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Phase transitions of colloid-polymer systems in two dimensions

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Phase transitions of systems consisting of colloidal particles and nonadsorbing polymer in a solvent are studied theoretically in two dimensions. The colloids are modeled as hard spheres and the polymer as an ideal gas. The imbalance in osmotic pressure induced by the depletion effect gives rise to an effective attraction tail for the colloid-colloid interaction. For a monodisperse polymer, liquid-liquid separation is predicted to occur for appropriate colloid concentrations when the ratio s of the radius of gyration of the polymer to the radius of the colloidal particle is greater than 0.31, while solid-liquid separation is predicted to occur for all colloid concentrations when s is smaller than 0.31. Polydispersity of polymer is found to increase the extent of liquid-liquid coexistence, and when the average s is smaller than 0.31, and for appropriate colloid concentrations, liquid-liquid coexistence occurs provided the polymer size distribution is broad enough. Partitioning and size distribution of polymer in coexisting phases are also predicted. [S1063-651X(99)10712-8]

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I. INTRODUCTION

Phase separation in colloidal suspensions, caused by the presence of nonabsorbing polymers, is a phenomenon of fundamental interest [1–5]. A theoretical study of this phenomenon was first made by Asakura and Oosawa [6] and further elaborated by Vrij [7]. In the Asakura-Oosawa model, the colloidal particles are assumed to be hard spheres and the polymers interpenetrate each other freely. The driving force for the attraction of colloidal particles is induced by the resulting imbalance in osmotic pressure, which occurs when two colloidal particles are so close to each other that no polymer can lie between them, giving rise to an effective attractive force between the colloidal particles, called the depletion force (see Fig. 1). At high enough polymer concentrations, the suspension separates into a colloid-rich and a colloid-poor phase. Several techniques have been utilized to directly measure the depletion force, such as laser radiation pressure [8] and digital video microscopy [9–12].

Previous studies [13–14] of the phase transitions of a colloid-polymer system used an effective pair interaction, in which the depletion attraction is added to a repulsive hard core. Compared to the hard-sphere system consisting of a colloidal suspension without polymer, the fluid-solid region is found to expand upon addition of polymer. For a large enough polymer to colloid size ratio, a fluid-fluid transition appears for a range of polymer concentrations. Although these predictions agree qualitatively with those of experiment [14–15], the polymer concentrations corresponding to phase separation deviate significantly from experimental values.

Several assumptions on the properties and distribution of the polymer made in the effective potential approach are believed to account for the disagreement between theory and experiment. Lekkerkerker *et al.* [16] studied polymer partitioning between coexisting phases, which is ignored in the effective potential approach, by using scaled particle theory [17–18] and perturbation theory [19]. The polymer is supposed to be at its theta condition, and the colloid particles are again taken to be hard spheres. The only effect of the interaction between colloid and polymer is to restrict the free volume in which the polymer can move. Mean-field approximation is used to replace the free volume by its average value in the corresponding unperturbed system of colloidal particles. Nonpairwise additivity of the polymer-induced interaction, especially for large polymers, is also taken into account. The location of phase boundaries is determined for various values of the polymer-colloid size ratio, and the predictions are found to be in closer agreement with experiment than those based on the effective potential [20]. More complex systems including rodlike colloids [21], colloids of a size small compared to that of the polymer [22], nonideal polymer [23], binary polymer mixture [24], and polydisperse polymer [25] have been studied in a similar fashion.

All above studies pertain to bulk, three-dimensional systems. Some recent studies have been made of the phase transition of hard spheres in confined systems [26–28], with an interest in the fluid-solid transition. Fluid-fluid phase separation, which was observed [15] in three-dimensional hard-sphere systems with an attractive tail, was of course not found in these studies, because of the absence of any attractive interaction.

In this work, we turn to two-dimensional systems consisting of colloidal particles and nonadsorbing polymers, in which the depletion force is taken into account, and study them using an approach similar to that of [16]. The effects of the inevitable polymer polydispersity are also investigated and the system is assumed to be strictly monolayered, which cancels wall effects. In Sec. II, the model is introduced and its assumptions and limitations are discussed. In Sec. III, the phase diagram for a system of colloid and monodisperse polymer is compared to that of a system in three dimensions. The effect of polymer polydispersity is also discussed.

