PHYSICAL REVIEW E **67**, 020401(R) (2003)

Phase behavior and crystallization kinetics of poly-12-hydroxystearic-coated polymethylmethacrylate colloids

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(Received 11 October 2002; published 26 February 2003; publisher error corrected 13 March 2003)

Polymethylmethacrylate (PMMA) colloids sterically stabilized by a layer of chemically grafted poly-12-hydroxystearic (PHSA) are widely used in experiments as model hard spheres. However, due to the coating, the interaction between particles is slightly soft. Here we report a numerical study of the effect of the PHSA coating on the phase behavior and crystallization kinetics of PMMA colloids based on parameters determined from surface-force measurements on PHSA-PMMA-coated mica surfaces [B. A. de L. Costello and P. F. Luckham, J. Colloid Interface Sci. **156**, 72 (1993); B. A. de L. Costello *et al.*, Langmuir **8**, 464 (1992)]. We find that the core volume fraction of particles at freezing measured by Pusey and van Megen [Nature **320**, 340 (1986)] can only be reproduced by using a thickness of the PHSA layer that is considerably larger than literature values. This may indicate that the particles are in fact slightly charged. Compared to perfect hard spheres, the crystallization rate in these slightly soft particles was found to be increased by about two orders of magnitudes.

DOI: 10.1103/PhysRevE.67.020401 PACS number(s): 82.70.Dd

A disordered collection of hard spheres is perhaps the simplest interacting fluid. The experimental realization of a colloidal suspension that closely mimics the phase behavior of hard spheres was a milestone in soft matter research [2–4]. Pusey and van Megen showed in the 1980s that polymethylmethacrylate (PMMA) particles stabilized by chemically grafted polyhydroxystearic acid (PHSA) reproduced closely the equilibrium phase behavior expected of hard spheres [2]. Other realizations are also known [5]. Recently, it was shown that the crystallization kinetics of hard spheres predicted by computer simulations [6] differed by several orders of magnitude from the crystallization rates measured in model colloids [7–9]. Polydispersity in the synthetic colloids cannot account for this discrepancy [10]. Another possible explanation is a slight softness in the interparticle potential. In this report, we investigate how such softness may affect phase behavior and crystallization kinetics.

The potential that we used to model the interaction between two PHSA-coated PMMA spheres was deduced from surface-force measurements. Costello *et al.* [1] measured the force between two mica surfaces coated with a PMMA-(backbone) PHSA (side chain) comb copolymer, with the PMMA backbone directly adsorbed on the mica and the PHSA side chains protruding into the solvent. The interaction thus mimics that between the surfaces of two PHSA-stablized PMMA colloids. Recently Bryant *et al.* [28] performed similar experiments, but there the PHSA was directly absorbed on the mica surface. Costello *et al.* [1] analyzed their measurements according to a model proposed by Alexander and de Gennes [11]. In this model, expected to be valid for high grafting densities, each chain is assumed to consist of connected semidilute blobs. The chains are stretched by osmotic repulsion between the blobs. This tendency is opposed by the increase in elastic free energy of the chain upon stretching. The resulting expression for the force per unit area between two parallel plates at a distance r is

$$F(r)=\frac{\alpha k_B T}{s^3}\left[\left(\frac{2L}{r}\right)^{9/4}-\left(\frac{r}{2L}\right)^{3/4}\right], \tag{1}$$

where s is the mean spacing between grafting points and L is the thickness of the polymer layer, α is a numerical prefactor, and k_BT is the thermal energy. The expression is supposed to hold for $0<r<2L$. Integration yields the corresponding energy density. From the distance of onset of the interaction, Costello *et al.* estimated that their layer thickness was $L=12.5$ nm. A fit of the Alexander–de Gennes model to experimental measurements yielded $\alpha=0.025$ and $s=2.8$ nm. By using the Derjaguin approximation (see, e.g., Ref. [12]) we can estimate the interaction potential between two spheres.

