RICE UNIVERSITY

Phase Equilibria, Microstructure, and Transport Properties of

Confined Colloid-Polymer Systems

by

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A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE

Doctor of Philosophy

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November, 2004
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ABSTRACT

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For two-dimensional geometries, computer simulations on a lattice based on the grand canonical Monte Carlo method, in combination with histogram reweighting and finite-size scaling, are used to determine the phase diagrams of colloid-polymer systems in which the colloids are modeled as hard spheres and the polymers as hard chains, and where an effective attractive interaction arises due to depletion effects. In contrast to the predictions of previous mean-field and other approximate theories, the nature of the coexistence phases is found to depend not solely on the polymer-to-colloid size ratio, but on the colloid diameter, the polymer radius of gyration, and the polymer monomer size. The threshold values of the polymer-to-colloid size ratio for the onset of liquid-liquid phase separation differ significantly from earlier predictions and from those of the corresponding three-dimensional systems. Extrapolation to the "protein limit" of very small colloid and very long polymer indicates that, in contrast to the case of three dimensions, immiscibility does not persist at this limit. The pair correlation functions, both positional and orientational, of the liquid and solid phases are determined
experimentally by video microscopy and image analysis for aqueous suspensions of colloids with nonadsorbing polymer. Finally the diffusion of colloids and polymer (bacteriophage \( \lambda \)-DNA) is studied experimentally by the same technique. The diffusivity of colloids as a function of polymer concentration exhibits a change of slope in the neighborhood of the overlap polymer concentrations.

For systems confined in one-dimensional channels, the colloid pair correlation function is determined experimentally as above. The diffusion of the colloidal particles is obtained by tracking individual colloidal particle and by determining their mean square displacement. For short times, the diffusion is of Brownian motion, Fickian type, with mean square displacement varying linearly with time. For long times, however, the mean square displacement is found to increase more slowly with time than linearly, in agreement with the theoretical prediction that diffusion in one dimension, in which mutual crossing of the particles is not possible, is non-Fickian and the mean square displacement increases as the square root of time. A crossover between short-time and long-time diffusion is observed, and is found to depend on the colloid and polymer concentrations.
Acknowledgements

The accomplishment of this thesis is the combination of the efforts of many people, in addition to myself. First of all, I would like to express my appreciation to my thesis advisor, Professor Marc A. Robert. His guidance and encouragement have inspired me to face many challenges not only in scientific research but also in life. I would like to express my gratitude to Professor Athanassios Z. Panagiotopoulos at Princeton University, for guiding me in computational studies of colloid-polymer systems and for his hospitality during my visit at Princeton University. I am grateful to Professor Clarence A. Miller and Professor Matteo Pasquali for the usage of their laboratory space and microscopy equipment. I thank Professor Clarence A. Miller and Professor Anatoly B. Kolomeisky for serving as my thesis committee members.

I thank Professor Li-Jen Chen for discussions and collaborations on the study of confined systems. I also appreciate Professor Walter G. Chapman’s helpful discussions on computer simulations. Next, I would like to thank all those who have helped me during this thesis: Professor Shi-Yow Lin for discussions on surfactants, Dr. Trinh T. M. Vo for discussions on computer simulations of colloid-polymer systems, and Elizabeth A. Lipke for help with the autoclave. I also thank Dr. Tai-Chou Lee for assistance and discussions on image analysis techniques, Joshua M. Mourot and Juan C. Araque Izaguirre for their support, and the undergraduate students who assisted me in the experimental work: Dana R. Pilaski, Steve M. Abel, Catherine Hoang, Chapman B. McDaniel, Prashant N. Setty, Laura E. Hall, Margot M. Herman, and Bruce C. Eng.

Next, I would like to express my thanks to the friends who have helped and supported me throughout, in particular: Elizabeth A. Lipke, Amanda G. Sekour, and Virginia A.
Davis. Their friendship, which I treasure most, made it much easier for me to adjust to the life style and studies in the United States. Many thanks to my friends Angela N. Hvitved, Damian E. Dalle Nogare, Marietta Buj, Inna A. Husain, Pei-Lun David Ting, Yi-Ju Wang, Chia-Hsing Tung, Lysandra Tarlow, Amanda Warwick, Bing-Hung Chen, Peggy Kuo and all the others from Rice University, National Taiwan University, and high school.

Finally, I express my deepest gratitude to my family, especially my parents, for their unconditional support and endless love, and my sisters and brothers for their encouragement. Also, I am very grateful to Ta Lin for his constant inspiration. I could not reach this far without them. This dissertation is dedicated to my family and to him.
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Chapter 1: Introduction

1.1 Background and Applications

Colloids are ubiquitous in many manufacturing processes and biological systems. They are studied and used in numerous fields such as analytical chemistry, physical chemistry, biochemistry and molecular biology, chemical manufacturing, materials science, environmental science, petroleum science, geology, imaging technology, coatings, cosmetics, food science, and household products [1]. Formulations of colloidal suspensions play important roles in product storage and processing.

Applications of colloids include microfluidic devices, protein crystallization, cataract prevention, synovial fluid remediation, photonic materials, polymer films, coatings, inks, colloidal nanoparticles for medical diagnosis, colloidosomes for drug encapsulation, cosmetics and foods.

For example, the eye lens cells constitute protein mixtures, named the crystalline proteins (α, β, and γ-crystallins). Under normal conditions, light passes through the lens and focuses on the retina. The formation of cataract results from the aggregation and microphase separation of the crystalline proteins. The aggregation of proteins creates a small cloudy area on the retina. Extensive attention [2-5] has focused on the studies of the phase diagrams of these proteins and of their mixtures. Polyethylene glycol (PEG) is a hydrophilic and nontoxic polymer, which appears to be a perfect candidate for a precipitation agent in protein crystallization and liquid-liquid partitioning of biomolecules [6, 7]. The driving force for the phase separation in these systems is the depletion attraction induced by the addition of nonadsorbing polymers in colloid
suspensions.

Clearly, a better understanding of depletion effects has a direct impact on controlling the stability and industrial yields in systems containing colloids. It is essential to investigate colloid-polymer systems at a fundamental level for optimizing these applications, and this requires in particular knowledge of colloid-polymer interactions, their microstructures and their phase behavior.

1.2 Interactions

Colloidal particles are large molecules with dimensions ranging from nanometers to micrometers. They are thus relatively large compared to solvent molecules, but still small enough to perform irregular Brownian motion when in solution. Unlike atoms, they are large enough to be tracked by optical microscopy.

The interactions between colloidal particles are generally divided into attractive and repulsive interactions. Attractive interactions, which may give rise to phase transitions of the liquid-vapor or liquid-liquid type, are considered to be destabilizing forces for colloidal dispersions. On the contrary, repulsive interactions, which keep particles apart and help molecules to disperse in solutions, are considered to be stabilizing forces [8]. Typically, the destabilizing attractive forces are of the van der Waals type, while the repulsive sterically stabilizing interactions and electrostatic interactions are two major interactions contributing to stabilization. The van der Waals forces arise from dipole or induced-dipole interactions between atoms, molecules and particles. Two models, the hard-sphere model and the Yukawa model, are typically used to describe steric and electrostatic stabilization, respectively. The repulsive hard-core interaction is due to the
increase in energy when the cores of two colloidal particles overlap:

\[
U_{\kappa}(r) = \begin{cases} 
0, & \text{for } r \geq \sigma_c \\
\infty, & \text{for } r < \sigma_c \end{cases},
\]

where \( r \) is the distance between the centers of the colloidal particles, and \( \sigma_c \) is the colloidal diameter.

The pair-interaction potential of charged colloidal particles is screened to some extent by the free ions in the solvent. This screened Coulomb potential, calculated by treating particles as points or spheres, can be expressed as a Yukawa potential \( \exp(-\kappa r)/r \), where \( \kappa \), the inverse screening length, measures the extent of screening. Screening is most effective for high concentrations of free ions. The van der Waals attraction and electrostatic repulsion are combined in the well-known DLVO theory of Derjaguin, Landau, Verwey and Overbeek [1, 8].

Apart from attractive and repulsive forces, new forces between colloidal particles arise in the presence of soluble polymer. The addition of soluble polymer to colloidal suspensions plays an important role for stabilization. In industrial manufacturing of inks and paints, for example, additives such as gelatin are widely used for stabilization. Stabilizing agents are charged polymeric molecules, which contribute both electrostatic and polymeric effects to stabilization. On the other hand, the addition of soluble nonadsorbing polymer to a colloidal dispersion can induce, under suitable conditions, an attraction between the colloidal particles. The pioneering work on this polymer-induced attraction is that of Asakura and Oosawa [9], which was further developed by Vrij [10]. Asakura and Oosawa modeled polymers as rigid spheres of radius of gyration \( R_g \). The
interactions between colloids in the absence of polymer and the interactions between colloids and polymers are assumed to be repulsive hard-sphere-like. Polymer-polymer interactions are ignored, and polymer molecules can thus interpenetrate each other freely.

This effective attractive interaction between colloids is due to the imbalance of osmotic force exerted by polymers, as illustrated in the following figure:

![Diagram showing depletion zones and effective attractive force between colloids.](image)

Fig. 1.1. The center of polymer molecules are excluded from depletion zones (hatched circles), leading to an effective attractive force between neighboring colloids.

When two colloidal particles approach each other closely, the depletion regions overlap. The strength of the depletion force depends on the osmotic pressure and the overlap cross-sectional area. In three dimensions, one has [10]:

\[
F_{\text{dep}} = -\Pi_p \frac{\partial V_{\text{overlap}}}{\partial r},
\]

\[
F_{\text{dep}} = \begin{cases} 
\infty & r < \sigma_c \\
-\frac{\pi}{4} (4\delta^2 - r^2) n_p k_B T & \sigma_c \leq r \leq \sigma_p + \sigma_c \\
0 & \sigma_p + \sigma_c < r
\end{cases}
\]

where \( F_{\text{dep}} \) is the depletion attraction induced by the polymer, \( \Pi_p \) is the osmotic pressure.
pressure of the polymer, and $V_{\text{overlap}}$ is the overlap volume of the depletion zones. If dilute, polymer acts as an ideal solvent, and the osmotic pressure can be expressed as a function of polymer concentration and temperature:

$$
\Pi_p = n_p k_B T,
$$

(1.4)

where $n_p$ is the number density of polymers and $k_B$ is Boltzmann’s constant. By integrating the depletion force, one obtains the depletion potential between colloidal particles in three dimensions [10]:

$$
U_{\text{dep}}(r) = -\eta_p k_B T \left( \frac{q+1}{q} \right)^3 \left[ 1 - \frac{3}{4} \left( \frac{r}{\delta} \right) + \frac{1}{16} \left( \frac{r}{\delta} \right)^3 \right],
$$

(1.5)

where $\eta_p = n_p \pi \sigma_p^3 / 6$ is the volume fraction of polymer, $q = \sigma_p / \sigma_c$ is the ratio of the polymer diameter of gyration ($\sigma_p = 2R_g$, with $R_g$ the radius of gyration) to the colloidal diameter, and $\delta = \frac{\sigma_c + \sigma_p}{2}$. The depletion potential and its range are seen to be dependent on the polymer concentration and the polymer-to-colloid size ratio. These effects are illustrated in Fig. 1.2. By increasing the polymer concentration, the depletion attraction can be strong enough to give rise to a phase transition of the condensation type, and thus to a phase separation into colloid-rich (polymer-poor) and colloid-poor (polymer-rich) phases.

The effective interaction potential can be expressed by combining a hard-core repulsive potential and the short-ranged attractive pair potential given above:

$$
U(r) = \begin{cases} 
\infty & r < \sigma_c \\
-\eta_p k_B T \left( \frac{q+1}{q} \right)^3 \left[ 1 - \frac{3}{4} \left( \frac{r}{\delta} \right) + \frac{1}{16} \left( \frac{r}{\delta} \right)^3 \right] & \sigma_c \leq r \leq \sigma_c + 2R_g \\
0 & r > \sigma_c + 2R_g
\end{cases}
$$

(1.6)
Fig. 1.2. Effects of size ratio and polymer concentration on depletion potential in three-dimensional systems.

The simplified model of Asakura and Oosawa assumes the polymer to behave like an ideal solvent and is thus only valid in the dilute regime. If the polymer concentration is increased to the semidilute regime, the above estimate of the osmotic pressure based on an ideal polymer solution is no longer valid, and consideration of effects of polymer concentration on osmotic pressure will be necessary to approximate the effective forces.
The second virial coefficient $B_2$, obtained from the derivative of the osmotic pressure:

$$\frac{1}{k_B T} \frac{\partial \Pi}{\partial \rho} = 1 + 2B_2 \rho + \cdots,$$  \hspace{1cm} (1.7)

yields the interaction potential $V(r)$ through the well-known statistical mechanical expression:

$$B_2 = 2\pi \int r^2 [1 - \exp(-\frac{V(r)}{k_B T})] dr,$$  \hspace{1cm} (1.8)

where $\rho$ is the particle number density. For hard spheres in three dimensions, $B_2$ equals four times the volume of a particle. Attractive forces will reduce the value of $B_2$. $B_2$ drops from positive to negative values with a significant increase of the attraction, and colloidal systems become unstable when $B_2$ is negative [11]. The interparticle interaction $V(r)$ can thus be obtained from the measurable second virial coefficient [12].

### 1.3 Phase Behavior

A number of researches, both theoretical and experimental [13], have shown the phase behavior of colloid-polymer mixtures to be highly sensitive to the strength and range of the depletion potential. In other words, the concentration of polymer and the size ratio of polymer to colloidal particles govern the phase diagram of these systems. Colloids will start to aggregate or even crystallize with the addition of sufficient polymer. Experimental results that show the crystallization of numerous globular protein solutions coincide with those of short-ranged hard spheres with an effective attractive potential [12, 14]. Theoretical investigations [15, 16] of attractive hard-sphere cores show qualitative agreement with experimental results [17]. Scaled-particle theory [18, 19] and
perturbation theory [20] were also used in investigations of colloid-polymer systems.

Calculations based on approximate theories predict [15, 16, 21] that when the polymer-to-colloid size ratio is smaller than 0.3, a solid phase can occur. From experiment, the lower size ratio of 0.24 produces coexistence of gas-liquid-crystal phases [13]. However, when the size ratio is greater than about 0.3, three-phase coexistence similar to that of gas, liquid and solid phases of simple materials becomes possible [13]. In monodisperse polymer solutions, if the range of attraction between colloidal particles is sufficiently large, fluid-fluid coexistence may also occur, apart from three-phase coexistence and gas-solid coexistence. All the above pertains to three-dimensional systems. Similar results should also apply to confined, two-dimensional systems, as indicated in a theoretical study of the present group [22]. For polydisperse polymer solutions, liquid-liquid coexistence is predicted to occur for appropriate colloid and polymer concentrations over a larger range than for monodisperse polymer solutions [22].

Finally, it is clear that at the limit of very large polymer-to-colloid size ratios, the so-called "protein limit", the above considerations of depletion effects are no longer valid, and the depletion attraction is expected to be significantly weakened or even to vanish [23, 24]. Correspondingly, at that limit, condensation (liquid-liquid phase separation) is expected not to occur. This conclusion is however contradicted by more recent calculations [25].