II. MODEL

Consider N_C colloidal particles and N_P polymer coils in a volume V. The colloidal particles are assumed to be mono-

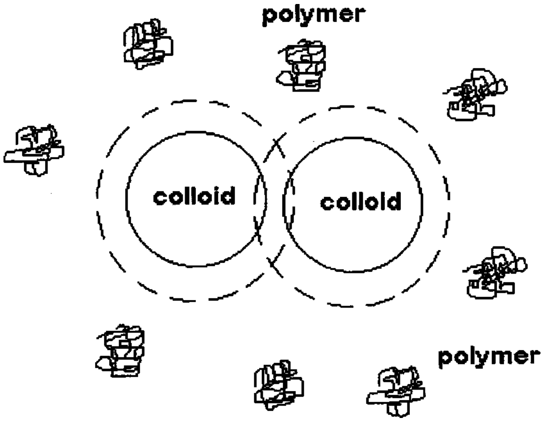

FIG. 1. Illustration of depletion force induced by polymer. The polymers cannot penetrate the overlapping region if two colloidal particles are too close to each other.

disperse and interact with each other as hard spheres of diameter σ_C, so that the colloid-colloid pair potential $\phi_{CC}(r)$ as a function of the separation r of the particle centers is

$$\phi_{CC}(r)=\begin{cases}0 & r>\sigma_C\\ \infty & r\leqslant\sigma_C.\end{cases}\tag{1}$$

The polymer is assumed ideal and at its θ condition. Polymer coils thus do not interact and interpenetrate each other freely.

The colloid-polymer pair potential $\phi_{CP}(r)$ is given by

$$\phi_{CP}(r)=\begin{cases}0 & r>(\sigma_P+\sigma_C)/2\\ \infty & r\leqslant(\sigma_P+\sigma_C)/2,\end{cases}\tag{2}$$

where σ_P is twice the gyration radius of the polymer. The depletion force induced by this potential is illustrated in Fig. 1. The coordinates of colloidal particles are denoted individually by r_i $(i=1,\ldots,N_C)$ and collectively by r_C. The center positions of the polymers are denoted similarly by r_k $(k=1,\ldots,N_P)$ and r_P. The total colloid-colloid pair potential $U_{CC}(r_C)$ is given by

$$U_{CC}(\mathbf{r}_C)=\sum_{i>j}\phi_{CC}(\mathbf{r}_i-\mathbf{r}_j).\tag{3}$$

U_{CP} has a similar meaning.

The canonical partition function for the system is

$$Z=Z_C^*Z_P^*\int\frac{d^3\mathbf{r}_C}{V^{N_C}}e^{-U_{CC}/k_BT}\int\frac{d^3\mathbf{r}_P}{V^{N_P}}e^{-U_{CP}/k_BT},\tag{4}$$

where Z^*'s are the partition functions of ideal gases:

$$Z_C^*=\frac{1}{N_C!}\left(\frac{V}{\lambda_C^3}\right)^{N_C},\tag{5}$$

$$Z_P^*=\frac{1}{N_P!}\left(\frac{V}{\lambda_P^3}\right)^{N_P},\tag{6}$$

with λ_C and λ_P the de Broglie thermal wavelengths of the colloid and polymer, respectively.

Consider the void function defined as.

$$\psi(\mathbf{r}_k;\mathbf{r}_C)=\prod_i\theta\left(|\mathbf{r}_k-\mathbf{r}_i|-\frac{\sigma_C+\sigma_P}{2}\right),\tag{7}$$

where $\theta(x)$ is the step function. The void function equals zero when r_k is located in the excluded volume of spheres of radius $(\sigma_C+\sigma_P)/2$ centered on each colloid, and equals unity when r_k is located in the free volume V_{free}. The void function ψ is a function of the collective colloid coordinates and yields an expression for the free volume fraction:

$$\alpha(\mathbf{r}_C)=\frac{1}{V}\int\psi(\mathbf{r};\mathbf{r}_C)d^3\mathbf{r}.\tag{8}$$

The Boltzmann factor of the total colloid-polymer potential can thus be expressed in terms of void functions as

$$\exp\left(\frac{-U_{CP}}{k_BT}\right)=\prod_k\psi(\mathbf{r}_k;\mathbf{r}_C).\tag{9}$$

Using the definition of α, the partition function (4) can be integrated over r_P:

$$Z=Z_C^*Z_P^*\int\frac{d^3\mathbf{r}_C}{V^{N_C}}e^{-U_{CC}/k_BT}\alpha^{N_P}(\mathbf{r}_C).\tag{10}$$