Different methods have been used to measure the thickness of the PHSA layer on PMMA colloids synthesized according to the method of Antl *et al.* [13], giving values of $L=7-13$ nm [14] and a maximum distance between grafting points of $s=2.0$ nm [15]. As a starting point in our calculations, we used $L=13.5$ nm and $s=2.0$ nm to yield the strongest repulsion compatible with these experimental data. Denoting the radius of a particle's PMMA core (without the PHSA hair) as R, we plot the interaction potentials for two cases, $R=305$ nm and 201 nm, in Fig. 1. These two radii are chosen to enable us to compare our calculations with the equilibrium phase behavior data of Pusey and van Megen [2,16] and the crystallization kinetics data of Harland and van Megen [7], respectively. We see that in both cases the interparticle interaction increases steeply to $10k_BT$ within 6–7 nm from the point of first contact.

We used the potential obtained above to calculate the freezing and melting densities of the colloidal suspensions from simulations using thermodynamic integration [17]. The resulting freezing and melting core volume fractions for our model potential were estimated to be $\phi_f=0.4137$ and $\phi_m=0.4579$ (for $R=201$ nm) and $\phi_f=0.4380$ and ϕ_m

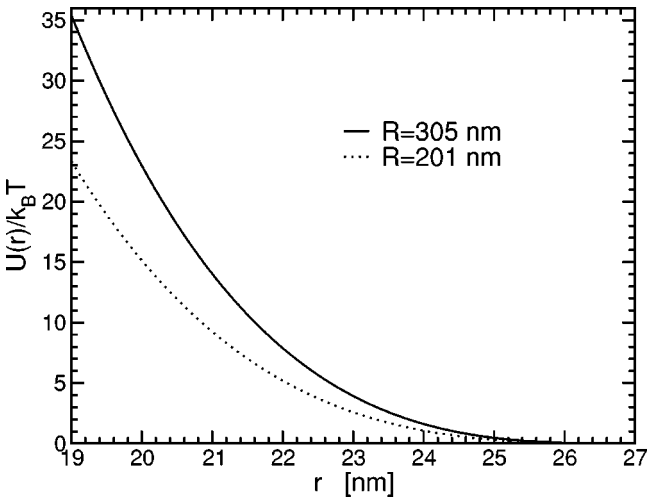

FIG. 1. Estimated interaction potential between two PMMA spheres coated with a layer of PHSA. Results are shown for particles with core radii of $R=201$ nm and 305 nm with the following values for the parameters: $s=2.0$ nm, $L=13.5$ nm, $\alpha=0.025$.

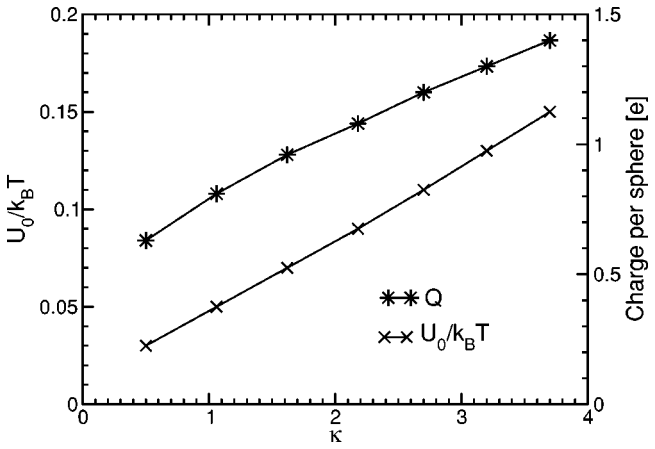

FIG. 2. Calculated parameter set $(U_0/k_BT,\kappa)$ of a hard-core Yukawa potential that accounts for the observed shift in the freezing density. The same curve but in units of charge per sphere is also shown.

$=0.4850$ (for $R=305$ nm). By scaling the freezing volume fractions to that of hard spheres, $\phi_f^{HS}=0.494$ [18], we obtain the effective hard-sphere diameter $\sigma_{\rm eff}=1.061\sigma$ and $\sigma_{\rm eff}=1.041\sigma$ of the two systems. We can compare these diameters to the effective hard-sphere diameter predicted by first-order perturbation theory: $\sigma_{\rm eff}=\int_0^\infty dr\{1-\exp[-U(r)/k_BT]\}$. The results $\sigma_{\rm eff}=1.061\sigma$ (for $R=201$ nm) and $\sigma_{\rm eff}=1.041\sigma$ (for $R=305$ nm) are identical to the estimate above. The values for the interaction potential at this distance are $U(r=\sigma_{\rm eff})/k_BT=0.7056$ and 0.7065. If we use the effective hard-sphere diameter to rescale the melting volume fractions of the soft systems to that of the hard spheres, we find $\phi_m=0.5469$ and $\phi_m=0.5463$ (to be compared with $\phi_m^{\rm HS}=0.545$ [18]).