1.4 Colloid Solutions in Confined Geometries

With the rapid development of nanoscience and the potential of nanotechnology, the systems surfaces and geometries become increasingly important. For example,
fabrication of novel materials can be achieved by deposition of colloid suspensions on a patterned substrate [26]. The phase behavior and dynamic properties colloids change significantly in the presence of geometric confinement [27] such as patterned substrates [28-30], lipid bilayers, strong light fields, channels [31, 32] or slit pore structures [33]. The studies of colloidal solutions in confined geometry can help to obtain a better understanding of many physical, biological and chemical processes in which confinement plays an essential role.
Chapter 2: Computer Simulation Study of Phase Behavior of Colloid-Polymer Systems in Confined Geometries

2.1 Introduction

The phase behavior of confined systems has received much less attention than that of bulk, three-dimensional systems. One of the questions of greatest interest is how the phase behavior of confined systems differs from that of bulk unconfined, three-dimensional systems. According to the Kosterlitz-Thouless-Halperin-Nelson Young theory [34-38], a fluid in a confined geometry differs from its bulk, three-dimensional in analog that it shows continuous second-order transition from solid to liquid phases. In the absence of attractive interactions, only the melting-freezing transition is observed for both bulk, three-dimensional, and confined systems.

The nature of two-dimensional transitions is significantly different from that of three-dimensional transitions. In some cases, liquid-liquid phase separation can be suppressed when the fluids are restricted to small regions. On the other hand, capillary condensation occurs when bulk vapor is confined in pores [39]. As mentioned above, confinement alters the nature of the first-order transition, including condensation and freezing transition, and shifts them away from their values in the bulk. By adding hard-chain polymer in the present confined geometry, the tunable attraction potential induced by polymer, along with geometric confinement, give rise to a rich phase behavior of colloid-polymer systems.
2.2 Simulation Techniques

2.2.1 Grand Canonical Monte Carlo Ensemble

In order to study phase transitions and critical phenomena, it is crucial to choose a suitable ensemble to have strong order parameter fluctuations near critical points. The liquid-liquid phase transition is the main focus of the present study, and therefore strong density fluctuations are expected when the critical point is approached. The grand canonical ensemble provides the freedom for the number of particles to fluctuate such that the near-critical density fluctuations are observable. In contrast to other properties such as pressure and configurational energy, the chemical potential is difficult to obtain from simulations. However, the method proposed by Widom [40] offers a straightforward way to calculate the chemical potential in Monte Carlo simulation and Molecular Dynamics. The chemical potential can be determined as following:

\[ \beta \mu = -\ln \left( \exp \left( -\beta U_{\text{test}} \right) \right) + \ln \rho \]  \hspace{1cm} (2.1)

where \( \mu \) is the chemical potential, \( U_{\text{test}} \) is the energy experienced by a "test" particle placed at a random position and \( \rho \) is the density. The chemical potential can also be obtained by grand canonical Monte Carlo (GCMC) simulations which are compatible with Widom test particle insertions. GCMC simulations are performed at fixed volume \( V \) under periodic boundary conditions. The inverse "temperature", \( \beta = 1/k_B T \), and the chemical potential, \( \mu \), are specific to the simulation. Besides the random particle movements, the insertions and removals of particles are also implemented in GCMC simulations. The addition and annihilation of particles are performed and accepted according to the following probability criteria: [41]
\[ \varphi(N \to N+1) = \min \left[ 1, \frac{V}{N+1} \exp(-\beta \Delta E + \beta \mu) \right] \]  \hspace{1cm} (2.2) \\
\[ \varphi(N \to N-1) = \min \left[ 1, \frac{N}{V} \exp(-\beta \Delta E - \beta \mu) \right] \]  \hspace{1cm} (2.3)

where \( N \) is the number of particles in the system.

```plaintext
PROGRAM gcmc
  do icycl=1,ncycl
    ran=int(randf()*(npav+nexc))+1
    if (ran.le.npart) then
      call mcmovе
    else
      call mcexc
    endif
    if (mod(icycl,nsamp).eq.0)
      call sample
  enddo
end
```

Basic \( \mu \)VT Monte Carlo ensemble simulation
Perform \( n_{cycl} \) MC cycles
Displace a particle
Exchange a particle with the reservoir
Sample averages

Fig. 2.1. Basic grand canonical ensemble simulation algorithm. Subroutine `mcmovе` attempts to move a particle; subroutine `mcexc` attempts to exchange a particle with the reservoir, and subroutine `sample` samples quantities every \( n_{samp} \) simulation cycles [42].

### 2.2.2 Histogram-Reweighting Method

#### A. One-Component Systems

The histogram-reweighting method collects data of the probability distribution
function $P(N, E)$ of occurrence of $N$ particles in the simulation box with configurational energy value around $E$. The probability distribution function can be written as:

$$P(N, E) = \frac{\Omega(N, V, E) \exp(-\beta E + \beta \mu N)}{\Xi(\mu, V, \beta)},$$  \hspace{1cm} (2.4)

where $\Omega(N, V, E)$ is the microcanonical partition function and $\Xi(\mu, V, \beta)$ is the grand canonical partition function. The ratio of two microcanonical partition functions can be determined by the histogram data collected from two runs with different values of $N$:

$$\frac{\Omega_1(N_1, V, E_1)}{\Omega_2(N_2, V, E_2)} = \frac{P(N_1, E_1)}{P(N_2, E_2)} e^{\beta \mu (N_1 - N_2) -(E_1 - E_2)}$$  \hspace{1cm} (2.5)

On the other hand, a simulation run with different values of the chemical potential and temperature should give a new distribution function $P'(N, E)$, with

$$\frac{P'(N, E)}{P(N, E)} \propto e^{(\beta \mu' - \beta \mu)N - (\beta' - \beta)E}$$  \hspace{1cm} (2.6)

The rescaled relationship in Eq. (2.6) can only apply over a narrow range of temperatures and chemical potentials, since the initial simulation only provides meaningful results over limited ranges of particle numbers and energies. From Eq. (2.4), the entropy can be written in terms of the microcanonical partition function as:

$$S(N, V, E)/k_B = \ln \Omega(N, V, E) = \ln P(N, E) + \beta E - \beta \mu N + C_n$$  \hspace{1cm} (2.7)

where $C_n$ is a run-specific constant, with $C_n = \ln \Xi(\mu_n, V, T_n)$.

The reweighting method [43] introduced by Ferrenberg and Swendsen provides an efficient approach to make predictions in a broader range of particle numbers and energies by combining multiple runs. Given $R$ overlapping runs available for a system, the composite probability of $N$ particles and energy $E$ can be determined as follows:
\[ f(N, E; \mu, \beta) = \frac{\sum_{n=1}^{R} P_n(N, E) \exp[-\beta E + \beta \mu N]}{\sum_{m=1}^{R} K_m \exp[-\beta_m E + \beta_m \mu_m N - C_m]} \]  \hspace{1cm} (2.8)

where \( K_m \) is the total number of observations \( (K_m = \sum_{N,E} f_m(N, E)) \) for run \( m \). The run-specific constant \( C_n \), which is also known as "weight", can be calculated by iterations:

\[ \exp(C_n) = \sum_{E} \sum_{N} f(N, E; \mu_n, \beta_n) \]  \hspace{1cm} (2.9)

From Eqs. (2.8) and (2.9), the final value of \( C_n \) is determined when convergence is approached after imposing an initial guess. The Ferrenberg-Swendsen method guarantees that there is minimum deviation between observed and predicted histograms from the combined runs. Based on \( C_n \), all the thermodynamic properties such as density and configurational energy, can be calculated. The mean density \( \rho(\mu, \beta) \) and the mean configurational energy \( U(\mu, \beta) \) are expressed as:

\[ \langle \rho \rangle_{\mu, \beta} = \frac{1}{V} \sum_{E} \sum_{N} f(N, E; \mu, \beta) N \]  \hspace{1cm} (2.10)

and

\[ \langle U \rangle_{\mu, \beta} = \sum_{E} \sum_{N} f(N, E; \mu, \beta) E \]  \hspace{1cm} (2.11)

To illustrate this problem further, consider one-dimensional histogram with fixed temperature. Eq. (2.4) can be simplified to:

\[ P(N) = \frac{Q(N, V, \beta) \exp(\beta \mu N)}{\Xi(\mu, V, \beta)} \]  \hspace{1cm} (2.12)

When two runs with respective chemical potentials \( \mu_1 \) and \( \mu_2 \) overlap over a range of
values of $N$, the function $\ln P(N) - \beta \mu N$ is related to the Helmholtz energy by:

$$\beta A(N, V, \beta) = -\ln Q(N, V, \beta) = \ln P(N) - \beta \mu N + C$$  \hspace{1cm} (2.13)$$

The information given by these two runs can be composed by shifting the data by the amount indicated with arrows in Fig. 2.3. The shifts in Fig. 2.3 are determined by an optimization method [44].

Fig. 2.2. Schematic diagram of probability of the occurrence of $N$ particles in two GCMC runs with different chemical potentials $\mu_1$ and $\mu_2$ for the same volume $V$ and temperature $T$ [45].
Fig. 2.3. The function $\ln P(N) - \beta \mu N$ for two runs of $\mu_1$ and $\mu_2$. The composite curve is obtained by shifting the data by the amount indicated by the arrows [45].

B. Multi-Component Systems

For a multi-component system, the histogram method is comparable to that for one-component systems. GCMC simulations are performed at fixed temperature $T$ and volume $V$ with chemical potentials $\mu_1$ and $\mu_2$ for the respective components. The numbers of particles $N_1$ and $N_2$ fluctuate during the course of the simulation. The histogram information is collected from each single run, and thereby the probability
distribution function for a given configurational energy and particle numbers \( N_1 \) and \( N_2 \) is written as:

\[
P(N_1, N_2, E) = \Omega(N_1, N_2, V, E) \exp\left[\beta(\mu_1 N_1 + \mu_2 N_2 - E)\right] / \Xi(\mu_1, \mu_2, V, \beta)
\]

Here the grand canonical partition function is given by

\[
\Xi(\mu_1, \mu_2, V, E) = \sum_{N_1, N_2} \frac{1}{N_1! \Lambda_1^{3N_1}} \frac{1}{N_2! \Lambda_2^{3N_2}} \times \exp\left[\beta(\mu_1 N_1 + \mu_2 N_2) \int d\mathbf{r}^N_{N_1+N_2} \exp\left[-\beta E(N_1 + N_2)\right]\right]
\]

where \( \Lambda_i = \sqrt{\hbar^2 / 2\pi m_i k_b T} \) is the de Broglie wavelength of particle of type \( i \). The dimensionality of the histogram increases from two to three as an additional component appears. The three-dimensional histogram arrays radically enhance the memory required for storage of data. Because it is computationally impractical to store large quantities of sampling data, the sampling of data should be implemented less frequently to ensure computational efficiency. Hence, sampling of histogram should only be exercised for essential simulation runs.

### 2.2.3 Critical Universality and Scaling Methods

Simple systems such as one-component simple fluids typically undergo phase transitions when the temperature goes below the critical temperature. At low temperature, the systems become more ordered. Second-order phase transitions have received much attention, in particular due to the similarity of criticality in widely diverse systems. In the vicinity of critical points, all simple fluids share the same, so-called universal critical behavior; which is identified as the Ising universality class.
Universality means that the critical behavior does not depend on the details of the systems, but only on general features such as dimensionality. Different physical systems such as the Ising ferromagnet and liquid-gas systems actually share the same critical exponents, which are the exponents measuring the nature of the thermodynamic singularities at the critical points. The universal behavior stems from the fluctuations of densities near the critical points, which extend over very large distances, so large that the details of the systems become irrelevant.

Another parameter, the order parameter, such as the magnetization and difference in concentrations (densities) of the coexisting phases in simple ferromagnets and simple fluids, respectively, is introduced to describe the critical behavior.

When a critical point is approached, the correlation length of the spontaneous fluctuations grows extremely large and usually exceeds the linear system size $L$ of the simulation box [46]. The mixed-field finite-size scaling method has proved efficient for determining critical parameters for fluids without special symmetries. The critical behavior at the thermodynamic limit is characterized by its singularities and discontinuities, and typically the critical parameters shifts in finite-sized systems such as those studied in computer simulations. Systems with short-ranged interactions are in the Ising universality class and are expected to exhibit the same critical exponents as those of the Ising model of a ferromagnet. The infinite-volume critical parameters of a system can be extracted by examining the size dependence of the thermodynamic observables with finite-size scaling theory.

The finite-size scaling computer simulation method [47] is based on performing a series of GCMC simulations in the vicinity of the expected critical point. The resulting
histograms are combined according to Eqs. (2.8) and (2.9) to obtain self-consistent estimates of the probability distributions \( P(N, E; \mu, \beta) \). Finite-size scaling is based on two relevant scaling fields, \( \tau \) and \( h \), where \( \tau \) is the thermal scaling field and \( h \) is the ordering scaling field. The scaling operators \( \varepsilon \) and \( M \) are conjugate to the scaling fields \( \tau \) and \( h \), respectively, and therefore the scaling operator \( M \) is also called the ordering operator. In the Ising model, \( \varepsilon \) is the energy density and \( M \) is the magnetization. For a fluid which does not possess the symmetry of the Ising model, the thermal operator \( \varepsilon \) and ordering operator \( M \) are linear combinations of the number of particles \( N \) and the total configurational energy \( E \):

\[
\varepsilon \propto E - rN, \quad M \propto N - sE, \quad (2.16)
\]

where \( r \) and \( s \) are the field-mixing parameters controlling the degree of the coupling between number and energy density fluctuations near the critical point. For multicomponent systems, an extra field-mixing parameter is introduced for every extra component.

\[
M \propto N_1 - sE - qN_2. \quad (2.18)
\]

The normalized probability distribution \( P_L(x) \) for a given system size \( L = V^{1/3} \) follows a universal shape \( x = A(M - M_c) \). The case-specific constant \( A \) and the critical value \( M_c \) of the ordering operator are assigned to yield zero mean and unit variance. The apparent critical temperature \( T_c(L) \) and critical density \( \rho_c(L) \) of a finite-size system deviate from their infinite-system values \( T_c(\infty) \) and \( \rho_c(\infty) \). The critical behaviors of the critical temperature and density follow scaling relationships with respect
to the simulated system size $L$:

$$T_c(L) - T_c(\infty) \sim L^{-(\theta+1)/\nu}$$

$$\rho_c(L) - \rho_c(\infty) \sim L^{(d-1)/\nu} = L^{(1-\alpha)/\nu},$$

(2.19)

where $\theta$, $\nu$ and $\alpha$ are, respectively, the correction-to-scaling exponent, the correlation length exponent and the exponent associated with the heat capacity divergence. The critical exponent values for three-dimensional systems are $(\theta, \nu, \alpha) \approx (0.54, 0.629, 0.11)$ and $(\theta, \nu, \alpha) \approx (0, 1, 0)$ for two-dimensional systems [48].

### 2.3 Simulation Model

In the present work, the colloids and polymer are modeled as hard-sphere particles and hard-sphere chains, respectively. The simulations are performed on lattices, and in order to imitate more closely behavior in the continuum, as well as to describe a high polymer flexibility, the colloid diameter is chosen sufficiently large, and the coordination number is chosen to be 26. The colloid diameter is chosen to be larger than one unit lattice spacing, and the monomer size of the polymer is taken equal to one unit lattice spacing.

