is that the monomers can only sense the local surface roughness. Although the overall particle size is changed, which leads to the change of surface curvature, the overall trend in terms of the dependence on fluctuation magnitude remains the same, but the absolute value of solubility will depend on the particle-monomer size asymmetry (typically grows strongly as an exponential), similar to the smooth HS cases [2].

Based on previous studies of smooth HS filler polymer nanocomposites, we know that the potential of mean force scales linearly with particle-monomer size asymmetry [2]. Thus,

$$\phi_s \sim -\frac{1}{B_2} \int d\mathbf{r} e^{-\beta W_{\text{sm}}(\mathbf{r})} \sim \frac{1}{\int d\mathbf{r} e^{-\beta K(D/d)}} \sim e^{-A(D/d)}$$  \hspace{1cm} (6.4)

and hence, we can roughly write the following relation:

$$\ln \phi_{s,\text{smHS}} = -A[D/d] + B$$  \hspace{1cm} (6.5)

where A, B are two constants. By fitting the theoretical data (see Fig.6.14 squares) for D/d=5, 7.8, 10 for smooth HS fillers, one has A=0.922, B=0.266. For soft and interfacially rough nanoparticle fillers, the dependence on size asymmetry D/d is also roughly exponential decay (see Fig.6.14).

$$\ln \phi_{s,\text{roughHS}} = -A(u)[D/d] + B(u)$$  \hspace{1cm} (6.6)
where \( A(u) \) and \( B(u) \) are now functions of the fluctuation magnitude, where \( A(u)<A \) and \( A(u) \) increases with increasing fluctuation magnitude while \( B(u) \) decreases.

Given the above analytic function forms, we can quantify the enhancement of solubility relative to the smooth HS filler cases via the ratio \( \phi_{\text{Rough}} / \phi_{\text{Smooth}} \). The relative enhancement for different nanoparticle sizes with matched bead-monomer size can thus be compared:

\[
\ln \phi_{\text{Rough},1} - \ln \phi_{\text{Rough},2} = (A - A(u)) \left[ \frac{(D_1 - D_2)}{d} \right]
\]

(6.7)

Since \( A>A(u) \), then if \( D_1 > D_2 \), one has \( \phi_{\text{Rough},1} > \phi_{\text{Rough},2} \), which is exactly the trend we observe from numerical calculations (see Fig.6.15). Larger particles result in stronger enhancements of dispersion compared to their smooth analogs. This difference decreases as the fluctuation magnitude increases because \( A(u) \) is approaching \( A \). Our physical understanding is that there are two competing forces that affect dispersion. One is the particle-monomer size asymmetry; the other is the bead-monomer size match. The larger the particle is, the bigger the particle-monomer size asymmetry is, which reduces dispersion. On the other hand, given the matched size condition, the larger the particle is, the more crevices there are on the surface of the particle, which enhances dispersion. As a result, when one normalizes the spinodal volume fraction by its value for smooth HS filler cases, we are subtracting the effect of size asymmetry and leaving only the effect of crevices.

We now consider the more general condition with mismatched bead-monomer size. The starting point is to compare with smooth HS fillers of the same particle-monomer size asymmetry.
First consider frozen surfaces. We have multiple corrugation sizes ranging from \( \sigma / d = 1\), 0.7 to 0.5 (the corresponding numbers of beads are 72, 162, 282). The trend is straightforward: At zero fluctuation (see Fig.6.16), the trend is as expected. As surface gets smoother (corrugation size shrinks), it approaches smooth hard sphere limit. The physical understanding is that surface looks smoother for the monomer as corrugation size shrinks. (Literally, it goes to smooth HS as corrugation size vanishes in a extremely slow manner.)

When surface fluctuation is present, the PMF displays complicated trends. At the matched size condition, depletion attraction is enhanced as the fluctuation magnitude increases, while the trend is reversed when beads become significantly smaller than monomer size (see Fig.6.17). We can then normalize the spinodal volume fraction by its value for smooth HS filler cases (see Fig.6.18) and explore the whole regime of mismatched size. As one varies the bead size from half the monomer diameter to twice the monomer diameter, the dependence on fluctuation magnitude changes from slightly increasing \( (\sigma = 0.5d) \) to dramatically decreasing \( (\sigma = 2d) \). The physical understanding is that fluctuation makes the surface “look smoother”. This effect is most pronounced when the surface is “rough” in the view of the monomer, which is when the bead size is significantly larger than the monomer size and the monomer can fit into the crevices and gain entropy.

**6.3.4 Comparison: Incoherent fluctuation vs. coherent fluctuation**

We have made an assumption about the way the surface beads fluctuate. It is the incoherent radial Gaussian fluctuation. Coherent fluctuation means that all beads on one particle fluctuation in the same phase, thus behaves effectively like “breathing”,

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essentially an opposite limiting picture. For real crosslinked nanogels, the surface is a crosslinked network with strands of monomers between nodal points. For small fluctuations, the incoherent assumption should be most relevant. However, if fluctuation gets significantly large, the connectivity between different monomers will be interfering and tangential fluctuation will matter. This will also induce correlation between different monomers. We are not trying to realistically address this effect in the present model. But we can consider the extreme case, which is the coherent fluctuation model.

Fig.6.19 compares the filler PMF based on incoherent and coherent fluctuation models. At small surface fluctuation, the coherent and incoherent calculations are close. At large fluctuations, coherent effective interactions tend to be less repulsive. The physical understanding is that how repulsive the inter-particle potential is largely depends on the probability of overlapped configurations. Thus, at large fluctuation magnitude the “dynamical disorder” generated by incoherent fluctuation would be most pronounced to induce more overlapped configurations than the case at small fluctuations.

We now further investigate this effect in terms of particle-particle potential of mean force (see Fig.6.20) and miscibility (see Fig.6.21(A) and (B)). Different from the relatively weak dependence on fluctuation magnitude for incoherent fluctuation cases, the coherent fluctuation models show much stronger dependence on fluctuation amplitude. For the PMF, both the depletion attraction strength and range increase dramatically as the fluctuation amplitude gets larger. This is a direct result of the interparticle potential, where coherent fluctuation generates much less repulsion for large fluctuation. In terms of miscibility, the coherent fluctuation cases can have solubility limits far below the values for their smooth HS counterparts. We also study the dependence of miscibility on
particle size. Despite the differences in terms of fluctuation magnitude, the incoherent fluctuation systems show a drop of miscibility of around one order of magnitude, while the miscibility for coherent cases drops even more dramatically as fluctuation amplitude gets large.