Our results can be compared directly with the observations of Pusey and van Megen [2,16]. These authors measured the core radius of their PMMA particles by static light scattering and electron microscopy, and found $R=305$ nm. Knowing the core radius R, Pusey and van Megen dried down their suspensions and converted the measured mass fraction to core volume fractions using literature values of the densities of PMMA and the suspending liquid. They found core volume fractions at freezing and melting, $\phi_{\rm f}=0.407$ and $\phi_{\rm m}=0.441$ [19]. The corresponding effective hard-sphere diameter is $\sigma_{\rm eff}=1.067$. The experimental volume fractions are some 3.1% lower than the freezing volume fraction determined in our simulations. If we consider the fact that the particles are polydisperse (5%) the discrepancy increases to 4.1% [20]. One may seek to obtain a better fit to experiments by varying the parameters s and L. The value of s used gives the minimum surface coverage (at areal density s^{-2}) necessary for steric stabilization to function [15]. In any case, we find that the effective hard sphere diameter is somewhat insensitive to variations in s. Instead, agreement with the hard-core freezing volume fraction of Pusey and van Megen can be obtained by using a value of $L\approx 22$ nm. While there was no direct determination of the PHSA chain length for the batch of PMMA particles used by these authors, this value of L is twice to three times as long as values obtained from a variety of experiments on PHSA-coated PMMA particles [14]. Pusey and van Megen, who estimated the effective hard-sphere diameter of their particles to be $\sigma_{\rm eff}=2R(0.494/0.407)^{1/3}$, also concluded [16] that the implied PHSA layer thickness of $L\sim 20$ nm was rather larger than expected. It is therefore possible that there is an additional source of weak repulsion, such as a slight charge on the colloids.

If we assume that the interaction between charged colloids is described by a repulsive hard-core Yukawa potential: $(U_0/k_BT)\exp[-\kappa(r/\sigma-1)]/(r/\sigma)$ for $r>\sigma$, we can use the previous equation for the effective hard-sphere diameter from first-order perturbation theory to estimate the values of the parameter U_0/k_BT and κ needed to account for the observed shift in the freezing volume fraction. Here U_0/k_BT is the value of the Yukawa repulsion at contact and κ is the inverse screening length in units of the hard-sphere diameter σ. We find that the added repulsion is indeed quite weak, and very soft (see Fig. 2). Note that such a weak, soft repulsion can hardly be detected in the surface-force measurement. We can estimate the charge on a particle from the contact value of the interaction potential: $U_0/k_BT=Q^2/4\pi\epsilon_0\epsilon\sigma$, where Q is the charge, ϵ_0 and ϵ are the permittivities of the vacuum and the solvent. A value $U_0/k_BT=0.1$ corresponds to an average colloidal charge of about one electron per sphere. In more polar solvents, long range repulsions have been observed for the same kind of particles [21].

We turn now to study how the softness of the potential affects the crystallization kinetics. When a liquid is compressed to densities beyond freezing, crystallization can be very slow. The reason is that the free energy of a crystalline nucleus that forms in a supersaturated solution is the sum of two competing terms. The first is a bulk term that favors the transformation from the liquid to the solid state. If n particles transform from liquid to solid, the free energy gain is $n\Delta\mu$, where $\Delta\mu$ is the chemical potential difference between the two phases. This term is counterbalanced by the surface