By reducing the length of the three-dimensional simulation box along one dimension to slightly more than a colloid diameter, and by replacing periodic boundary conditions with reflecting (hard) walls, colloid particles become confined into a quasi two-dimensional geometry, that of a slit pore. Box sizes of $L \times L \times L_z$ are used, where $L_z < L$ measures confinement in the $z$ direction. A typical configuration of colloids and polymers in the simulation cell is illustrated in Fig. 2.4.
Fig. 2.4. Typical configuration of a colloid-polymer mixture in a quasi two-dimensional cell.

2.4 Results

2.4.1 Validation of Simulation Codes

In order to have a reasonable number of molecules in the simulation box, $L$ is set to 60 for $\sigma = 7.071$, and to 40 for a smaller colloid diameter, respectively. The codes are first tested for pure colloid hard spheres in confined and bulk systems, in which system pressure as a function of colloid reduced density is examined, and good agreement for the phase diagram is found between these test results and those of previous studies [49]. Moreover, the difference between the values of the pressure for different box sizes proves
to be negligible (see Fig. 2.5).

Fig. 2.5. Pressure vs. dimensionless density ($\rho_0 = N\sigma^3/V$) for confined hard spheres.
2.4.2 Density Profiles

The study of confinement effects in colloid-polymer systems conveniently begins with the comparison of density profiles of colloids and polymers as a function of the dimensionless coordinate \( z/L_z \). Gap sizes of \( L_z=10 \) and \( L_z=16 \) are chosen for the colloid diameter \( \sigma = 7.071 \) and the polymer chain length is \( n=60 \) (see Fig. 2.6). In the present lattice models, the colloid positions are restricted to discrete lattice sites. When the gap size \( L_z \) is reduced from 16 to 10, the number available discrete \( z \) positions for the colloids drop from 9 to 3. In both cases, the colloid densities are seen to be highest near the walls, as is well known to typically occur for confined fluids [27]. When further reducing the gap size to \( L_z=4 \), with a colloid diameter \( \sigma = 2.828 \) and a polymer chain length \( n=47 \), the colloids are restricted to a single position.

In contrast to the situation in the continuum, the colloid particles are slightly shifted away from the walls due to the lattice constraint. In this work, the gap size is chosen to be \( 1.414 \sigma \). While the colloids are limited to monolayer, polymer monomers (with size of one unit lattice spacing) still have the freedom of forming multiple layers inside the slit pore.
Fig. 2.6. Density profiles of colloids as a function of the coordinate $z/L_z$ normal to the walls for $L_z=4$ to 16.

Fig. 2.7 illustrates the density profiles of the polymer center of mass along the gap direction $z$. For small gap sizes such as $L_z=4$ and 10, single layer distributions of polymers prevail. When the gap size is increased to $L_z=16$, multiple layers of polymers start to form. Polymer molecules show the largest density at contact with the walls only
when the gap is large enough to allow sufficient overlap of polymers. As seen in Fig. 2.8, which shows the density profiles for different concentrations of colloids and polymers for $L_z=16$, both species tend to stay near the walls, leading to the layering of liquid.

Fig. 2.7. Density profiles of polymers as a function of the coordinate $z/L_z$ normal to the walls for $L_z=4$, 10, and 16.
Fig. 2.8. Density profiles $\rho_i \sigma_i^3 \pi / 6$, $i=c, p$ for colloid and polymer, respectively as a function of the coordinate $z/L_z$ normal to the walls for $\sigma = 7.071$, $n = 60$ in $L_z = 16$, where $\sigma_p = 2R_g$, $\rho_c = 9.11 \times 10^{-4}$, $\rho_p = 9.28 \times 10^{-4}$ for state 1 and $\rho_c = 7.84 \times 10^{-4}$, $\rho_p = 1.24 \times 10^{-4}$ for state 2.
2.4.3 Radius of Gyration of Polymer

The size of polymer chains is characterized by the radius of gyration, $R_g$, which scales with the number $n$ of polymer segments as [50]:

$$R_g \sim n^{\nu_F}$$  \hspace{1cm} (2.20)

where $\nu_F$ is the Flory exponent. The values of $\nu_F$ equal 0.5 and 0.6 in three dimensions for ideal polymers and polymer with excluded volume effects, respectively. For bulk three-dimensional systems, extensive studies have been conducted on the radius of gyration in different concentration regimes. When the concentration of the system increases, polymers start to interpenetrate each other, and the radius of gyration decreases. As the semi-dilute regime (polymer critical overlap concentration) is reached, $R_g$ is independent of the degree of polymerization and is dominated by the correlation length $\zeta$. The correlation length measures the average spatial distance between two neighboring polymer entanglement points.

According to Flory-Huggins theory, the values of $\nu_F$ for three-dimensional and two-dimensional at the low density limits are 0.588 and 0.75, respectively. In three-dimensional systems, the scaling of the polymer radius of gyration with the polymer chain length is determined in the presence and absence of colloids (see Fig. 2.9). In the absence of colloids, the value of $\nu_F$ for polymer chain lengths $n \geq 24$ at dilute concentration is 0.5838, which agrees well with the theoretical predicated value of 0.588. In the presence of colloids, the accessible volume for polymer decreases and the value of $\nu_F$ drops to 0.5472, which indicates the reduction of excluded volume effects due to the presence of colloids. It signifies that the solvent quality worsens with the addition of
colloids. Therefore, polymers exhibit more attractive interactions in the presence of colloids.

![Graph showing scaling of polymer radius of gyration versus polymer chain lengths with and without colloids.](image)

Fig. 2.9. Scaling of polymer radius of gyration versus polymer chain lengths with, and without colloids.

In the present work, the polymer chains are confined in quasi two-dimensional geometries. The radius of gyration of the polymer is calculated based on the projection on the xy-plane as:
\[ R_g = \sqrt{R_{gx}^2 + R_{gy}^2} \]  \hspace{1cm} (2.21)

The values of the radii of gyration for each polymer chain lengths are determined at infinitely dilute concentrations. Gap sizes of \( L_z = 10, 6, \) and \( 4 \) are considered. The values of \( \nu_F \) in Eq.(2.20) for different gap sizes are listed in Table 2.1.

Table 2.1. Flory exponent \( \nu_F \) for different gap sizes.

<table>
<thead>
<tr>
<th>( L_z = 60 ) (3D)</th>
<th>( L_z = 10 )</th>
<th>( L_z = 6 )</th>
<th>( L_z = 4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu_F )</td>
<td>0.584 ( \pm ) 0.001</td>
<td>0.68 ( \pm ) 0.01</td>
<td>0.71 ( \pm ) 0.01</td>
</tr>
</tbody>
</table>

By further reducing the gap space to a pure two-dimensional surface, the scaling of the polymer radius of gyration was found to be \( 0.74 \pm 0.02 \) in a previous study [51]. These findings agree well with the theoretical prediction of 0.75. As found in [51], the Flory exponent \( \nu_F \) for quasi two-dimensional systems increases as the cutoff polymer chain length increases. This is because the quasi two-dimensional geometry exhibits more two-dimensional-like character for longer polymers.

2.4.4 Phase Behavior

It is well known that when thermal systems are confined, the critical temperature typically shifts to lower values [27, 52]. In the present study of athermal systems, the role of temperature is played, in accord with intuition, by the inverse polymer concentration. It is thus observed (see Fig. 2.10), also in accord with experiment, that the critical point shifts to higher polymer concentration upon the reduction of the gap size.
Fig. 2.10. Phase coexistence of the quasi two-dimensional colloid-polymer system with

\[ \sigma = 7.071 \text{ and } n = 60 \text{ for } L_z=10 \text{ to } 60. \]

Two parameters, to wit the polymer-to-colloid, and the colloid-to-monomer size ratios, are varied. The effect on the phase diagram of the polymer-to-colloid size ratio is investigated by respectively fixing the colloid diameter at 2.828, 4.243 and 7.071, and by varying the polymer chain length. The latter is varied from \( n = 30 \) to \( n = 200 \). Unlike
in the three-dimensional systems studied in our group by T. T. M. Vo [53], liquid-liquid coexistence does not occur for short polymer chain lengths such as $n = 30$ or $n = 40$. Fig. 2.11 shows the phase coexistence curves for a colloid diameter of 7.071 and for various polymer chain lengths. A liquid-solid phase transition emerges at a colloid volume (area) fraction of 0.89, and the liquid-liquid phase transition vanishes at a colloid volume (area) fraction of 1.03. For the polymer chain lengths $n = 30$ and $n = 40$, a liquid-solid transition occurs. By increasing the polymer chain length, a liquid-liquid transition emerges at a polymer chain length of 50 ($q = 1.245$). This threshold value of $q$ is larger than that found in three dimensions [53]. In contrast to the large variation of the threshold value of $q$ found in three-dimensional systems for different colloid diameters [53], the threshold value does not depend strongly on the colloid diameter in quasi two-dimensional systems (see Table 2.2). Liquid-liquid phase separation into colloid-rich and colloid-poor phases is observed up to a polymer chain length of 200. Equilibration times become impractically long for longer polymer chains.

The excluded volume interaction between polymers becomes more significant as the chain length increases (see Figs. 2.11-2.12). In Fig. 2.11, the polymer concentration, which is the volume concentration ($\eta_p = \frac{n_p N}{V}$) and accounts for the actual lattice space occupied by polymer monomers, decreases as the chain length increases. However, a different trend is observed using the variable $\rho_p R_g^2$ in place of $\eta_p$. This is caused by the strong excluded volume effects for longer polymer chains. As the chain length increases, the number of polymers required to induce liquid-liquid phase separation decreases, resulting in the decrease of polymer critical volume fractions. On the other hand, the polymer chains swell in the simulation box, yielding a large radius of gyration
due to the strong excluded volume effects. Fig. 2.11 shows the actual monomer volume fraction, and Fig. 2.12 indicates the volume occupied in terms of the polymer radius of gyration. For polymer chain lengths equal to or shorter than 100, the critical polymer volume fraction still lies in the dilute regime. However, it exceeds the polymer overlap concentration for $n=200$, as the semi-dilute regime is entered, in which the radius of gyration of the polymers is overestimated.

![Graph](image)

**Fig. 2.11.** Phase coexistence curves for quasi two-dimensional colloid-polymer systems with $\sigma=7.071$ and various $n$, for $L_z=10$. The hatched lines denote tie-line.
Fig. 2.12. Phase coexistence curves for quasi two-dimensional colloid-polymer systems with $\sigma=7.071$ and various $n$, for $L_z=10$, using the variable $\rho_p R_g^2$ in place of $\eta_p$ (See Fig. 2.11). The hatched lines denote tie-line.
Table 2.2. Dependence of nature of phase coexistence on $q$ and $\sigma$ in quasi two-dimensional systems. L-L denotes liquid-liquid coexistence and L-S liquid-solid coexistence.

<table>
<thead>
<tr>
<th>$\sigma$</th>
<th>L-L or L-S</th>
<th>L-S</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.828</td>
<td>$n \geq 10$</td>
<td>$n \leq 5$</td>
</tr>
<tr>
<td></td>
<td>$q \geq 1.216$</td>
<td>$q \leq 0.778$</td>
</tr>
<tr>
<td>4.243</td>
<td>$n \geq 25$</td>
<td>$n \leq 18$</td>
</tr>
<tr>
<td></td>
<td>$q \geq 1.400$</td>
<td>$q \leq 1.131$</td>
</tr>
<tr>
<td>7.071</td>
<td>$n \geq 50$</td>
<td>$n \leq 40$</td>
</tr>
<tr>
<td></td>
<td>$q \geq 1.245$</td>
<td>$q \leq 1.078$</td>
</tr>
</tbody>
</table>

For a colloid diameter of 4.243, the polymer chain length is taken to be 25, 53, 85 and 166 (see Figs. 2.13-2.14), and for a colloid diameter of 2.828, it is taken to be 10, 35, 47, 73 and 137 (see Figs. 2.15-2.16). While the colloid diameter changes, the corresponding gap size is varied as well, in order to maintain a gap-colloid size ratio of 1.414. For these colloid diameters of 4.243 and 2.828, both the colloid and polymer critical volume fractions decrease as the polymer chain length increases. This is analogous to the trend observed in three-dimensional systems for a colloid diameter of 7.071 [53, 54]. The shift of the critical points exhibits the same trend for a colloid diameter of 7.071 as the polymer concentration is changed.
Fig. 2.13. Phase diagrams of quasi two-dimensional colloid-polymer systems with $\sigma=4.243$ and various $n$ for $L_z=6$. 
Fig. 2.14. Phase diagrams of quasi two-dimensional colloid-polymer systems with

\[ \sigma = 4.243 \text{ and various } n \text{ for } L_z = 6. \]
Fig. 2.15. Phase diagrams of quasi two-dimensional colloid-polymer systems with $\rho = 2.828$ and various $n$ for $L_z = 4$. 
Fig. 2.16. Phase diagrams of quasi two-dimensional colloid-polymer systems with $\sigma = 2.828$ and various $n$ for $L_z = 4$ using the variable $\rho_p R_g^2$ in place of $\eta_p$. 
In order to investigate the effect of the colloid-to-monomer size ratio on the phase diagrams further, the projection of the polymer radius of gyration on the xy-plane is fixed, while the colloid diameter as well as the corresponding gap length is varied. In order to maintain a fixed radius of gyration when the gap size is varied, the polymer chain length is correspondingly adjusted. The colloid diameter is also adjusted in order to maintain a quasi two-dimensional geometry with the same colloid-to-gap size ratio. The values obtained for the radius of gyration of the polymer agree well with those found in previous work [55].

Three radii of gyration, \( R_g = 4.94, 6.92, \) and 11.66, are considered. For \( R_g = 4.94 \), simulations are performed for colloid diameters of \( \sigma = 2.828, 4.243, 7.071, \) and 11.314, with corresponding polymer chain lengths of 47, 53, 60, and 64, respectively. By reducing the colloid diameter at fixed polymer radius of gyration, another phase diagram is established for various polymer-to-colloid size ratios. For a colloid diameter of 11.314, which yields a polymer-to-colloid size ratio of 0.87, the only phase transition found is the liquid-solid one (Fig. 2.17). The same behavior is shown in Fig. 2.11 for a colloid diameter of 7.071 and polymer chain lengths of 30 and 40.
Fig. 2.17. Phase diagrams of various quasi two-dimensional colloid-polymer systems with \( R_g = 4.94 \).
Fig. 2.18. Phase diagrams of quasi two-dimensional colloid-polymer systems with $R_g = 4.94$ using the variable $\rho_pR_g^2$ in place of $\eta_p$.