A tentative simple interpretation concerning the above results is that the solubility of coherent bead fluctuation or breathing sphere might be understood by post-facto averaging the smooth HS filler solubility (or second virial coefficient) over particle size (D) fluctuation:

\[ P(D) \sim e^{\frac{(D-D_0)^2}{(2\sigma)^2}} \quad (6.8) \]

Thus we construct:

\[ <\phi_s(D)>_{D_0/D,d,u} \sim \int_0^\infty e^{-A(D/d)} P(D) dD \quad (6.9) \]

and the following equation can be derived and using method of steepest descents (valid if \( D/d \gg 1 \)) to analyze its dependence on particle-monomer size asymmetry D/d:

\[ <\phi_s>_{p(D)} = \lambda \int_0^\infty e^{-A(D/d)} e^{\frac{(D-D_0)^2}{(2\sigma)^2}} dD = \lambda \int_0^\infty e^{-A(D/d)} e^{\frac{(D-1)^2}{(2\pi(D_0/d))\sigma^2}} d\bar{D} = \lambda \Omega(D_0/d,\bar{d},\bar{u}) = \lambda \int_0^\infty \phi(D_0/d,I) e^{\frac{(D-1)^2}{(2\pi(D_0/d))\sigma^2}} d\bar{D} \quad (6.10) \]

where \( \bar{D} = D/D_0 \) and \( \bar{u} = u/d \), Then

\[ \Omega(D_0/d,\bar{d},\bar{u}) = \omega_{\text{MAX}}(D_0/d,\bar{D}^* = -2A(D_0/d)\bar{u}^2 + 1,\bar{u}) = \exp[-A(D_0/d) + A^2(D_0/d)^2\bar{u}^2] \quad (6.11) \]

\[ \Psi(D_0/d,\bar{d},\bar{u}) = \psi_{\text{MAX}}(D_0/d,\bar{D}^* = 1,\bar{u}) = 1 \quad (6.12) \]

Thus,
\[
\ln[\langle \phi \rangle_{\ln(\Omega)}] = \ln[\lambda e^{-\frac{D_0}{\sigma^2}}] = \ln[\lambda e^{-\frac{d_0}{\sigma^2}}] = -\frac{D_0}{d} + (A^2 \sigma^2 + \ln \lambda) \quad (6.13)
\]

This simple analytic analysis qualitatively agrees with our numerical calculation (see Fig. 6.21(C)) which shows that on a log-linear plot, the slope for the averaged results are the same as the smooth HS filler, but the intercept increases as fluctuation magnitude squared. This behavior is the opposite of the results for the coherent fluctuation calculations, which show that the miscibility decreases as fluctuation amplitude increases.

So far, we have compared the two models for the matched size case, we now move to mismatched size cases. For the D/d=5 filler, we can also vary the bead size while keep D and d constant (see Fig. 6.22(A)). Despite the complicated trend observed for incoherent fluctuation cases, the trend for coherent fluctuation is simple. The spinodal solubility volume fraction drops as the fluctuation magnitude increases. This is least pronounced when monomer size is larger than bead size. We can then normalize the spinodal volume fraction by its value for smooth HS filler cases (see Fig. 6.22(B)) and explore the whole regime of mismatched size. The trend is similar to the one observed for the incoherent fluctuation cases but is more pronounced.

6.4 Role of Interfacial Cohesion

6.4.1 Particle-monomer pair correlation function

Fig. 6.23 shows some examples of the particle-monomer pair correlation function for N=72 particle \((D/\sigma = 5)\) with matched size \((d = \sigma)\) and various attraction strengths. We study both the frozen and fluctuating \((u = 0.25\sigma)\) cases. One can define a closest approach distance as the separation at which the pair correlation function vanishes. Physically, this is the smallest center of mass separation distance between a monomer and
a nanoparticle. i.e. \( \sigma_{pn} = (D + d)/2 \) for smooth HS filler system and rough fluctuating surface nanoparticle system because monomers can touch particle core while \( \sigma_{pn} > (D + d)/2 \) for rough, frozen surface nanoparticle system, for which there is surface geometry constraints due to corrugation. e.g. \( \sigma_{pn} = 0.636D \) for \( D/d=5 \) system where \( (D + d)/2 = 0.6D \). As surface attraction strength grows, the primary ordering peak shifts to smaller separation distance and has a larger magnitude, indicating a selection of length scales corresponding to maximum adsorption of monomers on nanoparticle surface. The stronger the attraction strength is, the more adsorption onto the particle surface occurs. Surface fluctuation competes against this length scale selection by making the primary peak broader and less pronounced. This effect is stronger as interfacial attraction increases.

### 6.4.2 Particle-particle potential of mean force

We investigate the impact of surface corrugation and fluctuation on the local “bridging” of fillers by polymer chains by answering the following three questions:

1. How does surface fluctuation modify “bridging” phenomena given the same static corrugation? Let us look at Fig.6.24(A). Here we present the PMF for fixed surface static corrugation \( D/\sigma = 5 \) (N=72). We find that no matter what regime one studies, i.e. contact clustering, steric stabilization or bridging, surface fluctuation induces more attraction in the same manner as in the athermal limit. The underlying physics is common, fluctuation smears out surface corrugation and reduces interfacial cohesion, leading to stronger depletion attraction.

2. How does the PMF vary with particle size? Based on the answer to question (1), we can answer this by studying frozen surfaces. In Fig.6.24(B) results for two
particle sizes are shown for similar attraction strength both in the local bead-monomer level and particle-monomer level. Similar as under athermal conditions, the larger the particle is, the stronger attraction the PMF shows. This is due to the size asymmetry induced depletion attraction.

(3) How can we make connections with the prior studies of smooth HS fillers? In smooth HS filler PNCs, there are only three length scales D, d and \( \alpha \), as well as one energy scale \( \varepsilon \). In frozen, rough filler PNCs, there are four length scales D, d, \( \sigma \) and \( \alpha_{mb} \), as well as one local energy scale \( \varepsilon_{mb} \). There is no unique way to map the entire interfacial attraction profile to smooth HS cases where only \( \alpha \) and \( \varepsilon \) matter. This is due to the active involvement of new length scales in the problem associated with surface corrugation and fluctuation. Using the “first contact distance” \( \sigma_{mn} \) as a borderline, the effective interaction between one particle and one monomer \( U_{mn}^{eff}(r) \) can be divided into left (\( r < \sigma_{mn} \)) and right (\( r > \sigma_{mn} \)) branches. When we change the local bead-monomer attraction strength \( \varepsilon_{mb} , \varepsilon_{mn} \) and the left branch will be modified. However, the right branch (or literally, the attraction branch) almost remains the same, meaning the “attraction range” on the particle-monomer level remains the same despite the variation of the local bead-monomer attraction range, i.e. \( \alpha_{mn} \approx \alpha = \text{const} \). For example, \( N=72 \) and \( D/d=5 \), and \( \alpha_{mb} = 0.5d \), we find \( \alpha_{mn} \approx \alpha = 0.546d \). However, this constant \( \alpha \) changes with particle size: for \( N=162 \) and \( D/d=7.8 \), \( \alpha_{mb} = 0.5d \) and \( \alpha_{mn} \approx \alpha = 0.558d \); for \( N=282 \) and \( D/d=10 \), \( \alpha_{mb} = 0.5d \) and \( \alpha_{mn} \approx \alpha = 1.245d \). We then can make two possible connections or “mappings” to smooth HS filler calculations (see Fig.6.24(C)): 
(1) Ignore the effect of the left branch and replace this with a hard core interaction and shift the entire potential profile so that the hard core interaction enters at $\sigma_{pn} = (D + d)/2$, i.e. we map the frozen surface $U_{mn}^{\text{eff}}(r, \varepsilon_{mb}, \alpha_{mb})$ to $U_{pn}(r, \varepsilon_{mn}, \alpha_{mn})$ and compare the PMF of the latter case with the frozen surface calculations.