To consider the partitioning of polymer, the colloid-polymer mixture is assumed to be in osmotic equilibrium with a large reservoir containing a pure polymer solution at fixed chemical potential μ_P. Since the chemical potential of polymer, the temperature, and the total volume of the system are fixed, the proper thermodynamic ensemble is the semigrand canonical ensemble, with partition function given by

$$\Xi(N_C,V,T,\mu_P)=\sum_{N_P=0}^{\infty}e^{N_P\mu_P/k_BT}Z(N_C,V,T,N_P),\tag{11}$$

where $Z(N_C,V,T,N_P)$ is the canonical partition function of a system of N_C colloidal particles and N_P polymers.

Substituting Eqs. (5) and (6) into Ξ and summing over N_P gives

$$\Xi=Z_C^*\int\frac{d^3\mathbf{r}_C}{V^{N_C}}\exp\left[\frac{-U_{CC}}{k_BT}+a_P\alpha(\mathbf{r}_C)V\right],\tag{12}$$

where a_P is the polymer activity

$$a_P=\frac{e^{\mu_P/k_BT}}{\lambda_P^3}.\tag{13}$$

In mean-field approximation, in which the r_C-dependent terms are replaced by their averages over the unperturbed colloid system, we get the thermodynamic potential

$$\begin{aligned}\beta\Omega(N_C,V,T,\mu_P)&=-\ln\Xi\\&=\beta A_C-a_P\alpha V,\end{aligned}\tag{14}$$

where A_C and α are both functions of the colloid volume fraction η.

In the above, the polymer is assumed to be monodisperse. The effect of polymer polydispersity can also be determined from Eq. (14). Consider a mixture of N_C colloid particles and a polymer with density function $\rho_P(s)$, where $\rho_P(s)$ is defined such that the number density of polymer coils of size $s\sigma_C$ is $\rho_P(s)ds$. The potential Ω is generalized for the colloid/polydisperse-polymer mixture as follows:

$$\beta\Omega(N_C,V,T,\mu_P)=\beta A_C(\eta)-\int_0^\infty a_P(s)\alpha(s,\eta)Vds. \tag{15}$$

The polymer size distribution is assumed to be given by the Schultz distribution function [29]

$$f(s)=\frac{1}{z!}\left(\frac{z+1}{\overline{s}}\right)^{z+1}s^z\exp\left[-\left(\frac{z+1}{\overline{s}}\right)s\right], \tag{16}$$

with first moment

$$\begin{aligned} s_1&=\int_0^\infty sf(s)ds\\ &=\overline{s}, \end{aligned} \tag{17}$$

and the parameter z in Eq. (16) determines the broadness of the distribution. In the limit $z\rightarrow\infty$, the Schultz distribution tends to a δ function centered at $s=s_1$, and Eq. (15) reduces to Eq. (14).

Since the polymer is assumed to be ideal, its activity, which is also a function of s, can be expressed as

$$a_P(s)=\frac{\rho_R}{v_0}f(s), \tag{18}$$

where ρ_R is the total polymer number density of a polydisperse polymer system in a reservoir, which is in equilibrium with the colloid-polymer system, and v_0 is the volume of a colloidal sphere.

Substitution of the polymer activity into Eq. (15) yields

$$\frac{\beta\Omega(N_C,V,\rho_R;z,s_1)}{N_C}=\frac{\beta A_C(\eta)}{N_C}-\frac{\rho_R\alpha_{\mathrm{eff}}(\eta;z,s_1)}{\eta}, \tag{19}$$

where $\eta=N_Cv_0/V$ is the colloid packing density, and α_{eff} is defined as

$$\alpha_{\mathrm{eff}}(\eta;z,s_1)=\int_0^\infty ds\, f(s;z,s_1)\alpha(s,\eta). \tag{20}$$

An approximate expression for α can be obtained by using Widom's particle insertion method. Comparison with the scaled-particle expression [17] for the chemical potentials of a mixture of hard disks yields

$$\alpha(s,\eta)=(1-\eta)\exp[-(2s+s^2)\gamma-(cs^2+s^2)\gamma^2], \tag{21}$$

in which $\gamma=\eta/(1-\eta)$, $c=0.128$ and use has been made of Kratky's equation of state for hard disks [30].