For $R_g = 6.92$, the polymer chain lengths of 73, 85 and 100 for the corresponding colloid diameters yield the size ratios $q = 4.89, 3.26$ and 1.96, respectively (see Figs. 2.19 and 2.20). The radius of gyration is further increased to 11.66, and three different size ratios, $q = 8.25, 5.50$ and 3.30, are obtained for the polymer chain lengths of 137, 166 and
200, respectively (see Fig. 2.21). For these conditions of a fixed polymer radius of gyration and various colloid diameters, the critical colloid volume fraction decreases as the colloid diameter decreases. It is observed that while \( q \) increases, the polymer critical volume fraction increases instead of decreasing, as found in the case of fixed colloid diameter. This results from the strong colloid-polymer interaction as the colloid diameter approaches the polymer monomer size. In Fig. 2.18, using \( \rho_p R_g^2 \) for the polymer concentrations, the critical polymer concentration increases as the gap size decreases. This is because the reduction of the colloid size improves the solvent quality and favors polymer to swell in the solutions, and thus miscibility prevails. The increase of the critical polymer volume fraction becomes more significant as the chain length increases.
Fig. 2.19. Phase diagrams of various quasi two-dimensional colloid-polymer systems with $R_g = 6.92$. 
Fig. 2.20. Phase diagrams of various quasi two-dimensional colloid-polymer systems with $R_g = 6.92$, using the variable $\rho_p R_g^2$ in place of $\eta_p$. 
Fig. 2.21. Phase diagrams of various quasi two-dimensional colloid-polymer systems with $R_e = 11.66$.

Next, two cases with the same $q$ value are compared. For fixed $q$, both in two and three [53] dimensions, a higher polymer volume fraction is required to induce phase separation for $\sigma = 4.243$ than for $\sigma = 7.071$. For $q = 2.33$, $\sigma = 4.243$ and $n = 53$, the critical polymer volume fraction $\eta_p = 0.105$ is larger than that found in three dimensions.
The two cases $\sigma = 7.071$, $n = 60$ and $\sigma = 4.243$, $n = 25$ yield the same size ratio $q = 1.40$, but the phase coexistence curves of these cases exhibit quite different features. The critical volume fractions equal $\rho^* \sigma^2 = 0.445$ and $\eta_p^* = 0.070$ in the former case, while they equal $\rho^* \sigma^2 = 0.380$ and $\eta_p^* = 0.116$ in the latter case.

The size ratio $q$ can be increased to a value around 3.3 either by increasing the polymer chain length to $n = 200$ or by reducing the colloid diameter to $\sigma = 4.243$ and taking $n = 85$. The critical volume fractions change to $\rho^* \sigma^2 = 0.411$ and $\eta_p^* = 0.060$ in the first case, and to $\rho^* \sigma^2 = 0.353$ and $\eta_p^* = 0.100$ in the second case. It is seen that a much higher polymer volume fraction is required to induce phase separation when the colloid-to-monomer size ratio is reduced and confinement is increased.

2.4.5 Scaling and “Protein Limit”

The effects on the critical parameters caused by simulation boxes of varying sizes are next studied. Fig. 2.22 illustrates the changes in colloid and polymer critical volume fractions as the box size varies. It is observed that both colloid and polymer critical volume fractions decrease as the box size increases.

The critical parameters scale according to $\phi_c(L) - \phi_c(\infty) \propto L^{-(d-1/\nu)}$, with $\nu = 1$ for quasi two-dimensional systems. The case of $\sigma = 7.071$ and $n=60$ is studied for $L=60, 80, 100$ and $120$. The extrapolation of the critical volume fraction to infinite box size yields $\rho_c \sigma^2 (L = \infty) = 0.432 \pm 0.001$ and $\eta_p (L = \infty) = 0.683 \pm 0.003$. The deviations for critical parameters, colloid reduced density and polymer volume fraction, between $L=60$ and $L=\infty$ equal 2.9% and 2.8%, respectively.
The Asakura-Oosawa model of ideal polymer is usually valid for systems with large colloids and small polymers (colloid limit) in the dilute regime. If the polymer chain length increases to the extent that the size ratio $q$ becomes much larger than one, the so-called "protein limit" is reached. As the polymer chain length increases, the critical parameters (critical colloid volume fraction and critical polymer volume fraction) scale according to $\phi_c(n) \propto n^{-\gamma}$. For a colloid diameter of 7.071, the scaling of the critical colloid volume fraction yields an exponent $\gamma_c$ equal to $0.196 \pm 0.005$. The extrapolated critical colloid volume fraction at infinite polymer chain length is $0.256 \pm 0.004$ (see Table 2.3). The corresponding values for the smaller colloid diameter of 4.243 are also shown in Table 2.3. These values of critical exponent $\gamma$ are seen to be smaller than those of three-dimensional systems [53, 54]. The uncertainties take into account the deviations caused by both simulations and linear fitting. From the extrapolated values (see Table 2.3), immiscibility does not appear to persist with decreasing colloid diameter, in contrast to the case of three-dimensional systems [53, 54]. The scaling of the critical polymer volume fraction with chain length for quasi two-dimensional systems is found to be given by $\gamma_p = 1.61 \pm 0.09$ for $\sigma = 7.071$ and $\gamma_p = 1.10 \pm 0.02$ for $\sigma = 4.243$. These values are much larger than the previous findings of $\gamma_p = 0.11$ for polymers in two dimensions and $\gamma_p = 0.129$ for quasi two-dimensional geometries [51].

The polymer crossover concentration defined by de Gennes [56] is related to the chain length and radius of gyration by $\phi_p = \frac{n}{R_g} \sim n^{1-d\nu_p}$. For two-dimensional athermal
systems, \( \nu_p = 0.75 \) so that \( d\nu_p - 1 = 0.5 \). The exponent \( \gamma_p \) being greater than \( d\nu_p - 1 \) indicates that the critical polymer volume fraction is smaller than crossover concentrations, which is different from pure polymer systems. In pure polymer systems, the occurrence of immiscibility is caused by the interactions between polymers, and miscibility persists if polymers stay within the dilute regime [51], since no direct polymer interactions occur in this regime. The presence of colloid particles effectively worsens the solvent quality for polymers, and facilitates the emergence of phase separation at lower polymer concentration. When reducing the colloid size, the effects imposed by colloids weaken and a higher polymer concentration is required for phase separation; therefore the value of \( \gamma_p \) decreases, as shown here.

Table 2.3. Scaling of critical parameters with polymer chain length in quasi two-dimensional systems. \( \gamma_c \) is defined in the text; \( \rho^* \sigma^2 \) is the critical colloid density extrapolated to infinite polymer chain length.

<table>
<thead>
<tr>
<th>( \sigma )</th>
<th>( \gamma_c )</th>
<th>( \rho^* \sigma^2 )</th>
<th>( \gamma_p )</th>
<th>( \eta_p^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.071</td>
<td>0.196 ( \pm 0.005 )</td>
<td>0.256 ( \pm 0.004 )</td>
<td>1.61 ( \pm 0.09 )</td>
<td>0.0614 ( \pm 0.0003 )</td>
</tr>
<tr>
<td>4.243</td>
<td>0.029 ( \pm 0.007 )</td>
<td>-0.42 ( \pm 0.03 )</td>
<td>1.10 ( \pm 0.02 )</td>
<td>0.0957 ( \pm 0.0001 )</td>
</tr>
</tbody>
</table>
Fig. 2.22. The effect of system size on critical parameter in quasi two-dimensional geometries.
2.5 Conclusion

The phase behavior of colloid-polymer mixtures in confined geometries is found to differ significantly from that of bulk, three-dimensional systems. The present detailed simulations demonstrate that the phase diagrams of confined colloid-polymer systems are significantly more complex than those predicted by mean-field and other approximate theories. In particular, the occurrence of liquid-liquid phase separation depends not only on the polymer-to-colloid size ratio as found in previous studies, but in fact on both the colloid size and the polymer chain length. Moreover, in contrast to the predictions of mean-field theories, the phase diagrams strongly depend on the dimension of space, and the threshold value of the polymer-to-colloid size ratio for liquid-liquid phase separation is quite different in two dimensions and three dimensions. The critical temperature, whose role is played by the inverse polymer concentration, is found to shift to lower value, in accord with intuition and theoretical predictions. Driven by the geometric confinement, the threshold value of $q$ for the onset of liquid-liquid phase separation is shifted to a higher value. Finite-size scaling enables one to study the phase behavior at the “protein limit”. The extrapolation to infinite polymer chain length suggests the persistence of miscibility for quasi two-dimensional systems, in contrast to the case of three-dimensional systems [53].
Chapter 3: Positional and Orientational Correlation Functions in Quasi Two-Dimensional Systems

3.1 Introduction

The microstructures of complex systems such as those consisting of colloids and polymers can now be studied experimentally with high precision, due to the facts that large enough colloidal particles can be viewed by optical microscopy, and that image analysis can yield accurate statistics [57].

Modern image analysis coupled to video microscopy enables one to determine the nature of the ordering of the colloidal particles in confined, quasi two-dimensional systems and thus to determine both the positional correlations and the orientational correlations of the colloidal particles.

Numerous theoretical, experimental, and computer simulation studies have been performed on the nature of phase equilibria in two-dimensional systems such as those consisting of colloids [58-65]. These studies are largely motivated by the unusual features of the melting transition in two dimensions [66, 67], and the related fact that the ordering of systems in two dimensions presents unique characteristics due to the well-known absence of long-range positional order in two-dimensional systems with short-range interactions, and to the existence of long-range orientational order in these systems [68, 69].

These previous studies have dealt with systems consisting of simple elements. Here, in contrast, the focus is on liquid-liquid phase separation, and a complex system is considered, one in which long polymer molecules are added to colloidal suspensions, and
the soluble polymer does not adsorb onto the colloid. For such systems confined in quasi two-dimensional geometries, it is known from previous works [22, 70, 71] that liquid and solid phase equilibria, as well as liquid-liquid phase coexistence, occur for appropriate values of the polymer-to-colloid size ratio and of the polymer concentration. More precisely, denoting by $q$ the polymer-to-colloid size ratio, it is predicted that for $q$ smaller than 0.31, solid-liquid phase separation occurs, and that for $q$ greater than 0.31, liquid-liquid phase coexistence obtains [22]. These theoretical predictions are in agreement with experimental findings [70, 71].

In the present study, video microscopy and image analysis are used to determine the positional and orientational pair correlation functions of neutral colloidal particles in confined aqueous solutions containing soluble polymer. These correlation functions are obtained in both the liquid and solid phases.

3.2 Experiment

The experimental procedure has been described in detail in a previous study [70], and will thus only be briefly outlined here. The confined geometry is created by using a Mylar® film (DuPont) of appropriate thickness as a spacer between two microslides. The thickness of the Mylar film is large enough for the colloidal particles to move freely, but is not so large that any two particles may overlap each other (see Fig. 3.1). After introducing the various components at their desired concentrations, these quasi two-dimensional samples are sealed by using a UV-adhesive. Using enhanced video microscopy combined with the imaging software IDL, the position of each particle can be determined for each configuration; the image is then digitized and stored for further
analysis [72].

The colloid-polymer system used in this study consists of polystyrene spheres of 3.15 μm in diameter in aqueous polyethylene oxide (PEO) solutions. The thickness of the Mylar® (DuPont) film is 6 μm. To prevent the adsorption of polymer onto the colloid surfaces, and to screen any residual long-range electrostatic repulsion between colloidal particles, surfactant Triton X-405 (0.15%) and sodium chloride (0.004M) are added. The neutrality of the system is confirmed by electrophoresis. Deuterium oxide is also added to balance the difference between density of the colloidal particles and that of the solvent. The radius of gyration of the polymer lies between 0.139 μm and 0.372 μm. These are the longest synthetic polymers which are commercially available; they are therefore those most likely to give rise to liquid-liquid phase separation for a given colloidal diameter, and the latter must be chosen large enough to allow for microscopy observation, which reinforces the constraint on the polymer size. The colloid concentration is fixed at 5 w.t.%, and the polymer concentration is chosen to be either 0.05% or 0.06%, in order to investigate both liquid and solid phases. The correlation functions are determined by averaging over all configurations. Care must be taken to avoid the boundaries because of the limitation of the size of the images. 800 frames, containing between approximately 200 and 1000 particles depending on the nature of the phases, are used to calculate each correlation function.
Fig. 3.1. Two-dimensional cell.
3.3 Results

3.3.1 Positional Correlation Function

Fig. 3.2 shows two snapshots corresponding to the polymer concentrations of 0.06% and 0.05%. For the polymer concentration of 0.06% (Fig. 3.2a), the system exhibits a single solid phase. For the polymer concentration of 0.05% (Fig. 3.2b), the system separates into two liquid phases. The interface runs diagonally from the bottom to the upper right side.

The positional pair correlation function $h(r)$ is calculated by the histogram method [32]:

$$g(r) = \frac{N}{2\pi r \Delta r \rho},$$

(3.1)

where $h(r) = g(r) - 1$. Each image is discretized; $N$ is the number of particles in the shell between the circles of radii $r - \Delta r/2$ and $r + \Delta r/2$ centered at a reference molecule. $\rho$ is the total number density. The pair correlation is then averaged over each reference molecule for 800 frames. To avoid boundary problems, a molecule is chosen as a reference molecule only if it lies sufficiently far away from the edges of the image. Fig. 3.3 shows the correlation function of the colloid-poor phase of Fig. 3.2b, and Fig. 3.4 shows that of the colloid-rich phase. Fig. 3.5 shows the pair correlation function of the solid phase.
Fig. 3.2. (a) Solid phase and (b) Liquid-liquid phase separation in two dimensions.
Fig. 3.3. Colloid pair correlation function of colloid-poor liquid phase.
Fig. 3.4. Colloid pair correlation function of colloid-rich liquid phase.
3.3.2 Orientational Correlation Function

The orientational or bond correlation function depends upon the number and orientation of nearest neighbors to each particle. Considering the centers of colloids observed by video microscopy to be points in a plane, lines are constructed connecting each particle with other particles nearby. Perpendicular bisectors are constructed for each of these lines, and the smallest area enclosed by the bisectors defines the Voronoi polygon for each point. The number of nearest neighbors of a particle is given as the number of sides of a particle's Voronoi polygon.

A local order parameter at each particle is defined as

$$\Psi_\theta = N^{-1} \sum \exp^{i \theta}$$

(3.2)

where \(N\) is the number of nearest neighbors, the sum is taken over all nearest neighbors, and \(\theta\) is the angle between a reference line defined through the particle center and each nearest neighbor. The global pair orientational or bond correlation function is then defined as

$$g_\theta(r) = \left\langle \Psi_\theta(r) \Psi_\theta^*(0) \right\rangle,$$

(3.3)

where \(\Psi_\theta(0)\) is the local bond order parameter at a center particle, and \(\Psi_\theta(r)\) is the local bond order parameter at a distance \(r\) away. In almost all cases \(\left\langle \Psi_\theta(r) \Psi_\theta^*(0) \right\rangle\) is complex-valued, and its real part is taken as the value of \(g_\theta(r)\). This is related to Mermin's early definition of the pair orientational correlation function [68], which is based on the magnitude of the projection of vectors connecting nearest neighbors onto other vectors. The real part of \(g_\theta(r)\) gives the magnitude of such projections [68].

Fig. 3.6 shows the Voronoi polygon constructed from Fig. 3.2a. It is noticed that
there exist regions of nearly perfect order, while other areas show considerable departure from perfect order. Fig. 3.7 shows the pair orientational correlation function of the solid phase.