(2) Use thermal energy to determine a new length scale $\sigma_{eff}$ and carefully choose an attraction range $\alpha_{eff}$ such that the total cohesion energy is the same as $U_{mn}^{\text{eff}}(r, \varepsilon_{mb}, \alpha_{mb})$ ($\alpha_{eff} > \alpha_{mn}$ since it also accounts for the contribution from the left branch) and shift the entire potential profile so that the hard core interaction enters at $\sigma_{pn} = (D + d)/2$, i.e. we map the frozen surface $U_{mn}^{\text{eff}}(r, \varepsilon_{mb}, \alpha_{mb})$ to $U_{pn}(r, \varepsilon_{mn}, \alpha_{eff})$.

Based on the two mapping methods described above, one can compute the potential of mean force for the rough spheres and their mapping counterparts based on the smooth HS filler model and compare them. No matter what mapping method we apply, we can always recover almost all features given there is a shifted length scale due to the ambiguity of defining closest contact distances. Despite the somewhat complicated nature of such mapping procedure, the more detailed mapping (i.e. using mapping 2 instead of 1) we apply to the potential, the better agreement in terms of the PMF between smooth and rough sphere mapping can be achieved. (see Fig.6.24(D))

### 6.4.3 Second virial coefficient

Fig.6.25(A) shows that in the intermediate attraction strength, steric stabilization regime, the dimensionless second virial coefficients are not sensitive to the surface fluctuation amplitude. However, for both the contact clustering and strong bridging regimes, $\bar{B}_2$ strongly depends on fluctuation magnitude and decreases (more attractive)
with increasing fluctuation amplitude. Fig.6.25(B) further confirms the above conclusion by showing a strong non-monotonic dependence on attraction strength that ranges from contact clustering \((\beta e_{mb} = 0)\) to steric stabilization \((\beta e_{mb} \in [0.25,0.75])\) to strong bridging \((\beta e_{mb} = 1)\).

6.5 Summary and Discussion

In this chapter, we have presented representative results based on a new minimalist multi-scale model for soft nanoparticle fillers. This is the first theoretical study of the role of nanoparticle morphology associated with surface corrugation and fluctuation at one and two particle limit in polymer melts with/without interfacial cohesion.

Our results provide a physical basis for the unexpected ability to disperse chemically matched crosslinked polystyrene in linear polystyrene melt. The surface corrugation in the frozen surface regime results in a favorable entropic driving force for mixing which competes with unfavorable depletion, resulting in a major enhancement of nanoparticle dispersion, including a much larger spinodal solubility limit. Smooth hard sphere behavior is recovered when the number of beads are significantly large (N=282) and the relative corrugation size significantly reduced (from 20% to 10% of particle size). When surface fluctuation exists, the dependence of solubility limit on fluctuation magnitude is somewhat subtle, due to the relevance of multiple length scales. We find fluctuation suppresses dispersion for all particles sizes (or surface curvature) studied, and this effect is most pronounced when the monomer size is smaller than corrugation size. The extreme coherent fluctuation model shows dramatically enhanced dependence on
fluctuation magnitude at large fluctuation magnitude and less miscibility. When interfacial cohesion exists, we develop a model for local bead-monomer level attraction, which explicitly connects to particle-monomer level attraction through potential mapping strategies. By varying the interfacial attraction strength, we can still observe all three regimes reported in prior PRISM studies of smooth HS filler PNCs. The steric stabilization regime is not sensitive to surface fluctuation magnitude, while the contact clustering and strong bridging regimes are very sensitive to surface fluctuation magnitude. Surface fluctuation smears out surface corrugation and reduces interfacial cohesion, leading to stronger depletion attraction and more negative second virial coefficients.

Recent SANS experiments show that the dispersion of crosslinked polystyrene nanogels (with diameters that range from ~5 nm to 7 nm or larger) in chemically matched dense polymer matrix of linear chain-like polystyrene (monomer size~1 nm) is possible [%]. We know this not true if the filler is smooth HS with no interfacial cohesion. So it is now natural for us to believe the surface corrugation and fluctuation plays a major role to achieve this “high” dispersion (nanoparticle concentration of 2 wt %). Our multi-scale model explicitly studies the surface corrugation and fluctuation and our hybrid approach proves the possibility to achieve dispersion and predicts the necessary conditions required (large surface corrugation and small surface fluctuation). Our predictions of the second virial coefficient can be tested via dilute filler SANS experiments, which are in progress at Oak Ridge National Lab. Apart from experiments, full computer simulations (using our multi-scale modeling) of such soft, interfacially rough nanoparticle PNCs can also be designed to test the major results reported in this chapter, e.g. the validity of incoherent
fluctuation model versus coherent fluctuation model, the reduction of miscibility as surface fluctuation increases, the dependence of miscibility on multiple length scales, etc.

This work presented here was performed in the dilute particle limit. A natural extension of this hybrid small scale MC simulation plus PRISM theory approach is the determination of the mixture structure and the spinodal phase diagram beyond the low filler volume fraction regime. Prior PRISM studies have found qualitatively new insights concerning structure and phase behavior, e.g. the identification of critical points and construction of full spinodal curves, from the dilute filler to dilute polymer limits [3]. The many body particle correlation effects are perhaps important for understanding miscibility when the mixture has a positive filler second virial coefficient and repulsive dilute filler limit potential of mean force. This is an indication that the system can undergo a collective bridging driven phase separation [3]. Fourier space partial collective density fluctuations are experimentally measurable using selective labeling scattering methods, which can determine the system miscibility from dilute to ultrahigh filler volume fractions. [4]

The present work serves as a starting point for the development of a predictive theory of multiple phenomena in real soft filler polymer nanocomposites, such as crosslinked nanogels, chemically manipulated colloidosomes, and also motivates further generalization of NMCT and NLE theories [5-7] to treat the role of surface morphology for slow dynamics of soft colloid suspensions like crosslinked microgels (as discussed in next chapter) and micelles formed by block copolymers, which also has an impenetrable core and an outer soft coronal layer.
6.6 References


[4] B. Anderson and C. F. Zukoski recent experiments


6.7 Figures

Fig. 6.1

Conceptual scheme: A schematic representation of the hybrid simulation-theory approach to study soft, interfacially rough and fluctuating filler polymer nanocomposites. We start from the smooth hard sphere filler, then add surface beads to model static surface corrugation. The static surface corrugation can be varied by changing the number of beads on the surface. Surface fluctuation is then added by allowing beads to fluctuate radially either in an incoherent or coherent manner to vary the “dynamic” surface corrugation.
Fig. 6. 2

Effective pair potential between nanoparticle and monomer are shown for various fluctuation magnitudes. Lines indicate polynomial fitting results.
Fig. 6. 3

Effective pair potential between two nanoparticles are shown for various fluctuation magnitudes. Lines indicate polynomial fitting results.
Effective pair potential between two nanoparticles and between one particle and one monomer is shown for various D/d at fixed $D/\sigma = 5$ (N=72 particle). Open symbols indicate the cross monomer-filler pair potentials. We vary D/d = 10, 5, 2.5 by varying $\sigma/d = 0.5, 1, 2$. 