To calculate the colloidal compositions η_{I} and η_{II} of the coexisting phases, the equations $\mu_C(\eta_{\mathrm{I}},\rho_R)=\mu_C(\eta_{\mathrm{II}},\rho_R)$ and $\Pi(\eta_{\mathrm{I}},\rho_R)=\Pi(\eta_{\mathrm{II}},\rho_R)$ are solved numerically. The osmotic pressure Π and the chemical potential μ_C of the colloids can be derived from the grand potential

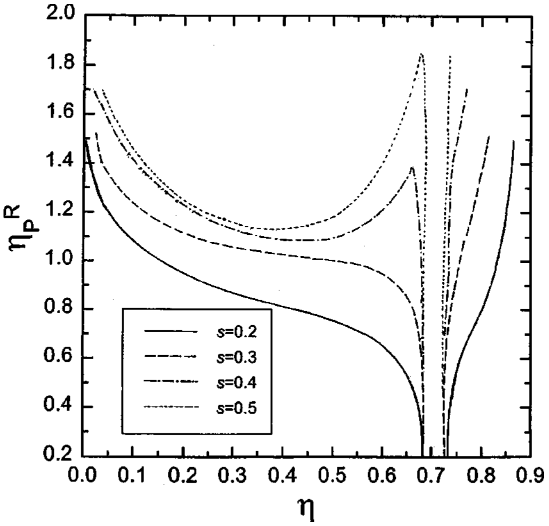

FIG. 2. Liquid-liquid coexistence for monodisperse polymer for various values of s. η is the volume fraction of colloid and η_P^R is the volume fraction of polymer in the reservoir. Both η and η_P^R are dimensionless.

$$\begin{aligned} \beta\Pi v_0&=-\beta v_0\left(\frac{\partial\Omega}{\partial V}\right)_{N,T,\mu_P}\\ &=\beta P_{HD}v_0+\rho_R\left[\alpha_{\mathrm{eff}}-\eta\frac{\partial\alpha_{\mathrm{eff}}}{\partial\eta}\right], \end{aligned} \tag{22}$$

$$\begin{aligned} \beta\mu_C&=\beta\left(\frac{\partial\Omega}{\partial N}\right)_{V,T,\mu_P}\\ &=\beta\mu_{HD}-\rho_R\frac{\partial\alpha_{\mathrm{eff}}}{\partial\eta}, \end{aligned} \tag{23}$$

where P_{HD} and μ_{HD} are the pressure and chemical potential of a hard-disk system, respectively, and are calculated from the equations of state for the hard-disk fluid and solid [30–31]. The freezing and melting compositions of a hard-disk system are taken as references for the chemical potential [32]. Thus, μ_C (fluid) and μ_C (solid) approach the same value at the expected coexistence compositions in the absence of polymer, namely $\eta\,(\mathrm{fluid})=0.689$, and $\eta\,(\mathrm{solid})=0.724$. It should be kept in mind that the solid phase is not crystalline, since long-ranged positional order is well known to be impossible in two dimensions for short-ranged forces.

III. RESULTS AND DISCUSSION

The coexistence curves in the $(\eta,\ \eta_P^R)$ plane, in which the polymer volume fraction in the reservoir, η_P^R, equals $\pi N_P\sigma_P^2/4V$, are given in Fig. 2. For $s=0.2$ and 0.3, only liquid-solid coexistence is observed. For $s=0.4$ and 0.5, liquid-liquid coexistence and critical points occur at high enough polymer volume fractions, which are larger than unity. Since in two dimensions the close-packing density for monodisperse polymers interacting as hard spheres is 0.906,

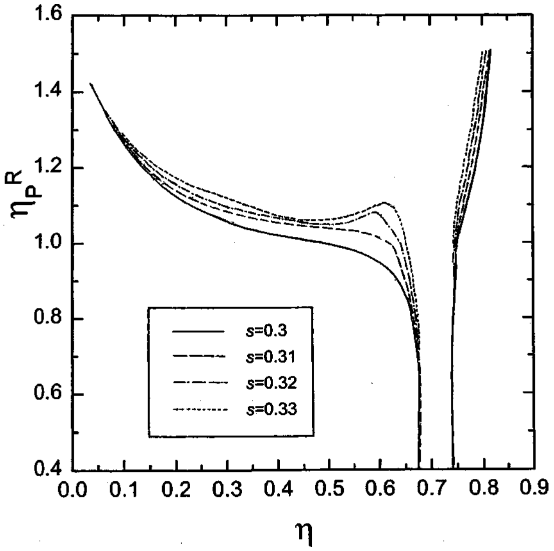

FIG. 3. Determination of s_m; detailed view of Fig. 2 for $0.3 < s < 0.33$.