Fig. 3.5. Colloid pair correlation function of solid phase.
Fig. 3.6. Voronoi diagram for solid phase. This diagram corresponds to the configuration of Fig. 3.2(a) p. 56.
3.4 Discussion and Conclusion

For the system containing two liquid phases (Fig. 3.2b), it is observed from Figs. 3.3 and 3.4 that, in accord with intuition, the positional correlation function of the colloid-rich phase is more structured than that of the colloid-poor phase, but the intensity of the first peak of the former is smaller than that of the latter. As shown by recent exact results on correlation functions for one-dimensional systems [73], no such trend is observed for the intensity of the first peak in relation to the strength of the interaction potential. From the depletion model [9], the effective attraction between two colloidal particles depends on the colloid-to-polymer size ratio and on the volume fraction of the
polymer solution. The colloid-rich phase is the polymer-poor phase, and vice versa. This implies that the polymer volume fraction is larger in the colloid-poor phase, and therefore that the attraction between colloidal particles is larger in that phase. The present experimental results shown in Figs. 3.3 and 3.4 confirm this prediction.

In a previous theoretical study [22], it was shown that polymer polydispersity significantly increases the size of the region in which liquid-liquid coexistence occurs. For the values of the colloid diameter and of the polymer radius of gyration of the present experiments, it is predicted [22] that no phase separation occurs for a strictly monodisperse polymer. The present observation of liquid-liquid phase separation thus implies that polymer polydispersity of the present system is high.

For the system consisting of a single solid phase, it is seen from Fig. 3.5 that, as expected, the positional correlation function is more structured and decays more slowly than that of the liquid (see Figs. 3.3 and 3.4). The orientational correlation function of the solid phase (Fig. 3.7) is similar to that found by Murray and van Winkle [74] in their study of quasi two-dimensional colloidal suspensions of polystyrene spheres confined between two glass plates in the absence of polymer. The presence of polymer at relatively low concentration is not expected to have a significant effect on the orientational correlation function of the solid phase, in accord with the phase diagram shown in Fig. 3.2 of Ref. [22], in which the solid phase boundary is very steep so that largely different polymer concentrations correspond to nearly the same colloidal concentration in the solid phase. Finally, the relatively rapid decay of the orientational correlation function seen in Fig. 3.7 is likely due to the large number of defects present in the solid phase.
Chapter 4: Microstructure of Colloid-Polymer Systems in Confined Geometries

4.1 Introduction

Traditional studies of colloid-polymer systems focus on bulk, three-dimensional systems [10, 15, 21, 75-77], for either charged [78-81] or neutral [82, 83] colloid particles. However, formulations of colloids suspensions in confined geometries play increasingly important roles in many engineering processes, in particular with the advance of nanotechnology. For instance, during the course of polymer film synthesis, depletion flocculation can contribute to the formation of poor film quality. Also, the colloid arrays constrained in quasi one-dimensional channels can be utilized for the fabrication of mesoscale wires [31]. Recent studies have correspondingly shifted attention to colloid particles in confined geometries. Colloid particles in confined geometries, unlike in a bulk three-dimensional environment, can be tracked with the aid of video microscopy [72], and the static and dynamic properties of the systems can therefore be obtained.

The interactions which induce the colloidal microstructures can be determined from the pair distribution function in the dilute regime. Indeed, according to statistical mechanics:

\[ g_2(r) = \exp[-U/k_B T] \]  

(4.1)

where \( g_2 \) is the pair distribution function, \( U \) is the interaction potential, \( k_B \) is Boltzmann’s constant, and \( T \) is the absolute temperature.

The presence of soluble polymer in colloidal solutions leads to a depletion interaction between colloid particles. Studies of depletion effects in confined systems have focused
on binary colloid mixtures [62, 64]; in contrast, experimental exploration of the correlation functions for colloid-polymer mixtures in confined geometries has apparently been rarely performed. In the present study, the microstructures of these complex mixtures are investigated experimentally in confined one-dimensional channels. On the other hand, colloids confined between walls are studied both by computer simulations and experiment.

### 4.2 Computational Studies of Colloid Correlation Functions

The Asakura and Oosawa depletion model for three-dimensional systems is well studied. However, the effects of depletion forces in two dimensions have not yet received much attention [22]. Here, the system is confined to two dimensions; the effective attractions between particles are analogous to those of three-dimensional systems. We can determine the effective potential in dilute solutions by following Asakura and Oosawa. The osmotic pressure and overlap volume are readily derived analytically, and yield the effective depletion force and potential in two dimensions.

\[
F_{dep} = \begin{cases} 
  \infty & r < \sigma_c \\
  -\sqrt{4\delta^2 - r^2} n_p k_B T & \sigma_c \leq r \leq \sigma_p + \sigma_c \\
  0 & \sigma_p + \sigma_c < r
\end{cases}
\]  

(4.2)

\[
U_{dep} = -2n_p k_B T \int_{0}^{\delta} \sqrt{(a + R_b)^2 - \left(\frac{r}{2}\right)^2} dr
\]

\[
= -4n_p k_B T \int_{0}^{\delta} \sqrt{\delta^2 - x^2} dx
\]

\[
= -4n_p k_B T \left( \frac{x \sqrt{\delta^2 - x^2}}{2} + \frac{\delta^2}{2} a \sin \frac{x}{\delta} \right) \bigg|_{r=0}^{r=\delta}
\]

\[
= -4n_p k_B T \left( \frac{x \sqrt{\delta^2 - x^2}}{2} + \frac{\delta^2}{2} a \sin \frac{x}{\delta} \right) \bigg|_{r=0}^{r=\delta}
\]
\[
-4n_p k_B T \left[ 0 + \frac{\delta^2}{2} a \sin(1) - \frac{r}{4} \sqrt{\delta^2 - \left( \frac{r}{2} \right)^2} - \frac{\delta^2}{2} a \sin\left( \frac{r}{2\delta} \right) \right]
\]

\[
= -4n_p k_B T \delta^2 \left[ \pi - \frac{r}{\delta} \sqrt{1 - \left( \frac{r}{2\delta} \right)^2} - 2a \sin\left( \frac{r}{2\delta} \right) \right]
\]

where \( x = r/2 \), \( \delta = \frac{\sigma_c + \sigma_p}{2} = \frac{\sigma_p (1+q)}{2q} \)

\[
U_{dep}(r) = -\phi_p k_B T \frac{1}{\pi} \left( \frac{q+1}{q} \right)^2 \left[ \pi - \left( \frac{r}{\delta} \right) \sqrt{1 - \left( \frac{r}{2\delta} \right)^2} - 2a \sin\left( \frac{r}{2\delta} \right) \right],
\]  \((4.3)\)

where \( \phi_p = n_p \pi \sigma_p^2 / 4 \) is the area fraction (i.e., two-dimensional volume fraction) of polymer. This depletion potential is shown in Fig. 4.1. It may be compared to the three-dimensional form shown above in Fig. 1.2. As shown in Fig. 4.1, \( q \) is the size ratio of the polymer radius of gyration to the colloid radius, \( \phi_p \) denotes the volume fraction of polymer components, and \( \sigma_c \) is the colloid diameter. The interaction potential obtained from Eqs.(1.5) and (4.3) is used next for the studies of correlation functions for colloids in slit pores and two-dimensional geometries, respectively.
Fig. 4.1. Effects of size ratios and polymer concentration, $\phi_p$, on the depletion potential in two-dimensional systems.
4.2.1 NVT Monte Carlo Simulations

In this section, computational studies of correlation functions of colloids in the presence or absence of polymers are carried out by implementing canonical \((N, V, T)\) Monte Carlo simulations. The confined, quasi two-dimensional, slit pore is considered. The polymer induced depletion interactions are modeled by an effective attractive potential added to a hard-sphere interaction between colloids. Colloids interacting via the Asakura-Oosawa potential are constrained by reflecting hard walls.

4.2.2 Results

A. Density Profiles

The colloids are confined between two reflecting hard walls. In comparison with previous experimental study of correlation functions for hard sphere mixtures [62], the gap size and polymer-to-colloid size ratio, \(q\), are chosen to be 1.3 \(\sigma\) and 0.34, respectively. The two-dimensional colloidal density is defined as \(\eta_2 = N_c \pi \sigma^2 / 4A\), where \(N_c\) is the number of colloid particles in the simulation box. Three colloid densities, \(\eta_2 = 0.06\), \(\eta_2 = 0.2\) and \(\eta_2 = 0.4\) for two different polymer-to-colloid number density ratio, \(N_p / N_c = 0.0825\) and \(N_p / N_c = 27\), are considered.

The studies of the microstructures of colloid-polymer systems conveniently begin with the density profiles of colloids in the gap. Since the gap is relatively narrow, most particles gather in the center of the gap under dilute condition. Since there is no attraction between the particles and the walls, the symmetric density peaks exhibit their
highest peak at contact at higher colloid concentration (see Fig. 4.2). When further increasing the polymer-to-colloid concentration ratio while fixing the colloid density, the density profiles do not change. The intensity of the density peak is dominated by the colloid concentration and shows no dependence on polymer concentrations.

Fig. 4.2. Density profiles for $N_p / N_c = 0.0825$ at various colloid concentrations.
B. Distribution (Correlation) Functions

The pair distribution function is defined by:

\[ g_2(r) = \rho^{-1} \left( \sum_i \sum_{j \neq i} \delta(r_i) \delta(r_j - r) \right) \]  

(4.4)

As noted above, for dilute solutions, the interaction potential can be obtained from the pair distribution function by:

\[ U/k_B T = -\ln(g_2(r)) \]  

(4.5)

According to the previous section, the study of the correlation functions proceeds with three different colloid densities at fixed polymer-to-colloid number density ratio, \( N_f / N_c = 0.0825 \) and \( N_s / N_c = 27 \).

In Fig. 4.3, three colloid densities, \( \eta_2 = 0.06 \), \( \eta_2 = 0.2 \) and \( \eta_2 = 0.4 \), corresponding to the polymer volume fractions \( \eta_p = 0.0001 \), \( \eta_p = 0.00034 \) and \( \eta_p = 0.00067 \), are considered. At these very low polymer concentrations, the correlation functions of colloid particles exhibit pronounced first peaks at contact, and show little difference from the hard-sphere correlation functions (see Fig. 4.3), in accord with intuition. For dilute colloid concentrations, the correlation functions based on the effective Asakura-Oosawa potential agree well with experimental results of hard sphere mixtures [62].
Fig. 4.3. Pair correlation functions for $N_p/N_c = 0.0825$ at various colloid concentrations.
Fig. 4.4. Pair correlation functions for $N_p / N_c = 27$ at various colloid concentrations.

However, with increasing polymer concentration ($\eta_p = 0.03 \sim 0.22$), the first peak shifts slightly away from contact to a larger particle separation due to the strong effective attraction between colloids.

It is seen in Fig. 4.4, that the magnitude of pair correlation function increases with increasing polymer concentration. It is easy to understand such behavior in a one-component Hamiltonian since the increase of polymer concentration leads to the attraction to be stronger at contact. It is worth noting that the comparison with the hard-sphere mixture [62] of the same size ratio and gap size, leads to a larger discrepancy as
the colloid concentrations increase. The strong ordering structure found in hard sphere mixture is not seen here. This is because the difference in spatial ordering between soft particles with attractive tails and hard spheres becomes more pronounced at higher concentrations.

4.3 Experimental Studies of Colloid Correlation Functions

4.3.1 Experimental Method

Silica particles (Duke Scientific) with a diameter of $1.58 \pm 0.04 \ \mu m$ are used for the experimental studies of correlation functions in both quasi two dimensions and one dimension. Silica particles (density $=2.18 \ g/ml$) in water or polymer solutions are dispersed in the cell, in which colloid particles stay on the surface due to the gravity, and polymers disperse freely in the cell. The hydrophobic substrate and cover slip prevent the silica particles and polymer molecules from sticking to the surface. The magnification of the objective lens used here is 40X, with a resolution of 0.25 $\mu m$/pixel. The experimental details of sample preparations and experimental procedures are described in Chapter 5. Figs. 4.5-4.7 illustrate the structures of quasi two-dimensional and one-dimensional cells.

![Diagram](Image)

Fig. 4.5. Cell for studies of colloid-polymer systems in quasi two dimensions.
4.3.2 Results

A. Correlation Functions of Colloids in Quasi Two Dimensions

Experimental investigation of colloid correlation functions begins with one-component silica solutions. As shown in Fig. 4.8, the intensity of the first peak of the pair correlation function for pure colloid solutions increases as the colloid concentration increases, in accord with intuition. The interaction potential of colloids shown in Fig. 4.10 shows the attractive potentials for negative charged silica particles. The small polydispersity of colloid particles may have some contribution for this attraction, but the effect should be negligible. The phenomenon of attraction arises between like-charged
particles was reported for charged particles in confined geometries [84-86]. The attraction is caused by the inhomogeneous redistribution of electric double layers. Previous study [86] suggests the attraction for like-charged particles only arises when particles are confined in one or two charged walls, which exert repulsive force to colloids. In this current study, the colloids are confined between the substrate and cover slip, which appear to be neutral. However, the repulsive force from the hydrophobic surfaces can account for the occurrence of attractive forces between silica in our systems.

![Graph](image)

Fig. 4.8. Pair correlation functions of one-component silica solutions in quasi two-dimensional systems.
Before adding the polymer solution, a nonionic surfactant polyoxyethylene glycol (C$_{12}$E$_{8}$), is used to prevent the adsorption of polymer on the silica particles. The addition of surfactant not only weakens the magnitude of the colloidal attraction, but also reduces its range. Fig. 4.9 shows the pair correlation functions of two sets of sensibly identical concentrations of colloids in the presence and absence of surfactants. The presence of the surfactant reduces the intensity of the first peak and shifts it to a smaller colloid separation. The changes in the interaction potentials are observed by extracting the interaction potentials from the pair correlation functions of these dilute systems (see Fig. 4.10).

![Graph](image)

**Fig. 4.9.** Pair correlation functions of quasi two-dimensional colloids with, and without surfactant.
Fig. 4.10. Interaction potentials of quasi two-dimensional colloids with, and without surfactant.

As described above, the addition of polymer introduces effective attractive forces between colloids. It is observed that at lower polymer concentration, the first peak is shifted significantly by the addition of polymer and the system becomes more structured. At higher polymer concentration, the shift of the first peak and the change of the structure become less noticeable. The highly pronounced first peak for colloids with 0.0005% PEO as shown in Fig. 4.11 comes from particle clustering. Instead of being evenly dispersed on the two-dimensional surface, colloids form small clusters of 3–4 particles.
Depletion force induced by the polymers evidently creates significant changes of the microstructures.

Fig. 4.11. Correlation functions of quasi two-dimensional colloids for various colloid and polymer concentrations.
B. Correlation Functions of Colloids in Quasi One-Dimensional Channels

Here, the microstructure of colloid-polymer systems in quasi one-dimensional channels is investigated. Colloid volume fraction in one dimension is defined as 
\[ \eta_c = \frac{N \sigma}{L}, \]
where \( N \) is the number of colloids, \( \sigma \) is the colloid diameter, and \( L \) is the length of the channel. The pair correlation function defined below is calculated from the histogram of particle pair separations from each digitized image:

\[ g_2(x) = \rho^{-1} \left( \sum_i \sum_j \delta(x_i) \delta(x_j - x) \right) = \frac{N(x)}{2 \rho \Delta x}, \]  

(4.6)

where \( N(x) \) is the average number of particles within a distance range of \( x - \Delta x/2 \) to \( x + \Delta x/2 \) from a reference particle, and \( \rho \) is the average number density. To avoid edge effects, the reference particles for any separation are chosen to be at least a distance \( x \) from the edges of the images.