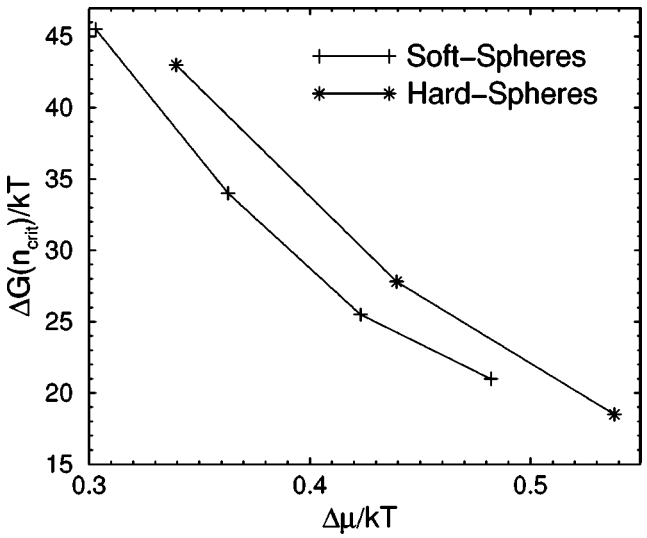

FIG. 3. Computed crystal nucleation barriers for the slightly soft spheres plotted as a function of supersaturation. In addition, we also show results from previous simulation on the hard-sphere system.

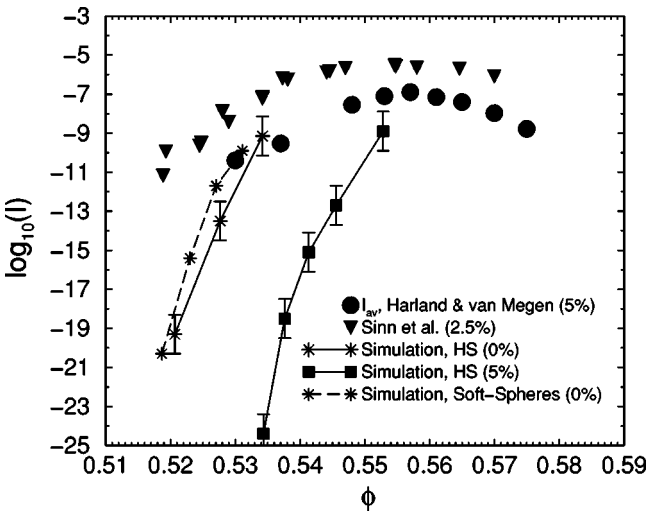

FIG. 4. Reduced nucleation rates I as a function of the rescaled volume fraction of the metastable fluid. We show the experimental results of Ref. [7] (●) and Ref. [8] (▼). The simulation data for the monodisperse colloids are indicated by *, where the solid and the dotted lines correspond to the hard-sphere system and the slightly soft system. The results of the hard-sphere system that has a polydispersity of 5% are shown as (■).

term, which describes the free energy required to create a liquid-solid interface $A\gamma$, where A is the surface area and γ is the surface free energy density. For small crystallites, the surface term dominates and the free energy increases. The free energy has a maximum at the critical cluster size n_{crit},

$$\Delta G(n_{\mathrm{crit}}) = \frac{16\pi}{3} \frac{\gamma^3}{(\rho_s |\Delta\mu|)^2}, \tag{2}$$

where ρ_s is the number density of the solid. For larger sizes, the bulk term dominates and the free energy decreases. The crystal nucleation rate per unit volume, I, is given by the product of the probability for the formation of a critical nucleus $P(n_{\mathrm{crit}}) \propto \exp[-\Delta G(n_{\mathrm{crit}})/k_B T]$ and a kinetic prefactor Γ,

$$I = \Gamma \exp[-\Delta G(n_{\mathrm{crit}})/k_B T]. \tag{3}$$

To compute the nucleation barrier, we require the (Gibbs) free energy of a nucleus of size n, given by $\Delta G(n) = \mathrm{const} - \ln[P(n)]$. The equilibrium cluster size distribution $P(n)$ is obtained using a biased Monte Carlo scheme in combination with a local bond-order analysis for the identification of crystal nuclei [6]. For the system with $R = 201$ nm, we computed the crystal nucleation barrier at four different pressures $P\sigma^3/k_B T = 12.5$, 13, 13.5, and 14, corresponding to volume fractions of the liquid $\phi_l = 0.43441$, 0.43803, 0.44144, and 0.44480. In Fig. 3 we show the results for the crystal nucleation barrier as a function of $\Delta\mu$. In the figure we also show the results for the hard-sphere system. As can be seen, despite the only slight softness, the crystal nucleation barrier is reduced by about $2-4k_B T$ at constant $\Delta\mu$. This is largely the result of a lowering of the surface tension compared to the case of hard spheres. If we assume that the nuclei are spherical, we can use Eq. (2) to calculate the surface free energy density of the critical nuclei. The results are $\gamma = 0.592 k_B T/\sigma^2$, $0.608 k_B T/\sigma^2$, $0.629 k_B T/\sigma^2$, $0.636 k_B T/\sigma^2$ (in order of increasing density).