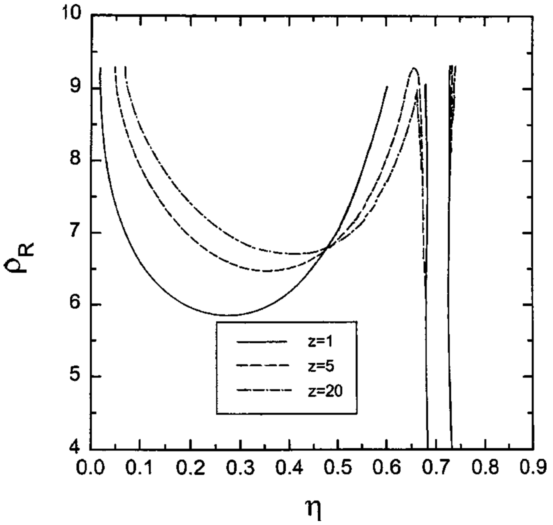

FIG. 4. Effect of polymer polydispersity on liquid-liquid coexistence for $s_1 = 0.4$. η is the volume fraction of colloid. ρ_R is the total number density of the polydisperse polymer in the reservoir. Both η and ρ_R are dimensionless.

liquid-liquid equilibrium is predicted never to occur. However, the polymers in the present model are assumed interpenetrable and noninteracting, and volume fractions above unity are therefore theoretically possible, although the assumption of ideal behavior of polymer is clearly no longer valid at such high concentrations.

In Fig. 3, the phase diagram for the colloid-polymer system is shown in detail in the range $0.3 < s < 0.33$. The minimal size ratio for the system to exhibit liquid-liquid coexistence, s_m, is found to be 0.31, which is slightly smaller than that found for the corresponding three-dimensional system [16,19]. The polymer volume fraction at the critical point is, again, larger than unity, implying that only liquid-solid coexistence could occur in a two-dimensional system. The polymer volume fraction has been transformed to $\rho_R = \eta_P^R / s^2$, which enables future comparison with polydisperse polymer systems (see below).

For polydisperse systems, the first moment s_1 of the Schultz distribution function [see Eqs. (16) and (17)], which reduces to the polymer size in monodisperse systems, is the average polymer size. Figure 4 shows the coexistence curves for $s_1 = 0.4$ for different values of the parameter z. Comparison of the latter with that of a monodisperse system (Fig. 2) reveals that with decreasing z, i.e., with broader polymer size distributions, the triple point is shifted toward higher colloid concentrations while the critical point is shifted toward lower colloid concentrations. Polydispersity is thus seen to increase the extent of liquid-liquid coexistence. A similar trend is observed in three dimensions [27]. Moreover, for smaller values of z, liquid-liquid coexistence occurs at smaller values of ρ_R. However, even for the broadest polymer-size distribution investigated here, the value of ρ_R at the critical point lies again above that of closest packing, at which $\rho_R = 5.65$. Thus, for $s_1 = 0.4$, no liquid-liquid coexistence is predicted to occur, even in the presence of polymer polydispersity.

The coexistence curves for the polydisperse system with $s_1 = 0.25$ are shown in Fig. 5 for different values of z. When $z < 5$, both liquid-liquid and liquid-solid coexistence are found. The approximate value of z below which liquid-liquid coexistence can occur is 4~5. Recall that only liquid-solid coexistence occurs in the monodisperse system for this value of s_1.