The pair correlation functions of pure silica particles, silica particles with the addition of surfactant and silica particle polymer solutions are the focus of the present study. The channel width employed here is \( \sim 2.75 \mu m \) to prevent mutual passing of particles inside the channel. The pair correlation functions of pure silica colloidal solutions are shown in Fig. 4.12. The systems display more ordered structures as the colloid concentration increases in accord with intuition. The displacement of the first peak to a closer pair separation as the packing density increases and the reduction of the ordering structures with the addition of surfactants as shown in Figs. 4.12 and 4.13, respectively, are consistent with the above findings in quasi two-dimensional experiments (see Fig. 4.8).
Fig. 4.12. Pair correlation functions of quasi one-dimensional silica colloidal particles for various colloid concentrations in pure water.
Fig. 4.13. Pair correlation functions of quasi one-dimensional Si solution in the presence of the surfactant C_{12}E_8.

The addition of polymer strengthens the intensity of the first peak and shifts it to a larger pair separation (see Fig. 4.14). However, when further increasing the polymer concentration to 0.0005 wt% and 0.0007wt%, the position of the first peak is displaced to a smaller particle separation. This implies the dispersion of polymers between colloids.
at dilute concentration, which leads to a greater increase of the attraction range than its magnitude. At the higher polymer concentration of 0.0005wt % ($\eta_p = 0.683$) and 0.0007wt% ($\eta_p = 0.957$), the significant increase of the depletion attraction pushes colloids to closer positions and creates more pronounced structures at larger particle separations (see Figs. 4.15 and 4.17).

Fig. 4.14. Correlation functions of quasi one-dimensional silica particles in polymer solutions for various colloid and polymer concentrations.
Fig. 4.15. Correlation functions of quasi one-dimensional silica particles in polymer solutions.
The interaction potential of silica colloid particles in polymer solutions is indicated in Fig. 4.16. The potential between the colloids illustrates the increase of the attraction force as polymer concentration increases. At intermediate polymer concentration, the presence of polymers between colloids increases the range of the attractive forces.

Fig. 4.16. Interaction potential of sensibly identical concentrations of quasi onedimensional silica colloids in polymer solutions of various concentrations.
Fig. 4.17. Correlation functions of quasi one-dimensional silica colloid particles for two polymer concentrations.
To further study the effects of geometric confinement, the channel width is increased to a marginal width of \(~3.25 \text{ \(\mu\)m}\) to allow particles to pass each other within the channel. Figs. 4.18- 4.19 illustrate the correlation functions of colloids inside wider channels.

Fig. 4.18. Correlation functions of quasi one-dimensional silica colloid particles for various polymer concentrations in wider channels.
Fig. 4.19. Correlation functions of quasi one-dimensional silica particles of various concentrations in 0.00015% PEO solution in wider channels.

When the channel width is increased to about 3.25 μm, a surprisingly structure is observed in the pair correlation functions. The pronounced ordering structure, which was not seen in regular channel width appears for the colloids in 0.0005wt% PEO
solution (see Fig. 4.18). The clustering of particles caused by the depletion effect occurs in wider channels. In Fig. 4.19, the first peak of the pair correlation function splits into two peaks for the colloid dispersed in 0.00015wt% PEO concentration. The splitting of the first peak was found in quasi two-dimensional colloid mixtures in a previous study [62]. The occurrence of peak splitting was interpreted there as the appearance of small colloid particles between two large colloid particles. The individual particle trajectory is shown in Fig. 4.20, which reveals the distribution of colloids along the channel. The splitting of the first peak corresponds to an inhomogeneous particle distribution, which may result from the uneven dispersion of the polymer along the channel.
Fig. 4.20. Colloid trajectories (x-axis: position, y-axis: time) in a quasi one-dimensional channel.
Another distribution quantity of interest is the nearest-neighbor distribution function, which is calculated from the histogram of nearest-neighbor separations for each digitized image. The nearest-neighbor distribution function, \( H(x) \), estimates the probability for any given particle of finding another particle at distance \( x \) to be its nearest neighbor. Since there is no mutual passing for particles in narrow one-dimensional channels, particles remain in their initial order and the complex algorithm is simplified. By definition,

\[
H(x) = \sum_i \delta \left( \text{Min}(x_i) - x \right)
\]

\[
= \sum_i \delta \left( \text{Min}(x_{i-1}, x_{i+1}) - x \right)
\]

(4.7)

The mean nearest-neighbor distance qualitatively agrees with that of a previous study [32]. The magnification of the objective lens used here is 40X, which compromises the determination precise particle positions and causes the deviation in the peak position compared with those found in previous studies.
Fig. 4.21. Nearest-neighbor distribution functions for quasi one-dimensional silica colloid solutions.
Fig. 4.22. Nearest-neighbor distribution functions of quasi one-dimensional silica colloid solutions in the presence of the surfactant C_{12}E_8.
Fig. 4.23. Mean nearest-neighbor distance vs. packing fraction of quasi one-dimensional colloids.

The comparison of the colloidal interaction potential in one and two dimensions can provide more insights on the effects of geometric confinement on the microstructure. Fig. 4.24 illustrates the interaction potential of silica colloids in quasi two and one dimensions. For pure silica solutions, the range of the attraction potential decreases as the confinement increases. Since no mutual passages in one-dimensional are allowed,
the interactions between colloids are dominated by near-neighbor pair-wise effects. The confinement highly hinders the movement of colloids and therefore reduces the range of the interactions.

Fig. 4.24. Interaction potential between colloids in quasi two-dimensional and one-dimensional geometries.

However, the addition of polymer alters the interaction between colloids. With the introduction of polymers, depletion attraction arises between colloids. The colloid-polymer concentration is relatively enhanced by the geometric confinement to yield a higher packing fraction (see Fig. 4.25). In the dilute regime, the polymers are evenly
dispersed in between colloids or in the cell. It is more appropriate to state that the range of attraction is relatively increased due to the presence of the polymer between the particles than concluding that the range of interaction is increased by the confinement.

Fig. 4.25. Interaction potential between colloids in the presence of polymer in quasi two- and one-dimensional geometries.
4.4 Conclusion

The microstructure and the interaction potential of the confined colloid-polymer systems are studied here. The addition of the polymers and the presence of geometric constraint significantly alter the system properties. The microstructure of the particles indicates that particles become more correlated in the presence of polymer. Geometric hindrance also helps to induce the attraction forces between like-charged particles and relatively increases the range of the interaction potentials at dilute regime. However, the range of the depletion potential is reduced as the polymer concentration enters semidilute regime.

The degree of confinement significantly alters the microstructure of the systems. When more than one layer of colloids are allowed in the channel, clustering of particles are observed due to the depletion effect, which is not seen for monolayer of colloids. The nature of microstructure is interplayed by both polymer concentration and geometric confinement.
Chapter 5: Diffusion in Confined Colloid-Polymer Systems

A. Colloid-DNA Systems in Quasi Two Dimensions

5.1 Introduction

From a fundamental point of view, while the diffusion in unconfined, three-dimensional systems has been extensively studied, that in confined, quasi two-dimensional systems has not. Practical examples are diffusion through biological membranes [1], diffusion of DNA molecules on lipid bilayers [87-89], diffusion in polymer thin films.

A particularly interesting system is that of a mixture of colloid and polymer, which offers the advantage that the individual particles can be tracked by ordinary light microscopy. For colloid-polymer systems confined to two dimensions, either on substrates with a free surface [87-89] or between two walls [70, 71], ordinary or fluorescence microscopy, coupled to image analysis make it possible to study the dynamics of individual colloidal particles or polymer.

In this work, the polymer is taken to be DNA, and the diffusion of colloidal particles in quasi two-dimensional colloid-DNA systems confined between two glass plates is studied as a function of DNA concentration. The diffusion of DNA in the same systems with a free surface is studied by tagging the DNA molecules with fluorescent probes [90].
5.2 Experiment

Polystyrene spheres of 1.96 µm diameter are prepared in a 1.25% solution of equal amounts of H$_2$O and D$_2$O to reduce the effect of gravity, thereby preventing precipitation of the colloid out of solution. DNA is chosen because of its monodispersity. Bacteriophage λ-DNA (New England Biolabs) has cohesive sites at its head and tail, which allows them to join intra or intermolecularly to form circular or linear polymers [91]. The DNA chain length equals 22 µm. The DNA is buffered with TBE (Tris-EDTA) and prepared at various concentrations with equal amounts of H$_2$O and D$_2$O; it is then heated at 75°C for 15 minutes [92]. Cooling the solution slowly to room temperature forms cyclic DNA. Quenching the solution in ice water melts the end of the polymer without allowing them to intramolecularly join, thus forming linear DNA. Experimental solutions of colloid-polymer systems contain a surfactant, Triton X-405, to prevent polymer coils from adsorbing onto the colloidal surfaces, as well as sodium chloride to increase the ionic strength in order to minimize residual long-range electrostatic repulsions between the colloidal particles. The pH values of the DNA solutions range from 8.40 at low DNA concentrations to 8.46 at a DNA concentration of 50 µg/mL. The fraction of the DNA which remains linear in the final circular DNA solutions is approximately 16% [91, 92].

For the investigation of the diffusion of the colloidal particles, neutral colloidal particles in nonadsorbing polymer solutions are next prepared in a two-dimensional system, in such a way that the colloidal particles can not overlap each other in the spacer. The details of the two-dimensional cell preparation have been reported elsewhere [22, 71]. Enhanced video microscopy is used to record the movements of the colloidal particles
and to store the data in digital form for further analysis. Macro-implanted imaging software IDL helps to identify the trajectory of each colloidal particle [72]. Finally, the displacement of each particle at different time intervals is calculated to determine the diffusion coefficient of the colloidal particles.

For the investigation of the diffusion of the DNA molecules, λ-DNA is tagged with fluorescent YOYO dye within its double helix. Linear and circular DNA molecules are prepared by the procedure described above. A small amount of YOYO molecules (0.5 μL) is next mixed overnight with DNA and TBE buffer solutions (2.6 μL DNA and 1mL TBE) with the ratio of 4 base pairs (bp) of DNA per one YOYO molecule. Mercaptoethanol is added to slow photobleaching. Finally, the solution is mixed with the DNA + TBE buffer solution to the desired concentration. Fluorescence microscopy is used to track the motion of the dyed DNA molecules in order to obtain the diffusivity of DNA molecules. The software Metamorph is used to analyze the data.

5.3 Results and Discussion

Linear and circular DNA of different concentrations ranging from 0 to 50 μg/mL are listed in Table 5.1. The concentration of the colloidal particles are kept at 1.25 w.t. %. Each particle on the screen is tracked for 10 seconds (30 frames per second). Histograms are then plotted for each time interval of movement (1/30 to 10/30 second). Finally, histograms are fitted to a Gaussian distribution in order to obtain the diffusion coefficient. Detailed calculations have been reported elsewhere [22, 71].

Fig. 5.1 shows the diffusivity of the colloidal particles for different concentrations of linear and circular DNA. The diffusivity decreases monotonically with DNA
concentration in both cases. An abrupt change in the slope of the colloid diffusivity occurs close to the concentration of 4 µg/mL for circular DNA, and a less abrupt change occurs close to the concentration of 15 µg/mL for linear DNA. Above these concentrations, the diffusivity of the colloidal particles is found to decrease much more slowly with DNA concentration. The uncertainty on the values of the diffusivity is estimated from the error on the mean-square displacement of the colloidal particles. The latter is approximately 0.5.

Table 5.1. DNA concentrations prepared for study of colloid diffusivity.

(X: Prepared concentration)

<table>
<thead>
<tr>
<th>Concentration (µg/mL)</th>
<th>0</th>
<th>0.625</th>
<th>1.25</th>
<th>2.5</th>
<th>11.25</th>
<th>30</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear DNA</td>
<td>X</td>
<td>–</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Circular DNA</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>

Fig. 5.1. Diffusivity of colloidal particles in various DNA solutions.
Fig. 5.2. Diffusivity of linear DNA in various concentrations of linear DNA solutions.

Fig. 5.2 shows the diffusivity of dyed linear DNA molecules in pure linear DNA solutions, for concentrations ranging from 5 to 15 μg/mL. The trend is similar to that of the diffusivity of colloidal particles in colloid-DNA solutions.

From Fig. 5.1 it is seen that the diffusivity of the colloidal particles in concentrated DNA solutions is lower for linear DNA than for circular DNA. For dilute colloidal solutions, such as those studied in the present work, the colloid diffusivity is inversely related to the viscosity of the polymer solution. For dilute DNA solutions, the viscosity of linear DNA solutions is larger than that of circular DNA solutions [92], and it increases with the concentration more rapidly than that of circular DNA [93], as is supported by theory [94] and by the fact that the molecular weight of circular DNA is smaller than that
of linear DNA [95], it follows that the diffusivity of colloidal particles is smaller in linear DNA solutions than in circular DNA solutions. The results of Fig. 5.1 at high concentration are in agreement with this suggestion.

For pure colloidal suspensions (in the absence of polymer), it is known [96] that an abrupt change of the colloid diffusivity occurs at high enough concentration due to a cage effect, the diffusing particle getting trapped in cages formed by surrounding colloidal particles. It appears natural to link the slope change of the diffusivity as a function of polymer concentration to the proximity of the overlap concentration, $C^*$, at which the polymers begin to entangle. For pure linear DNA, $C^*$ is estimated from electrophoresis measurements to lie between 30 and 40 $\mu$g/mL [97]. In that study, it is not specified whether the DNA is linear or circular, but the experiment description of that work suggests that the DNA is linear. Theoretically, the overlap concentration for the pure linear DNA system is estimated to be 37 $\mu$g/mL, assuming a radius of gyration of 0.7 $\mu$m [98].

For the present mixtures of colloids and DNA, the apparent slope changes (Fig. 5.1) occur at slightly lower values for linear DNA and significantly lower values for circular DNA. For the present pure DNA systems, it is not possible from the data (Fig. 5.2) to determine a precise concentration at which the change in slope occurs. The reasons for the different DNA concentration ranges in which the change in slope takes place are on one hand the presence of the colloid in the DNA solutions, and on the other hand the interactions between the colloid and polymer. It should be kept in mind that the radius of gyration, and consequently the overlap concentration, depend on the pH of the DNA solution, which varies slightly in different experiments.
B. Colloid-Polymer Systems in Quasi One Dimension

5.4 Introduction and Theory

Diffusion processes in complex systems such as those containing colloids and polymers exhibit remarkable features not found in systems of simple molecules [56, 94]. In many cases, the motion of the diffusing particles is confined. Diffusion of particles in confined, quasi one-dimensional, geometry is usually referred as single-file diffusion, where particles exhibit random-walk movements in channels so narrow that no mutual passage is allowed. Single-file diffusion is ubiquitous in many systems such as Markov chains in statistics [99], microfluidic devices [29], highway traffic flow [100], molecules in zeolites [101], and ion transport in biological membranes [102].