Fig. 6. 4
Fig. 6. 5 (A)

The effective pair potential between nanoparticle (N=72) and monomer for frozen and fluctuating rough surfaces is shown as a function of particle displacement for various attraction strengths.
The effective pair potential between nanoparticle (N=282, D/d=10) and monomer for frozen and fluctuating rough surfaces is shown as a function of particle displacement for various attraction strengths.
The effective pair potential between nanoparticle and monomer for frozen and fluctuating rough surface non-dimensionalized by the corresponding local attraction strength are shown as a function of particle displacement.

Fig. 6. 5 (C)
The effective pair potential between nanoparticle and monomer for frozen and fluctuating rough surface non-dimensionalized by the corresponding local attraction strength are shown as a function of particle displacement.
Particle-monomer pair correlation function for the frozen surface is shown as a function of particle-monomer separation at fixed $D/\sigma = 5$ (N=72 particle) for various D/d. We vary D/d =10, 5, 2.5 by varying $\sigma/d = 0.5, 1, 2$. 

Fig. 6.6
Nanoparticle potential of mean force for the athermal case is shown for various D/d. Smooth hard sphere fillers calculations are also shown for reference.
Nanoparticle-monomer pair correlation function is shown as a function of separation distance for various fluctuation magnitudes for D/d=5.
Fig. 6.9 (A)

Nanoparticle potential of mean force for D/d=10 is shown as a function of particle separation distance for various fluctuation magnitudes. The monomer size is chosen to be half the surface corrugations size. Smooth HS result for the same size asymmetry (D/d=10) is also shown for comparison.
Nanoparticle potential of mean force for $D/d=5$ (solid) and $D/d=2.5$ (dash) is shown as a function of particle separation distance for various fluctuation magnitudes. The monomer size is chosen to be equal to or twice the surface corrugations size. Smooth HS results for the same size asymmetry ($D/d=5, 2.5$) are also shown for comparison.
Fig. 6.10

Negative of the dimensionless second virial coefficient is shown as a function of bead fluctuation amplitude for N=72 particle and various monomer sizes. Smooth HS calculation for the same size asymmetry is also shown for reference.
Fig. 6.11 (A)

Spinodal solubility limit volume fraction is shown as a function of beads fluctuation magnitude for N=72 particle and various monomer sizes. Smooth HS calculation for the same size asymmetry is also shown for reference.
Fig. 6. 11 (B)

Spinodal solubility limit volume fraction is shown as a function of bead fluctuation amplitude for N=72 particles and various monomer sizes. Smooth HS calculation for the same size asymmetry is also shown for reference.
Fig. 6. 11 (C)

Spinodal solubility limit volume fraction normalized by its smooth hard sphere value of the same size asymmetry is shown as a function of bead fluctuation amplitude for N=72 particles with varying monomer sizes.
Fig. 6. 12

Comparison of PMF for fluctuating spheres with $D/\sigma=5, 10$ for various fluctuation magnitudes.
Spinodal solubility limit volume fraction as a function of bead fluctuation magnitude for N=72, 162 and 282 particle. Smooth HS calculation for the same size asymmetry is also shown for reference.
Spinodal solubility limit volume fraction as a function of bead fluctuation magnitude for \( N=72, 162 \) and \( 282 \) particle. Smooth HS calculation for the same size asymmetry is also shown for reference.
Spinodal solubility limit volume fraction as a function of particle-monomer size asymmetry for various fluctuation magnitudes. Smooth HS calculation is also shown for reference.
Spinodal solubility limit volume fraction normalized by its smooth hard sphere value of the same size asymmetry is shown as a function of bead fluctuation magnitude for $d = \sigma$ with varying nanoparticle sizes.

Fig. 6. 15
Fig. 6.16

Comparison of nanoparticle PMF for rough hard spheres with $D/\sigma=5, 7.8, 10$ are shown.

Smooth hard sphere calculation is also presented for reference.
Fig. 6. 17

Nanoparticle PMF for $D/d=5$ with various surface corrugation sizes and fluctuation magnitudes as a function of particle displacement.
Fig. 6. 18
Spinodal solubility limit volume fraction normalized by its smooth hard sphere value of the same size asymmetry as a function of bead fluctuation magnitude for various bead-monomer size ratios.
Fig. 6. 19

The effective pair potential between two nanoparticles for the incoherent and coherent surface fluctuation models as a function of particle displacement.
Fig. 6. 20

Nanoparticle potential of mean force for D/d=5 as a function of particle separation for various fluctuation magnitudes for both the incoherent and coherent fluctuation models.
Spinodal solubility limit volume fraction normalized by its smooth hard sphere value of the same size asymmetry as a function of bead fluctuation magnitude for N=72, 162 and 282 particles. Results for both the incoherent and coherent fluctuation models are shown.
Fig. 6. 21 (B)

Spinodal solubility limit volume fraction as a function of size asymmetry for smooth HS and rough HS and various fluctuation magnitudes. Dashed lines indicate the coherent counterparts for the corresponding fluctuation magnitudes.
Fig. 6. 21 (C)

Spinodal solubility limit volume fraction as a function of size asymmetry for smooth HS and rough HS and various fluctuation magnitudes. Solid lines indicate results for the breathing smooth sphere models and dashed lines indicate the rough counterparts for the corresponding fluctuation magnitudes.
Fig. 6. 22 (A)

Spinodal solubility limit volume fraction as a function of bead fluctuation magnitude for D/d=5. Open symbols represent incoherent fluctuation cases, while solid symbols represent coherent fluctuation cases. Smooth HS calculation for the same size asymmetry D/d=5 is also shown for reference.
Fig. 6. 22 (B)

Spinodal solubility limit volume fraction normalized by its smooth hard sphere value of the same size asymmetry as a function of beads fluctuation magnitude for various bead-monomer size ratios and the coherent surface fluctuation model.
Nanoparticle-monomer pair correlation function for $D/d=5$ as a function of reduced separation for various surface attraction strength (black, red, green, blue: 0, 0.25, 0.75, 1) for frozen surface fillers. Smooth HS filler result (dash) is also shown for comparison.

Inset: The same calculations for fluctuating surface fillers ($u = 0.25\sigma$)
Nanoparticle potential of mean force for $D/d=5$ is shown as a function of particle separation for various attraction strength and fluctuation magnitudes.