To estimate the crystal nucleation rate we also need to compute the kinetic prefactor Γ. In reduced units, Γ has the form $\Gamma = Z\rho_l f^+_{n_{\mathrm{crit}}} (\sigma^5/D_0)$ [22]. Here $Z = [|\Delta G''(n_{\mathrm{crit}})|/(2\pi k_B T)]^{1/2}$ is the Zeldovich factor, which is a quantity that can be computed once the nucleation barrier is known. ρ_l is the number density of the liquid phase. The only unknown quantity is the reduced attachment rate of particles to the critical cluster $f^+_{n_{\mathrm{crit}}}/D_0$, where D_0 is the diffusivity of colloids at infinite dilution. To compute this quantity we used [6] a kinetic Monte Carlo scheme [23]. In such simulations, the effect of hydrodynamic interactions between the particles is usually neglected. To correct for this, we followed the approach proposed by Medina-Noyola [24]. In this scheme the computed $f^+_{n_{\mathrm{crit}}}$ is multiplied by a factor D_S^S/D_0, where D_S^S is the short time self-diffusion coefficient. For the hard-sphere system we could use the approximate expression $D_S^S/D_0 = (1-\phi/0.64)^{1.17}$ [25]. In order to apply this expression to slightly soft spheres, we used the rescaled volume fraction of the corresponding effective hard-sphere diameter. The result for the crystal nucleation rates as a function of $\Delta\mu$ is that the decrease in the nucleation barrier transforms into an increase of the crystal nucleation rate of about two orders of magnitudes. Our simulations can be compared directly with the experimental results of Harland and van Megen [7], who measured nucleation rates by time-resolved static light scattering for PMMA spheres of radius 201 nm [27]. To make this comparison, we show in Fig. 4 the crystal nucleation rate as a function of the rescaled volume fraction of the metastable fluid. Comparing first the results for monodisperse hard spheres [6] and monodisperse soft spheres (this work), we see that there is again an increase of the nucleation

rate by more than one order of magnitude. However, the particles used by Harland and van Megen were 5% polydisperse. Previous simulation results for 5% polydisperse hard spheres [6] are reproduced in Fig. 4: these disagree with Harland and van Megen's data by up to ten orders of magnitude. If we assume that the effect of softness on the nucleation rate is also an upward shift of a little over an order of magnitude, then the results for polydisperse soft spheres would agree somewhat better with the data, but substantial disagreement remains. We also show the results of experiments by Sinn *et al.* [8]. The particles they used are larger (435 nm, and, therefore, less soft) and have a polydispersity of 2.5% (i.e., more monodisperse than the particles used by Harland and van Megen). The simulation results for monodisperse hard spheres can therefore be expected to be more comparable. Even here, however, there remain many orders of magnitude disagreement.

The fact that the particles may be weakly charged and the system has a large Debye screening length might have two additional effects on the crystallization kinetics. First of all, the charge further lowers the surface free energy, which increases the nucleation rates. Second, as both the surface charge and the Debye screening length may depend on density this can qualitatively change the dependence of the nucleation rate on supersaturation [26]. A better agreement with experimental nucleation rates would be obtained if we make the (not unreasonable) assumption that the colloids become more hard-sphere-like at higher densities.

In summary, using parameters from surface-force measurements as input, we have calculated from simulations the effect of softness on the phase behavior and crystallization kinetics of a frequently used experimental model system—PMMA cores stabilized by PHSA. Experimental freezing and melting densities could only be reproduced if we assume a small amount of charge on the particles; whilst the gap between simulated and measured nucleation rates was reduced compared to the case of hard spheres, significant discrepancies remain.

W.C.K.P. thanks AMOLF for hospitality. We thank J. Hoogenboom, A. Yethiraj, and A. van Blaaderen for inspiring discussions and a critical reading of the manuscript. This work was supported by the Division of Chemical Sciences (CW) of The Netherlands organization for Scientific Research (NWO). The work of the FOM Institute is part of the research program of FOM, and was made possible by financial support from NWO.

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