Due to the inhibition of mutual passage, particles are restricted to their initial order. The motions of individual particles are correlated to an extent that for long times they no longer obey Fick's law. In single-file systems, the mean square displacement is predicted theoretically, as will be seen below, to be proportional to the square-root of time for a time much longer than the direct interaction time $\tau$, in contrast to a linear increase with time in systems with allowed passing [103]. Subsequent theoretical studies obtained the same predictions for hard rod systems. Recent experimental studies [104-109] confirmed the non-Fickian behavior predicted by theory.

The studies of single-file diffusion began with Jepson's theoretical derivation [110] for one-dimensional hard-rod systems, in which he obtained several exact expressions for the time-dependent distribution. In particular, $p(x, t)$, the probability of finding a rod at position $x$ at time $t$ if it initially starts from the origin, has received most attention. Lebowitz and Percus [19] elaborated these results and obtained the conditional
probability, \( f_s(x,v,t/v') \) that a particle, which was at \( x=0 \) with velocity \( v' \) at time \( t=0 \), is at \( x \) with velocity \( v \) at time \( t \). Levitt [111], relying mainly on physical arguments, developed a simpler derivation, which gives the results with more physical significance. These exact solutions provide useful tests to validate the mathematical approaches used for three-dimensional systems.

In the following, a derivation is given of the main theoretical predictions. Consider hard rods of length \( a \) with the number density \( \rho \) in an infinitely long one-dimensional channel, as shown in Fig. 5.3. Hard rods are initially labeled with consecutive numbers with a probability distribution \( \rho dx \) and a velocity distribution \( g(v) dv \). When hard rods collide, the trajectories simply pass each other with the exchange of velocities and labels of rods on the trajectories; thus the spatial and velocity distributions remain the same.

![Diagram of hard rods trajectories](image)

Fig. 5.3. Trajectories of hard rods in a one-dimensional channel. The dashed line is the "test" trajectory with initial velocity \( v_0 \).
The dashed line in Fig. 5.3 is the “test” trajectory with velocity \( v_0 \). Whenever a trajectory crosses the “test” trajectory from the left to the right, the number of this trajectory should be raised by one, and vice versa. Therefore, the number of rods in the immediate vicinity of the “test” trajectory will be changed by an integer \( \alpha \) if the “test” trajectory has been crossed \( \alpha \) times more from the right than from the left. \( A_\alpha(v_0, t) \) is defined as the probability that the number of rods in the immediately adjacent vicinity of the “test” trajectory has changed by an integer \( \alpha \) in time \( t \):

\[
A_\alpha(v_0, t) = \sum_{n=0}^{\infty} P_R(v_0, n, t) P_L(v_0, n - \alpha, t)
\]  

(5.1)

where \( P_R(v_0, n, t) \) and \( P_L(v_0, n, t) \) are the probabilities that in time \( t \) the test trajectory is crossed \( n \) times from the right or the left, respectively. Consider the probability that a trajectory with velocity \( v \) crosses the test trajectory between the time interval \( t \) and \( t + dt \) at the position between \( x \) and \( x + dx \), where \( x = (v_0 - v)t \) and \( dx = (v_0 - v)dt \). With a uniform distribution of particles, the probability of finding a rod with velocity \( v \) in the area \( dx \) is \( \rho g(v)dxdv \). Therefore, the probability for a rod crossing the “test” trajectory from the right in time interval \( dt \) is:

\[
\rho dt \int_{-\infty}^{v_0} (v_0 - v)g(v)dv.
\]  

(5.2)

Equation (5.2) can be written as \( B_R dt \), with \( B_R = \rho \int_{-\infty}^{v_0} (v_0 - v)g(v)dv \).

The number of crossings can be expressed by a Poisson distribution, since \( B_R \) is independent of time:

\[
P_R(v_0, n, t) = e^{-B_R t} (B_R t)^n / n!
\]  

(5.3)

Likewise, \( P_L(v_0, n, t) = e^{-B_L t} (B_L t)^n / n! \)  

(5.4)
with \( B_L = \rho \int_{v_0}^{\infty} (v - v_0) g(v) dv \)

Substitute Eqs. (5.3) and (5.4) into (5.1), to get:

\[
A_2(v_0, t) = \sum_{n=0}^{\infty} \frac{e^{-B_R t} (B_R t)^n}{n!} e^{-B_L t} (B_L t)^{n-\alpha} (n-\alpha)!
= e^{-(B_R t + B_L t) v_0} \left[ (B_L \cdot B_R)^{1/2} t^{n-\alpha} \right] \sum_{n=0}^{\infty} \frac{[B_L B_R]^{1/2}}{n! (n-\alpha)!} t^{n-\alpha}
= e^{-(B_R t + B_L t) v_0} \left[ \frac{B_R}{B_L} \right]^{1/2} \sum_{n=0}^{\infty} \frac{n!}{n(n-\alpha)!} (B_L \cdot B_R)^{1/2} t^{n-\alpha}
\]

(5.5)

Consider that a particle initially at the origin with the velocity \( v' \) will be in the interval \( \Delta x \) of proximity of the “test” trajectory \( x = v_0(t + \Delta t) \) at time \( t + \Delta t \) if:

1. It started to the left of test trajectory \( (v_0) \) with no net crossings at time \( t \) and now, at time \( t + \Delta t \), it is going to the right of the “test” trajectory with the velocity, \( v \), greater than \( v_0 \). The contributions to the distribution function \( f_s(x, v, t / v') \) is

\[
\rho dx g(v) dv u(x - v' t) u( vt - x) A_0(x / t, t),
\]

where \( u \) is the unit step function.

2. It started to the right of the “test” trajectory with no net crossings at time \( t \) and it is now going to the left.

3. It started to the right and there was one crossing from the right with probability \( A_1 \) and it is now going to the left.

4. It started to the left and there was one crossing from the left with probability \( A_{-1} \) and it is now going to the right.

Summing the contributions from those four conditions and the possibility that the particle started off at origin without any net crossings yields:
\[ f_s(x, v, t / v') = \rho g(v)\{u(x - v't)u(vt - x)A_0 + u(vt - x)u(x - vt)A_0 \\
+ u(v't - x)u(vt - x)A_1 + u(x - vt)A_{-1}\}, \tag{5.6} \]

where \( \delta \) is the Dirac delta function.

Then the general possibility \( p(x, t) \) that the particle initially at the origin is now at \( x \) can be represented as:

\[ p(x, t) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f_s(x, v, t / v')g(v')dv'dv. \tag{5.7} \]

For the long-time limit, consider the probability that a trajectory initially at \( x_0 \) will cross the "test" trajectory at time \( t \)

\[ B_R(x_0)dx_0 = \rho dx_0(4\pi Dt)^{-1/2} \int_{-\infty}^{\infty} e^{-(x-x_0)^2/4Dt}dv \\
= \rho dx_0 / \sqrt{\pi} \int_{-\infty}^{\beta} e^{-\alpha^2}d\alpha \tag{5.8} \]

where \( \beta = (v_0t - x_0) / 2(Dt)^{1/2} \)

Applying Eq. (5.8) to each \( dx_0 \), the probability that \( n \) trajectories start at \( x_0 > 0 \) and end at \( x < v_0t \) can be expressed by a Poisson distribution with an average of

\[ \overline{B}_R = \int_0 B_R(x_0)dx_0 \]

\[ = 2\rho(Dt/\pi)^{1/2} \int_0^{\gamma} (\gamma - \beta^2) e^{-\beta^2}d\beta \tag{5.9} \]

where \( \gamma = v_0t / (4Dt)^{1/2} \) and

\[ P_R(v_0, n, t) = e^{-\overline{B}_R} \left[ (\overline{B}_R)^n / n! \right], \tag{5.10} \]

and \( P_L(v_0, n, t) = e^{-\overline{B}_L} \left[ (\overline{B}_L)^n / n! \right] \) with \( \overline{B}_L = 2\rho(Dt/\pi)^{1/2} \int_{\beta}^{\gamma} (\beta - \gamma)^{-3/2}d\beta \).

Therefore:
\[ A_\alpha(v_0,t) = \sum_{n=0}^{\infty} \frac{e^{-\overline{B}_R} (\overline{B}_R)^n}{n!} \frac{e^{-\overline{B}_L} (\overline{B}_L)^{n-\alpha}}{(n-\alpha)!} \]

\[ = e^{-(\overline{B}_R + \overline{B}_L)} \left( \frac{\overline{B}_R}{\overline{B}_L} \right)^{\alpha/2} I_\alpha \left[ 2(\overline{B}_L \overline{B}_R)^{1/2} \right] \quad (5.11) \]

\( A_0(v_0,t) \) is the probability that the number of rods in the immediately adjacent vicinity of “test” trajectory is now in the neighborhood of \( x = v_0 t \). Therefore \( A_0 \) gives the spatial probability distribution of the line connecting two neighboring particles which were at initially at the origin. At the long-time limit, since the difference between position \( x = v_0 t \) and its nearest neighbors is negligible compared to \( x \), this distribution is equivalent to \( p(x,t) \).

When \( t \to \infty \), \( I_\alpha(z) \to e^z / (2\pi z)^{1/2} \), where \( z = 2t(\overline{B}_R \overline{B}_L)^{1/2} \)

\[ A_0(t) \to (4\pi \overline{B}_L^{1/2} \overline{B}_R^{1/2})^{-1/2} e^{-\left(\overline{B}_L^{1/2} - \overline{B}_R^{1/2}\right)^2} \quad (5.12) \]

For the long-time limit, \( \gamma = x / (4Dt)^{1/2} \ll 1 \).

(5.9) can be written as:

\[ \overline{B}_R = 2\rho(Dt / \pi)^{1/2} \left[ \int_{-\infty}^{0} (\gamma - \beta) e^{-\beta^2} d\beta + \int_{0}^{\infty} (\gamma - \beta) e^{-\beta^2} d\beta \right] \]

\[ = 2\rho(Dt / \pi)^{1/2} \left[ \left( \frac{1}{2} + \frac{1}{2} \sqrt{\pi \gamma} \right) + \left( \frac{1}{2} \gamma^2 \right) \right] \]

\[ = \rho(Dt / \pi)^{1/2} \left[ 1 + \sqrt{\pi \gamma} \right] \]

\[ = K(1 + \alpha), \quad (5.13) \]

where \( K = \rho(Dt / \pi)^{1/2} \) and \( \alpha = \sqrt{\pi \gamma} \ll 1 \).

Likewise, \( \overline{B}_L = K[1 - \alpha] \).

\[ (5.14) \]

Substitute Eqs. (5.13) and (5.14) into (5.12), to get

\[ A_0(t) \to (4\pi K)^{-1/2} e^{-Ka^2} \quad (5.15) \]
With \( D = (1/\rho) \int_0^\infty v g(v) dv \),

\[
p(x,t) = \frac{\sqrt{\rho}}{2(\pi D t)^{1/4}} \exp \left\{ -\rho x^2 \left[ \pi/(16 D t) \right]^{1/2} \right\}
\]

(5.16)

The probability distribution in Eq. (5.16) shows that the mean square displacement in one-dimensional systems is proportional to the square root of time instead of linearly proportional to time. The comparison the experiment for colloid-polymer systems work with these theoretical predictions will be carried out in the next section.
5.5 Experimental Method

The present experimental study of one-dimensional diffusion is performed by confining colloid particles in quasi one-dimensional channels. Colloid particles positions are recorded by video microscopy into video tapes after settling in the confined channels for 6 hours. The overall procedure is illustrated in the following figure (Fig. 5.4).

![Procedure diagram]

Fig. 5.4. Procedure for study of one-dimensional colloid systems.

5.5.1 Preparation of Colloid-Polymer Solutions

Silica colloid particles ($\sigma = 1.58 \pm 0.04 \mu m$, density=$2.18 g/cm^3$, Duke Scientific) are used for the present studies of one-dimensional diffusion. For the study of colloid
diffusion, the silica particles are dispersed in deionized water (specific resistance 18 MΩ-cm, Millipore) to yield 0.0025 wt%, 0.006 wt%, 0.012 wt% and 0.02 wt%. However, extra care is exercised with the addition of polymer in the colloid suspension. Poly(ethyleneoxide) (PEO, Aldrich Inc) with the molecular weight of 8,000,000 is chosen as the polymer added to the solution. The 0.01 wt% PEO solution is prepared as follows.

1. Measure the water and PEO
2. Autoclave the bottle
3. Place the bottle with the water on a hotplate with a magnetic stirrer
4. Place PEO powder on a paper sheet with wedge like shape
5. Raise the stirrer speed to form a deep vortex in the beaker and slowly sprinkle PEO powder
6. After the PEO powder is dissolved, turn the stirrer down
7. Seal the bottle and transfer it to a rotating drum and let it roll for 2 days.

The nonionic surfactant polyoxyethylene glycol $\text{C}_{12}\text{E}_8$ is introduced in the colloid solution before adding polymer, to prevent polymer adsorption on the silica particles. The surfactant molecules and colloid particles are well mixed on the rotating drum for 4 hours. Finally, the PEO solution is added and rolled on the rotating drum over night.

5.5.2 One-Dimensional Cell

The quasi one-dimensional channels used in the experiment are provided by the Microtechnology laboratory of University of Minnesota. The features of the channels are printed on Si wafer with the photolithography technique followed by dry etching. Prior to the usage of making patterns out of silicon wafers, each wafer is first cleaned by
heating at 90 °C in the piranha solution, a mixture of 30% H2O2 and concentrated H2SO4 (30:70 v/v), and subsequently treated with silanizing reagent [112], which octadecyltrichlorosilane (OTS) solution is applied in our experiment. Dodecane is used as a solvent to prepare the 1.0 wt% OTS solution. Before the preparation of the solution, dodecane is purified by percolating through a column of anhydrous aluminum oxide. This percolating process removes certain amount of water in the dodecane. The hydrated silicon wafer is then immersed in a 1 wt% OTS solution for 3 minutes and then removed and rinsed by dichloromethane and trichloromethane to remove any un-adsorbed OTS molecules. All the preparations of the adsorbate (OTS) solution and silanization reactions are conducted in a glove-bag filled with dry nitrogen to exclude the amount of water traces in the surrounding atmosphere.

![Fig. 5.5. The configuration of one-dimensional channels on silicon wafers.](image)

The following procedures are followed to fabricate one-dimensional grooves from the master silicon wafer. The sylgard 184 elastomer base and its curing agent (Dow Corning) are well mixed to achieve transparent elastomeric polymer, poly(dimethysiloxane) (PDMS). The procedure is:

1. Weight ratio of 10:1 (sylgard 184:curing agent)
2. Mixed well for 5 minutes
3. Place in a vacuum pot for 30 minutes to remove the bubbles
4. Carefully pour into a Petri dish with the pattern facing up
5. Place the Petri dish in the vacuum pot for 1 hour to remove the remaining bubbles
6. The elastomer is cured at 60 °C in the oven for 12 hrs
7. Carefully strip the film from the silicon wafer

Fig. 5.6. Illustration of the fabrication procedure of slides.