Fig. 6. 24(A)
Fig. 6. 24 (B)

Nanoparticle potential of mean force for D/d=5 and 7.8 frozen surface model as a function of particle separation for various attraction strengths.
The effective interfacial attraction is shown as a function of particle displacement. The two smooth HS mappings are also shown for comparison. Mapping one (red): Hard core interaction at \( \sigma_{pn} = (D + d)/2 \) plus an exponential attraction with an attraction range \( \alpha_{mn} \) extracted from the right branch of \( U_{mn}^{\text{eff}}(r) \). Mapping two: Hard core interaction at \( \sigma_{pn} = (D + d)/2 \) plus an exponential attraction with an attraction range \( \alpha_{eff} \) extracted by maintaining the total cohesion energy, i.e. taking into account the effect of the left branch of \( U_{mn}^{\text{eff}}(r) \).
Fig. 6. 24(D)

Nanoparticle potential of mean force for D/d=5 frozen surface (rough HS) as a function of particle separation for various attraction strengths. The two smooth HS mappings are also shown for comparison.
Fig. 6. 24(E)

Nanoparticle potential of mean force for D/d=5 frozen surface (rough HS) as a function of particle separation for various attraction strengths. The smooth HS mapping is also shown for comparison.
Fig. 6. 25(A)

Dimensionless second virial coefficient as a function of bead fluctuation magnitude for N=72 particle and various attraction strengths.
Fig. 6. 25(B)

Dimensionless second virial coefficient as a function of attraction strength for N=72 particle and various bead fluctuation magnitudes.
Fig. 6. 25(C)

Dimensionless second virial coefficient as a function of attraction strength for N=72 and N=162 particles with frozen surfaces.
CHAPTER 7

MULTI-SCALE MODELING OF
SOFT COLLOID MELTS

7.1 Introduction

Novel polystyrene nanoparticles were synthesized by the controlled intramolecular crosslinking of linear polymer chains to produce well-defined single-molecule nanoparticles of varying molecular mass and particle sizes. [1] These nanoparticles are ideal to investigate the relaxation dynamics and rheology of high molecular mass polymer melts in the absence of chain entanglements. Kratky plots obtained from Small Angle Neutron Scattering (SANS) data show a shift toward particle-like nature with increasing molecular mass and crosslink density. The viscoelastic behavior of the particles in a 1-component liquid state was found to be strongly dependent on both the extent of intramolecular crosslinking and molecular mass (correlates with particle size), with a colloidal gel-like behavior at low frequencies evident for a large degree of crosslinking where the nanogels are compact. The low frequency elastic shear modulus, $G'$, grows as nanoparticle size, $D$, increases, in contrast to the well established behavior for hard colloids, where flocculated suspensions exhibit a modulus that scale inversely to the particle radius raised to a power of typically 2 or so [2,3]. For jammed particle systems at zero temperature, a scaling inversely proportional to the radius raised to the power of the system dimensionality [4] is present, i.e. $G' \propto k_B T / D^3$. These and other results suggest the presence of a secondary non-chain-
like mode of polymer dynamics relaxation, which is influenced by the total number of crosslinks in the nanoparticle.

Our perspective in applying the methods developed in Chapter 5 to dense suspensions of crosslinked nanogels is that although we still rely on center of mass level interparticle potentials, the multi-scale modeling enables us to explicitly study the role of particle size and crosslink density with regards to surface fluctuation or softness. This variable is buried in the models of many arm stars or Hertzian spheres because there is only one length scale, overall size. A melt or suspension of nanogels is an ideal system to utilize the two-length-scale bead-core model because the internal degrees of freedom indeed is not as relevant as the surface corrugation in the context of interparticle interaction.

This chapter is focused on the slow dynamics of dense soft colloidal suspensions based on the multi-scale modeling approach constructed in previous two chapters. Section 7.2 discusses the model, theories and definition of effective volume fraction. A study of the effect of particle size and surface fluctuation on mean alpha relaxation time and the kinetic arrest map is presented in section 7.3. An application of NLE theory of mechanical response to study the effect of particle size and surface fluctuation on linear shear modulus is established in section 7.4. The chapter concludes in section 7.5 with a summary and discussion. Section 7.6 and 7.7 present the references and figures, respectively.

7.2 Model, Theory and Effective Volume Fraction
7.2.1 Multi-scale modeling, effective interaction and connections to real crosslinked nanogels

We apply the theoretical approach developed in Chapter 5 to model soft, interfacially rough nanoparticles with corrugated and incoherent fluctuating surfaces. We use the same techniques used in Chapter 6 to calculate the effective interactions at center of mass level to mimic the interaction between two soft nanoparticles. Fig. 7.1 presents representative potentials for the frozen and most fluctuating surfaces studied for three particle sizes at fixed static surface corrugation. All cases show soft repulsive interactions and surface fluctuation makes it even softer. Large nanoparticles interact more like hard-sphere than small nanoparticles, i.e. the repulsion increases faster as one decreases the separation distance.

A natural question one may have is why we are doing this calculation given that we already performed calculations based on center of mass level interparticle potentials like Hertzian model? The answer is we indeed used Hertzian model at the center of mass level to capture the soft jamming, slow dynamics, and elasticity. But that model is based on viewing a microgel as an elastic smooth sphere. This renders it is impossible to a priori study the particle size dependence given it is the only length scale in the model which is subsumed in the volume fraction. This stands in contrast to real nanogels where there are site (monomer) level length scales. However, the Hertzian model does account for the fact that these nanoparticles are soft and deformable spheres and thus all “soft jamming” related properties appear to be qualitatively correctly captured. In this chapter, we take one step further towards a microscopic model, and view the nanogels as spheres with rough and fluctuating surfaces. We are not treating all sites level lengths scales due
to its complexity, but rather focus on the nanoparticle size and surface corrugation length scale which is directly related to interactions due to contacts, a key characteristic for dense suspension of microgels/nanogels.

7.2.2 Naïve MCT, NLE and Effective Volume Fraction

As discussed in Chapters 2, 3 and 4, suspensions of repulsive hard and soft spheres tend to kinetically arrest (vitrify) at very high volume fractions due to the local cage effect. This phenomenon has been theoretically addressed based on ideal mode coupling theory (MCT), and the beyond MCT barrier hopping nonlinear Langevin equation (NLE) approach. Glass formation is a consequence of strong interparticle ordering on the local cage scale. The signature of the latter is well developed solvation shells in the radial distribution function, or a large enough cage scale peak in the static structure factor.

Viewing the soft, interfacially rough spherical particles as effective colloids at the CM level, one can ask if they also form glasses, or at least show a dynamic crossover (the ideal MCT ‘‘transition’’) to transient localization and slow activated barrier hopping? We have explored this question by applying the well-documented CM version of naive MCT (NMCT) [5]. This methodology has been shown to accurately capture the soft jamming transition, slow activated dynamic and elastic properties for dense fluids of Hertzian spheres [6,7].

To connect with experiment and take into account the existence of geometric constraints due to bumpy particle surfaces requires some idea how the volume of one object can be defined. Moreover, the fluid volume fraction can take on values in excess of the hard sphere random close packing value due to soft repulsive particle overlap. Two
“local” length scales of a single particle follow directly from the hard core aspects of the interactions: (1) surface bead diameter, $\sigma$ and (2) core diameter, $D$.