The occurrence of liquid-liquid coexistence in a two-dimensional system thus appears to be a delicate matter. Polymers must indeed have an average size which is large enough to induce strong enough depletion forces, but small enough to reduce the concentration needed at the critical point. Polydispersity of polymer is also indispensable. The values of the coefficient of variance (CV), a normalized standard deviation (SD) defined by

$$\mathrm{CV} = \mathrm{SD}/\mathrm{Mean}, \tag{24}$$

of the polydisperse polymers which induce liquid-liquid coexistence at $s < 0.31$, are shown in Fig. 6. For polymers with

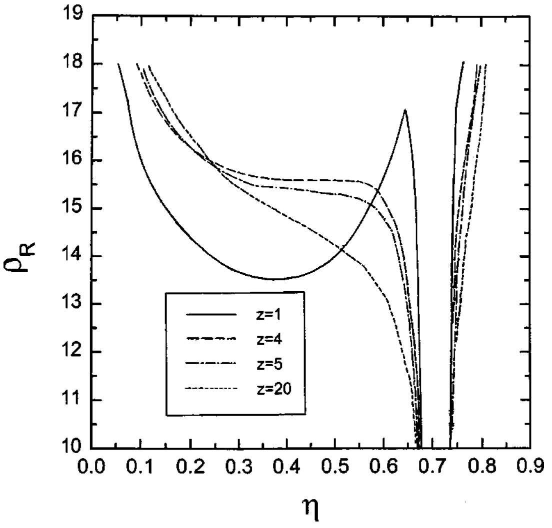

FIG. 5. Effect of polymer polydispersity on liquid-liquid coexistence for $s_1 = 0.25$. η is the volume fraction of colloid. ρ_R is the total number density of the polydisperse polymer in the reservoir. Both η and ρ_R are dimensionless.

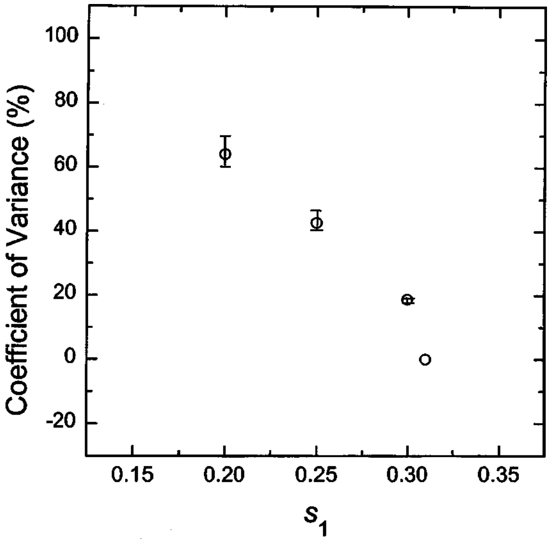

FIG. 6. Minimal polydispersity needed to induce liquid-liquid coexistence, for different values of s_1.

smaller average sizes s_1, a larger coefficient of variance, which corresponds to a broader size distribution, is needed to produce liquid-liquid coexistence.

The partitioning of polymer size distribution in coexisting phases is also studied. Figure 7 gives the size distributions of the polymers in the colloidal suspension at the triple point for $s_1 = 0.2$ and $z = 1$. The vertical line at $s = 0.2$ corresponds to a monodisperse polymer. The polymer density $\rho(s)$ is equal to $a_p(s) v_0 \alpha(s,\eta)$ and thus determined from the above. The partitioning and shifting of the polymer-size distributions are similar to those found in three dimensions [27].

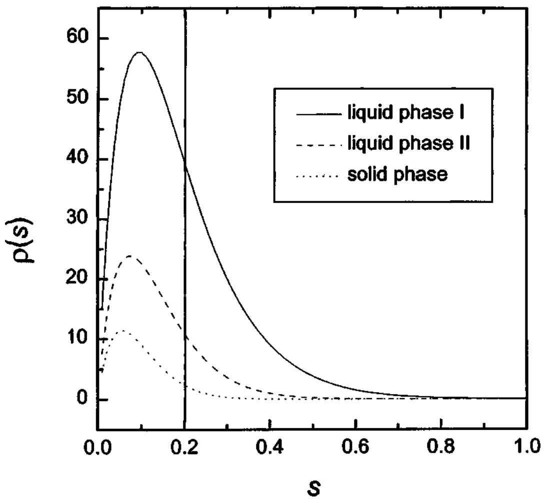

FIG. 7. Polymer size distributions at the triple point for $s_1 = 0.2$ and $z = 1$. $\rho(s)$ is the polymer density and is dimensionless.

A colloid-rich phase has a higher polymer density than a colloid-poor phase. Furthermore, the polymer-size distributions are also different in the coexisting phases. The maxima of the polymer-size distribution shift to lower values with increasing colloid densities, that is, smaller polymer coils have more free volume than larger ones in the colloid-rich phases, and thus occupy more space than the latter.

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