The sample cells are created by dispensing colloid solutions on the surface of channels and applying them with hydrophobic cover slips. The cover slips are treated to be made become hydrophobic [113] with following procedures:
1. Prepare 10wt% Octadecyltrichlorosilane (OTS) solution (n-undecane as solvent)
2. Place OTS solution in a 500ml beaker vial with cover slips on a rack
3. bubble nitrogen through the solution on each side between cover slips for 20 minutes
4. Rinse cover slips with n-undecane for 20 minutes
5. Rinse cover slips with methanol for 20 minutes
6. Rinse cover slips with pure water for 20 minutes
7. Bake cover slips in the oven at 60°C for 12 hours.
The colloid system studied in the present work is an aqueous solution of silica particles. All the experiments are performed at temperature $T \approx 25^\circ C$. The following experimental procedures are followed to determine the pair correlation functions and diffusion coefficients for confined colloid systems.

5.5.3 Video Microscopy and Image Analysis

Fig. 5.7. Experimental setup for study of colloid solutions in confined systems.

The images are recorded into VHS tapes by video microscopy. The magnifications of the objective lens employed in this research are 40X and 20X, which give the resolution of 0.25μm/pixel and 0.4842μm/pixel, respectively. The image analyses
include digitizing images with Scion Image, extracting particles information with IDL and tracking particles’ trajectories, and calculating the diffusivity and correlation functions with C++. The algorithm is sketched below in Fig. 5.8.

<table>
<thead>
<tr>
<th>Record microscopy images into VHS</th>
<th>Scion Image</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grab the images with macro “VCRgrab”</td>
<td>Scion Image</td>
</tr>
<tr>
<td>Subtract the background images of channels with macro “SubBack”</td>
<td>IDL (Interactive Data)</td>
</tr>
<tr>
<td>Process the image and output particle positional information to data files with IDL</td>
<td>Language 5.1</td>
</tr>
<tr>
<td>Determines channel positions and assign particles into each channel</td>
<td>C++</td>
</tr>
<tr>
<td>Link the particle trajectories and calculate the diffusivity</td>
<td>C++</td>
</tr>
</tbody>
</table>

Fig. 5.8. Image analysis algorithm

5.6 Experimental Results

The experimental study of diffusion of colloids in confined geometry is next carried out. Due to the constraint of the computer memory, the images are captured at the rate of 3 frames per second from each 2 hour VHS. The digitized images are further processed by Scion image and IDL to extract the positions of each particle in each frame. C++ first allocates particles into each corresponding channel from the positional information of each concentration. The trajectories of particles in each channel are determined by adjusting the parameters to yield optimized links (see Fig. 5.9). The mean square displacement is determined by averaging over $2.16 \times 10^4$ frames of images
for each channel. The order of the particles remains the same throughout the tracking period, as shown in Fig. 5.9. The resolution of the mean square displacement for times shorter than 3 seconds is 30 frames per second in order to capture the subtle movements of particles in the short-time regime. However, the data for times shorter than 0.3 second are not shown here due to the constraints of objective lens’ resolutions.

The present studies cover the diffusive behavior of colloids dispersed in pure water and polymer solutions in quasi one- and two-dimensional geometries.
Fig. 5.9. Trajectories of colloid particles in a one-dimensional channel (the $x$-axis describes the particles positions within the channel, and the $y$-axis describes time).
The mean square displacement of quasi one-dimensional silica solution inside channels of ~2.75 μm wide is first considered here (see Fig. 5.10). The magnitude and slope of the mean square displacement decrease significantly with the increase of colloidal volume fraction, in agreement with a previous study [114]. The slope of the logarithmic mean square displacement decreases as the concentration increases. It indicates that the subdiffusion regime emerges earlier as the concentration increases, due to the hydrodynamic interaction.

Fig. 5.10. Mean-square displacement of quasi one-dimensional colloids for various volume fraction $\eta_c$. 
Before the addition of the polymer, the effect of surfactant on the diffusion is also investigated. The surfactant (C\textsubscript{12}E\textsubscript{8}) molecules adsorbed onto the colloid surfaces suppresses the attractive force between the particles. The presence of the surfactant in the aqueous solution enhances the hydrodynamic interaction between colloids and the emergence of the subdiffusion regime occurs relatively early as shown in Fig. 5.11.

![Graph showing mean-square displacement of quasi one-dimensional colloids in the presence of surfactants.](image)

Fig. 5.11. Mean-square displacement of quasi one-dimensional colloids in the presence of surfactants.
The transport properties of colloid particles in the polymer solution are next studied. Fig. 5.12 illustrates the mean square displacement of colloids with sensibly identical concentrations in PEO solutions. The movement of particles slows down as the polymer concentrations increases in accord with intuition. On the other hand, the increase of the colloid concentration consistently agrees with the finding decrease of the colloidal diffusion as above one-component solutions. The colloid concentration also plays a role in the diffusion of the colloid-polymer mixture. The diffusion of colloids is influenced by both the colloid and polymer concentrations. In this study, the radius gyration of the polymer is about 0.227\(\mu\)m, which yields the polymer-to-colloid size ratio of 0.287. Therefore, the colloid concentration plays the dominating role in the colloid diffusion, due to its larger geometric hindrance because of the size asymmetry between these two components.
Fig. 5.12. Mean-square displacement of quasi one-dimensional colloids for various polymer concentrations.
In order to investigate the effects caused by the geometric confinement, a larger channel width of \( \sim 3.25 \, \mu \text{m} \) is considered. The width of the channels is equal to about the marginal width to allow for mutual passage of particles. However, the passing of particles in the dilute solution is not observed since it is energetically unfavorable. The increase of the channel width provides particles more space to perform random movements of Brownian motion. The particles diffuse faster in the wider channel, as anticipated (see Fig. 5.13).

Fig. 5.13. Mean-square displacement of quasi one-dimensional colloids with surfactant in regular and wider channels.
Fig. 5.14. Mean-square displacement of quasi one-dimensional colloids for various polymer concentrations in normal and wider channels.

With addition of the polymer, the diffusion of colloids is anticipated to slow down due to the hydrodynamic interaction and the depletion effect induced by the polymer. When comparing the mean-square displacement of colloids in the polymer solutions for regular channels and slightly wider channels, the phenomenon of particles slow-down is surprisingly more pronounced in the wider channels. In contrary to the one-component colloid solution, the presence of the polymer imposes more hindrance on the long term
diffusion of the colloid particles in wider channels, as shown Fig. 5.14. The depletion attraction force between colloids is governed by both the polymer concentration and the geometric confinement. It was shown that the enhancement and de-enhancement of the mean-square displacement by the repulsive and attractive interaction are caused by the hydrodynamic interaction of particles [63, 80]. The increase of the geometric confinement is believed to shorten the range of the attraction potential. This accounts for the further slowing down of the mean-square displacement of colloids in wider channels, due to the longer range of the attraction potential induced by the polymers.
Fig. 5.15. Mean-square displacement of quasi one-dimensional colloids for various polymer concentrations.

5.7 Discussion

In the short-time regime, the particles diffuse according to Fick’s law, $<x^2(\tau)\propto t^\gamma$ with $\gamma=1$. After a time longer than the particle direct interaction time, the spheres enter a subdiffusion regime with $\gamma<1$. The theoretical prediction of long time non-Fickian
behavior is examined here. The mean-square displacement of colloids versus time in one-dimensional channels is shown in Figs. 5.10-5.15. As seen in Fig. 5.10, the diffusive behavior follows Fick's law for low colloid concentrations, and gradually shifts to the subdiffusion regime for higher colloid concentrations. It is found in present work, although not shown here, that data obtained by a low magnification of objective lens, 20X, fail to capture the short-time Fickian behavior for all concentrations. This deviation is caused by the insensitivity of 20X objective lens to the subtle movements of particles at short times.

The short-time diffusivity $D_s$ is determined by linear fitting of the mean-square displacement versus time at low concentration. Conventionally, the diffusivity is displayed as a function of the volume fraction $\phi$. Therefore, the packing fraction of colloids $\eta_e$ is converted to $\phi$ with the relationship $\phi/\eta_e = \frac{\pi \sigma^3}{6AL} / \frac{\sigma}{L} = 0.223$, where $A$ is the cross-sectional area of the channel. The diffusivities for pure colloid systems are fitted with the volume fractions to a polynomial of second order. The minimum time step chosen here is 0.033 second. The fitted value for $D_s^5(0)$ equals $0.142 \pm 0.033 \ \mu m^2/sec$, which is larger than $0.110 \pm 0.002 \ \mu m^2/sec$ of a previous work [114]. This discrepancy results from the resolution of the objective lens (40X) employed in this work. The low resolution of the objective lens overestimates the movement of particles and increases the value of the diffusivities.
Fig. 5.16. The short-time diffusion coefficient as function of colloid volume fraction in one-dimensional channels.

The diffusion coefficient $D_0$ for a sphere in a bulk system is given by the well-known Stokes-Einstein relation:

$$D_0 = \frac{k_B T}{6\pi \eta a},$$  \hspace{1cm} (5.17)

with $k_B$, $\mu$ and $a$ denoting Boltzmann’s constant, the solution viscosity and the particle
radius, respectively. This gives the diffusion coefficient equal to 0.276 \( \mu m^2/sec \) for silica solutions in bulk systems. It is observed to much larger than the diffusivities in quasi two-dimensional (see Table 5.2) and that of 0.142 \( \mu m^2/sec \) in one-dimensional geometries. The diffusion coefficient is found to decrease with increasing confinement.

Table 5.2. Diffusivity of colloids in quasi two-dimensional geometry.

<table>
<thead>
<tr>
<th>( \rho \sigma^2 )</th>
<th>Polymer concentration</th>
<th>Diffusivity (( \mu m^2/sec ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0512</td>
<td>0.0000%</td>
<td>0.174</td>
</tr>
<tr>
<td>0.0376</td>
<td>0.0001%</td>
<td>0.163</td>
</tr>
<tr>
<td>0.0366</td>
<td>0.0003%</td>
<td>0.159</td>
</tr>
<tr>
<td>0.0395</td>
<td>0.0005%</td>
<td>0.138</td>
</tr>
</tbody>
</table>

Table 5.3. Change of \( \gamma \) values (in the regime \( t<2 \ sec \)) versus colloid packing fraction in pure silica solutions.

<table>
<thead>
<tr>
<th>Si packing fraction (( \eta_c ))</th>
<th>( \gamma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.106</td>
<td>0.9728</td>
</tr>
<tr>
<td>0.204</td>
<td>0.8706</td>
</tr>
<tr>
<td>0.349</td>
<td>0.8438</td>
</tr>
<tr>
<td>0.441</td>
<td>0.8207</td>
</tr>
</tbody>
</table>

The change of \( \gamma \) values for pure silica solutions shown in Table 5.3 indicates that the crossover from short-time to long-time regime emerges earlier as the colloid
concentration increases. The nonionic surfactant C$_{12}$E$_8$ is employed again to prevent polymer adsorption onto colloids. The presence of the surfactant does not produce a significant effect on one-dimensional diffusion (see Fig. 5.11). In order to understand the influence of polymer, we study the change of the exponent $\gamma$ as the colloid and polymer concentrations increase. In the short-time regime, the accuracy of the value of $\gamma$ is strongly dependent on the magnification of the objective lens. In order to avoid the errors introduced from the short-time movement and long-time instability due to the limited length of data, only the mean-square displacements between $10<t<100$ are considered. The decrease of $\gamma$ with the increase of colloid and polymer concentrations is shown in Table 5.4. For instance, for two sensibly identical colloid packing fractions of 0.129 and 0.127 dispersed in 0.0005% and 0.0007% PEO, respectively, the value of $\gamma$ substantially decreases in the latter case.

Table 5.4. Variation of $\gamma$ (in the regime $10<t<100$ sec) versus colloid packing fraction in PEO solutions.

<table>
<thead>
<tr>
<th>$\eta_p$</th>
<th>$\eta_c$</th>
<th>$\gamma$</th>
<th>$\eta_c$</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0001%</td>
<td>0.099087</td>
<td>0.9401</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>0.0003%</td>
<td>0.079956</td>
<td>0.9192</td>
<td>0.218005</td>
<td>0.7555</td>
</tr>
<tr>
<td>0.0005%</td>
<td>0.129111</td>
<td>0.8916</td>
<td>0.146892</td>
<td>0.8497</td>
</tr>
<tr>
<td>0.0007%</td>
<td>-</td>
<td>-</td>
<td>0.126639</td>
<td>0.6909</td>
</tr>
</tbody>
</table>
5.8 Conclusion

The study of the diffusive behavior of colloids in one-dimensional colloid-polymer solutions is reported here. The presence of polymers not only alters the microstructures of the systems, but also reduces the diffusion coefficient of colloids. The non-Fickian behavior of one-dimensional diffusivity is shown to occur earlier with the addition of polymer. In accord with intuition, the diffusion coefficient for one-component systems is found to increase with increasing system dimensionality. However, a different trend is observed with the addition of the polymer. The discrepancy is attributed to the difference of depletion attractive potentials caused by the geometric confinement.
Appendix A

<table>
<thead>
<tr>
<th>SUBROUTINE mcmove</th>
<th>attempts to displace a particle</th>
</tr>
</thead>
<tbody>
<tr>
<td>o=int(ranf()*npart) + 1</td>
<td>select a particle at random</td>
</tr>
<tr>
<td>call <em>ener</em>(x(o),eno)</td>
<td>energy old configuration</td>
</tr>
<tr>
<td>xn=(x(o)+ranf()-0.5)*delx</td>
<td>give particle random displacement</td>
</tr>
<tr>
<td>call <em>ener</em>(xn,enn)</td>
<td>energy new configuration</td>
</tr>
<tr>
<td>if (ranf().lt.exp(-beta *(enn-eno)))</td>
<td>acceptance rule</td>
</tr>
<tr>
<td>x(o)=xn</td>
<td>accepted: replace x(o) by xn</td>
</tr>
<tr>
<td>return</td>
<td></td>
</tr>
<tr>
<td>end</td>
<td></td>
</tr>
</tbody>
</table>

Subroutine *ener* calculates the energy of a particle at a given configuration.

If a configuration is accepted, the old configuration will be discarded; otherwise, the old one will be retained.

Ranf() is the random number uniform in [0,1].
SUBROUTINE mcexc

If (ranf() .lt. 0.5) then
  If (npart .eq. 0) return
    o=int(ranf()*npart)+ 1
    call ener(x(o),eno)
    arg=npart*exp(beta*eno)/(zz*vol)
    if (ranf() .lt. arg) then
      x(o)=x(npart)
      npart=npart-1
    endif
  else
    xn=ranf()*box
    call ener(xn,enn)
    arg=zz*vol*exp(-beta*enn)/(npart+1)
    if (ranf() .lt. arg) then
      x(npart+1)=xn
      npart=npart+1
    endif
  endif
return
end

attempts to exchange a particle with a reservoir
decide to remove or add a particle
test whether there is a particle
select a particle to be removed
calculate the energy of particle o
apply acceptance rule
accepted, then remove particle o

new particle at a random position
calculate the energy of new particle
apply acceptance rule
accepted: add new particle

zz is defined as $zz = \exp(\beta\mu) / \Lambda^3$ where $\Lambda$ is the de Broglie thermal wave length
References


Prog. Colloid Polymer Sci. 97, 80 (1994).