For a fluid of such particles, there are multiple ways to define volume fraction, all motivated, more or less, by an effective diameter idea in analogy with the hard sphere fluid. In colloid science, the interparticle separation ($D_{\text{eff}}$) at which the effective interparticle potential equals zero or thermal energy is often used to define an effective diameter, and based on the latter an effective volume fraction:

$$\phi_{\text{eff}} = \rho_c \frac{1}{6} \pi D_{\text{eff}}^3$$  \hfill (7.1)

Despite the ambiguities of choosing the criteria to define the effective particle diameter [8], we find our conclusions are not qualitatively sensitive to the precise choice.

### 7.3 Effect of Particle Size and Softness on Mean Alpha Relaxation Time and Kinetic Arrest

Using Eq.(2.8) the mean barrier hopping time is computed as a function of surface fluctuation magnitude and volume fraction. All times are expressed in terms of the elementary short Brownian time scale, $\tau_s$. To make quantitative comparisons with experiment, we need to estimate the time unit, the elementary short Brownian time scale, $\tau_s$. This quantity is influenced by the complicated polymeric nature of nanogels. If we believe this short Brownian time corresponds to a polymer chain equilibrium time scale for the internal degrees of freedom to relax, then we can write:

$$\tau_s = D_s^2 / D_s$$  \hfill (7.2)
where $D_s$ corresponds to the short time diffusion constant and $D$ is nanoparticle size. Based on a Rouse model of unentangled polymer dynamics as a crude estimate of the global shape (confirmation) equilibration relaxation time, then

$$\tau_R = N_W^2 \tau_0$$  \hspace{1cm} (7.3)

$$D_s \sim \frac{D^2}{6\tau_R} \sim \frac{D^2}{6N_W^2 \tau_0}$$  \hspace{1cm} (7.4)

where $\tau_R$ is the Rouse time, $N_W$ is the number of monomers in a chain, and $\tau_0$ is the elementary Brownian time for monomers. Given the temperature for the experiments is at T~440K, one has $\tau_0 \sim 10^{-7}$ sec as the segment relaxation time. For polystyrene with a molecular weight of 100 kDa, given the styrene molar mass is 104.15 g/mol, $N_W = 1000^1$. As a result, the elementary short Brownian time is of order 1 sec.

Fig.7.2 presents the dimensionless mean hopping times as a function of volume fraction for a range of particle surface fluctuation magnitudes (u). Results are shown over a wide range of relaxation times (7 orders of magnitude, as relevant to typical experiments and simulations.). In real colloidal suspensions (and often simulations too), a relaxation time range of only typically 4-6 orders of magnitude can be probed, perhaps up to $\tau_{hop} / \tau_s \sim 10^2 - 10^5$ (roughly 100 sec to 1 day) which represents a practical threshold used to define kinetic vitrification consistent with the limitations of low frequency rheometers. Fig.7.2 shows the relaxation times generally grows with $\phi_{eff}$, and more weakly as they soften, i.e. u increases.

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$^1 N_W = \frac{\text{MolarMass(PS)}}{\text{MolarMass(S)}} = \frac{\text{MolecularWeight(PS)} \times N_A}{\text{MolarMass(S)}} = \frac{10^4 \times 1.66 \times 10^{-27} \times 6.022 \times 10^{23}}{104.15 \times 10^{-3}} \approx 10^3$
As the particle size increases at fixed local corrugation, the relaxation time also increases. In addition, the increment of relaxation time is getting larger as the fluctuation magnitude increases. We use $\frac{\tau_{hop}}{\tau_x} = 10^X$ $(X=2, 3, 4, 5)$ as a practical threshold to define kinetic vitrification volume fraction and construct the kinetic arrest map. As a result, at the same relaxation time threshold, the bigger particle undergoes a kinetic vitrification at a lower volume fraction. This trend of easier solidification for large particles is qualitatively consistent with the polystyrene nanogel melt experiments [1]. Moreover, the more fluctuating the surface is, the higher volume fraction the system is required to be kinetically arrested.

7.4 Effect of Particle Size and Softness on Linear Shear Modulus

The linear elastic shear modulus of the transiently localized system, $G'$, is computed using a standard Green-Kubo-like statistical mechanical formula (Eq.(2.12)). Fig.7.3(A) presents calculations of $G'$, in units of $k_B T D_2^{-3}$, as a function of effective volume fraction for 3 particle sizes and over a wide range of particle surface fluctuation magnitude, $u$. The growth of the modulus with effective volume fraction does not display any simple functional form over a wide range.

To make qualitative contact with nanogel experiments, based on our $D/\sigma = 5, 7.8, 10$ model systems (so $D = 5, 7.8, 10$ nm for a polystyrene-like $\sigma \sim 1$ nm), we note that the theory predicts that larger particle has a higher elastic modulus, agreeing with the nanogel melt experiment [1]. This modulus increase with soft particle size is considered to be related to primarily one factor [1]. The larger molecular weight (larger particle size) system is more ‘‘particle-like’’ in nature based on SANS experiments. We
believe that the more “particle like” can be interpreted as more “smooth hard sphere” like. The interaction range decreases, with harshness of the repulsive force growth as two nanogels collide, as particle size increases. This is physically understood in our model because if the corrugation size is fixed, then increasing particle size means less importance lies in the surface corrugation and thus more smooth-hard-sphere like behavior.

We can make quantitative estimations of $G'$. Take $D_{72} = 5nm$ and temperature $T=443K$ (reported particle size and temperature in [1]) and $\tau_{hop} = 10^3$ sec to define a kinetic glass, we can replot Fig.7.3 (A) in absolute unit. Based on Fig.7.3 (B), by enforcing the theory to recover the low frequency plateau value of elastic modulus for tightly crosslinked nanogels: $10^4$ Pa for 5nm particle, we find a volume fraction ranges (depending on the fluctuation magnitude, larger fluctuation magnitude corresponds to higher volume fraction) from 52% to 64%; and $3 \times 10^4$ Pa for 7nm particle, we find a volume fraction ranges from 47% to 55%. These volume fractions are typical for melt condition, so the interpretation seems plausible.

7.5 Summary and Discussion

In this chapter, we have applied the multi-scale model for soft nanoparticle developed in Chapter 5 and 6 to study the role of nanoparticle surface corrugation and fluctuation on the slow dynamics of dense suspensions. This methodology allows us to study the dependence on particle size, which can not be explicitly investigated in the simple models like Hertzian spheres [9] where only one length scale exists.
Our results provide a physical basis for the striking phenomena observed in the experiment of crosslinked polystyrene nanogel melts (with diameters that range from ~3 nm to 7 nm or larger). (1) Larger nanogel melts form soft solids easier and have larger low frequency shear modulus than smaller particles. This “counterintuitive” based on classic hard colloids is the consequence of two competing factors: the scale of stress storage $k_B T / D^3$ decreases with particle size but the “hardness” of interparticle repulsion increases.

We plan to combine the current advance with mechanical response theories to describe the shear rheology of soft glasses from our multi-scale perspective. Although polymer entanglement, osmotic deswelling etc. are not included in the model, it is still the first of its kind study that encodes the basic aspects of surface corrugation and fluctuation and extreme limiting cases of dynamic surface fluctuations. In particular, the Maxwell viscosity, defined as the product of elastic shear modulus and mean barrier hopping time (see Fig.7.4), shows an even more pronounced dependence on particle size. This is a direct result of the combination of the enhanced dependence on particle size for elastic modulus and alpha relaxation time.

### 7.6 References


[8] There is no unique way to define the effective diameter. We choose the thermal energy condition for all calculations but we also tried other definition, e.g. the separation distance where the potential is equal zero. No qualitative difference exists.

Effective pair potentials between two nanoparticles are shown as a function of particle separation distance for a frozen corrugated surface and fluctuating surface ($u = 0.25\sigma$ i.e. $\sqrt{\langle (r-R)^2 \rangle} = 0.17\sigma$ see Chapter 5) for three particle core sizes of the same surface corrugation size.
Fig. 7.2

Dimensionless hopping time is plotted against effective volume fraction for various particle sizes and fluctuation magnitudes. The four horizontal lines indicate four kinetic glass transition criteria.
Dimensionless elastic modulus is plotted against effective volume fraction (defined under $k_BT$ condition) for various particle sizes and fluctuation magnitudes.

Fig. 7.3 (A)
Fig. 7. 3 (B)

Elastic modulus is plotted against effective volume fraction (defined under $1 \ k_B T$ condition) for various particle sizes and fluctuation magnitudes. The two horizontal lines indicate the elastic modulus reported in experiment for 5nm and 7nm crosslinked nanogels [ ].
The Maxwell viscosity is plotted against effective volume fraction for various fluctuation amplitudes and three particle sizes.

\( \eta_{\text{Maxwell}} \) vs. \( \phi_{\text{eff}} \)

- \( \phi_{\text{eff}} = \frac{\pi D_{\text{eff}}^3}{6} \)
- \( D_{\text{eff}} \sim U_{\text{eff}} = k_B T \)
- \( u = 0, \text{ frozen surface} \)
- \( u = 0.0625 \sigma \)
- \( u = 0.125 \sigma \)
- \( u = 0.25 \sigma \)

Solid N=72 \( D/\sigma = 5 \)
Dash N=162 \( D/\sigma = 7.8 \)
Dot N=282 \( D/\sigma = 10 \)
CHAPTER 8

SUMMARY AND OUTLOOK

This dissertation has explored the key role of particle softness in two types of soft condensed matter systems of importance in materials science and engineering: dense suspensions of soft colloids and soft filler polymer nanocomposites. We attempted to do so at a microscopic, predictive, single-length-scale to multi-length-scale level.

Although the experimental studies of soft colloids and nanoparticles have been extensively carried out [1-8], unfortunately there has been little theoretical work done to understand the role of particle softness on equilibrium structure and slow activated dynamics. This statement has two aspects. The first concerns the way one models or quantifies particle “softness”, i.e. at the particle-particle interaction level or at the surface local interactions level. The second aspect deals with how one connects the interparticle interaction to equilibrium structure, and later to thermodynamics and activated dynamics. We have approached these aspects by combining the center-of-mass level pair potentials, either well established based on connecting polymer coils to hard spheres [9] (many arm stars interaction used in Chapter 3), or effectively mimicked with a one-length-scale continuum mechanics model [4] (Hertzian model used in Chapter 4), or our new multi-scale modeling method (our methodology developed in Chapter 5), with liquid state theory. The computed structure is used as input to either nonlinear Langevin equation theory to capture the slow activated dynamics (Chapter 2, 3, 4, 7), or the PRISM integral equation approach to describe dispersion properties (Chapter 5, 6) in polymer nanocomposites.
The first part of this thesis lies in the realm of glassy soft colloidal dynamics. We applied the single-particle NLE theory [10] of activated dynamics to study the role of particle softness in the context of dense suspension of either many arm stars [11] or microgel-like Hertzian spheres [12,13]. Such model soft particle systems are key tools to understand a wide variety of novel experimental phenomena that are labeled as “soft glasses”. We are able to qualitatively and quantitatively describe many such glassy features, such as: the alpha relaxation time in the activated hopping regime is a rich function of volume fraction and temperature, including approaching a maximum value at ultra-high volume fraction due to a soft jamming crossover that signals local packing disorder due to particle overlap. A kinetic arrest diagram is constructed, and its qualitative features agree with the dynamic crossover (MCT) analog. The isothermal dynamic fragility varies over a wide range, and soft particles are predicted to behave as strong glasses, as experimentally observed [1].

Below the soft jamming threshold, the shear modulus roughly follows a power law dependence on volume fraction with an apparent exponent that grows with repulsion strength. The shear modulus varies inversely with the transient localization length under all conditions studied. For the barrier and alpha relaxation time, to a first approximation these local properties are controlled by a single coupling constant determined by local fluid structure which quantifies the effective mean square force on a tagged particle. In contrast to the behavior of hard spheres, an approximately linear relation between the elastic modulus and activation barrier is predicted. This suggests a microscopic foundation for the often observed, in both thermal liquids and soft microgel suspensions, connections between a (relatively) short time/distance property and the long time/length
scale relaxation process [14]. For the Hertzian model, yield strains were found to be relatively weakly dependent on volume fraction and single particle stiffness for parameters relevant to typical microgel suspensions. Shear thinning is predicted to commence at Peclet numbers far less than unity, a signature of relaxation via stress-assisted activated barrier hopping. Power law thinning of the viscosity over many orders of magnitude of shear rate is generically predicted but with an apparent exponent smaller than unity. Approaching the soft jamming threshold, a nearly universal master flow curve can be constructed at fixed repulsion strength which exhibits a power law form over many intermediate orders of magnitude of reduced shear rate. The breadth and apparent exponent in this regime systematically increases and decreases, respectively, as repulsion strength and/or volume fraction grow.

Comparisons with available simulations and colloid experiments reveal at least qualitative agreement. In particular, we found the non-monotonic change of the primary peak of the pair correlation function, agreeing with both 2 dimensional microgel experiment and 3 dimensional Hertzian sphere simulation [2], indicating the so-called “soft jamming” transition. We also predict power law dependence of the elastic modulus below the “soft jamming” volume fraction and the apparent power law exponent is quantitatively close to experiment values. Above the “soft jamming” transition volume fraction, a generally weaker dependence emerges, which agrees with recent experiments on many arm stars (linear dependence) and microgels (weaker, some cases decreasing). The scaling collapse of the mean barrier hopping time is achieved by using simulation reported fitting parameters (Hertzian spheres). A general point is that by applying microscopic theory for activated barrier hopping with an intuitive picture of center of
mass level interactions between two soft particles, we have made concrete, structure-based connections with diverse glassy behaviors of dense suspensions of soft particles.

The second half of the dissertation studied the effective forces, equilibrium structure and dispersion properties of soft filler polymer nanocomposites. Here, it is not the interaction at particle scale, but rather the interaction and geometry constraints at the surface corrugation scale comparable to monomer length scale, that largely determine entropic depletion attraction between nanoparticles.

Multi-scale descriptions of polymer nanocomposites have been exceptionally challenging to formulate, largely because exactly including all the internal and external degrees of length scales exist in polymeric nanoparticles is too computationally massive and conceptually difficult for surface morphology. Early attempts to understand the thermodynamics of such nanocomposites relied on viewing the nanogel as a hard sphere, and the entropically unfavorable dispersion is offset by an enthalpy gain due to an increase in molecular contacts at dispersed nanoparticle surfaces as compared with the surfaces of phase-separated nanoparticles [7]. But this idea ignores the fact that the chemistry is matched, and the particle surface is corrugated and fluctuating on a scale roughly of order the monomer size. As such, a multi-scale modeling that explicitly studies the role of surface morphology is desirable.

The core of our theoretical advances combined the small-scale MC simulation with PRISM theory that accounts for the surfaces of such nanoparticles are corrugated and fluctuating. This allowed the construction of the first minimalist, but representative, multi-scale model that embeds the corrugation and fluctuation at the center-of-mass level interparticle potentials: a soft repulsive interaction. However, whereas the first part of the
thesis (Chapter 4) uses one-length-scale potential (obtained, for example, from continuum contact mechanics), this multi-scale modeling method allows for prediction of the particle size dependence of all structural and dynamical (briefly discussed in Chapter 7) quantities. Simple mappings are proposed between the rough HS filler (multi-scale) and smooth HS filler (one scale) PNCs, which enabled a connection between local surface interaction to three physical regimes in terms of bridging phenomena predicted by prior PRISM studies [15]. This approach surely provides a better microscopic description of real nanogel fillers.

Our results provide a physical basis for the unexpected ability to disperse chemically matched crosslinked polystyrene in linear polystyrene melt. The surface corrugation in the frozen surface regime results in a favorable entropic driving force for mixing which competes with unfavorable depletion, resulting in a major enhancement of nanoparticle dispersion, including a much larger spinodal solubility limit. Smooth hard sphere behavior is recovered when the number of beads are significantly large (N=282) and the relative corrugation size significantly reduced (from 20% to 10% of particle size). When surface fluctuation exists, the dependence of solubility limit on fluctuation magnitude is somewhat subtle, due to the relevance of multiple length scales. We find incoherent surface fluctuation suppresses dispersion for all particles sizes (or surface curvature) studied, and this effect is most pronounced when the monomer size is smaller than corrugation size. The (presumably) less realistic extreme coherent fluctuation model shows dramatically enhanced dependence on fluctuation magnitude at large fluctuation magnitude and less miscibility. When interfacial cohesion exists, we have developed a model for local bead-monomer level attraction, which explicitly connects to particle-
monomer level attraction through potential mapping strategies. By varying the interfacial attraction strength, one can still observe all three regimes reported in prior PRISM studies of smooth HS filler PNCs. Interestingly, the steric stabilization regime is not sensitive to surface fluctuation magnitude, while the contact clustering and strong bridging regimes are very sensitive to surface fluctuation magnitude. Surface fluctuation smears out surface corrugation and reduces interfacial cohesion, leading to stronger depletion attraction and more negative second virial coefficients.

With the advance of our multi-scale modeling of soft particles to treat two length scales, we use the effective interaction to revisit the problem of slow activated dynamics and elasticity of soft colloidal dense suspension in the context of the crosslinked nanogels, focusing on the particle size dependence. Our shear elastic modulus calculations are in qualitatively agreement with a recent experiment [8], in contrast with the well-known smooth HS result. The elastic modulus grows with increasing particle size, while for smooth HS suspensions the modulus is inversely proportional to the particle size cubed in three dimensions. We plan to combine this advance with mechanical response theories to describe the shear rheology of soft glasses from our multi-scale perspective. In particular, the shear viscosity shows an even more pronounced dependence on particle size, which is a direct result from the combination of the enhanced dependence on particle size for elastic modulus and alpha relaxation time. This and other questions provide directions for future research.

Our perspective in applying the multi-scale modeling developed in Chapter 5 to melt of crosslinked nanogels is that although we still rely on center of mass level interparticle potentials, the multi-scale modeling enables us to explicitly study the role of
particle size. The hope is that in the context of a two-length-scale center of mass potential, one can capture information about the whole crosslinked network with a coarse-grained description of hard spheres with corrugated beads that fluctuate incoherently. It is in this sense we expect the explicit studies on monomer scale interaction will make us one step closer to the real world nanogels.

Concerning possible future work, we note that single particle Brownian dynamics simulation solution of Eq.(2.6) have previously been successfully employed to establish the full trajectory level predictions of the nonlinear stochastic Langevin equation theory of activated hopping dynamics in glassy hard sphere suspensions and fluids [16]. This method can be used to explore the role of particle softness on the transport properties, incoherent dynamic structure factor and dynamic heterogeneities of systems composed of soft particles. Comparison of the results with experiments on many-arm stars and crosslinked microgels could be performed, e.g. self-diffusion in a suspension of multi-arm star 1,4-polybutadiene (267 arms) with an arm molecular weight of 4490 g/mol [17]. The experiment finds star self diffusive coefficients strongly decrease (but in a non-hard sphere colloid manner) as the particle concentration increases, which is linked to the strong increase of the viscosity [17]. The computed dynamical mean square displacement can also be compared to confocal measurements on repulsive microgels [18].

The results and advances discussed in Chapter 2, 3, 4, 7 set the stage for investigating more complicated situations for dense soft colloidal suspensions beyond the two basic system parameters, volume fraction and particle softness. For example, one can add short-range attractions of variable strength, or equivalently reduced temperature. For hard spheres, this problem has been addressed based on MCT and NLE theories [10],
simulations [19] and experiments [20]. Many interesting behaviors have been found, such as the emergence of gels and attractive glasses, a reentrant glass-fluid-gel transition, nonmonotonic diffusivity as a function of attraction strength, and two-step yielding [21]. Different from hard spheres, now another type of complexity exists. Attractions exist on the length scale of surface corrugation due to the polymeric nature of such soft particles. We know that for attractive spheres, high volume fraction is no longer a necessary condition to trap particles. As long as the attraction is strong enough, particles will be transiently localized due to bonding to neighboring particles. However, whether this physical bonding occurs on the particle length scale or on the surface corrugation length scale perhaps largely determines the strength of such bonding and thus may strongly modify the dynamic phase diagram.

Obtaining numerical converged solutions of PRISM theory for finite filler volume fractions is a challenge. Finding a better algorithm is crucial for wider applications of the PNC integral equation theory. If improved numerical methods work, then one can address many body effects on miscibility and calculate the scattering structure factors that can be compared with X-ray and neutron scattering data, and the phase diagrams can be constructed.

The investigation of filler surface corrugation and fluctuation of PNCs systems has already provided some guidelines to produce various desirable and undesirable equilibrium structural behaviors. Since the dynamics is largely dependent on structural input, we believe multi-scale modeling method can further provide guidance on the viscoelasticity of polymer nanocomposites, which is of great importance to industry. With stronger computational power, we can construct models that include more detailed
monomer level information. A possibly fruitful approach is to obtain effective interactions based on our multi-scale modeling method, and determine mixture structure, and input it to dynamical theories.

References


