PHYSICAL REVIEW E VOLUME 62, NUMBER 2 AUGUST 2000

Phase behavior of a model of colloidal particles with a fluctuating internal state

Richard P. Sear*
Department of Physics, University of Surrey, Guildford, Surrey GU2 5XH, United Kingdom

(Received 14 February 2000)

Colloidal particles are not simple rigid particles; in general an isolated particle is a system with many degrees of freedom in its own right, e.g., the counterions around a charged colloidal particle. The behavior of model colloidal particles, with a simple phenomenological model to account for these degrees of freedom, is studied. It is found that the interaction between the particles is not pairwise additive. It is even possible that the interaction between a triplet of particles is attractive while the pair interaction is repulsive. When this is so the liquid phase is either stable only in a small region of the phase diagram or absent altogether.

PACS number(s): 82.70.Dd, 78.30.Cp

I. INTRODUCTION

Theories for the behavior of systems of particles usually apply to a model for the interaction between particles in which the energy of interaction is pairwise additive. The Hamiltonian is of the form

$$H(\mathbf{r}^N)=\sum_{i,j=1}^{N}{}' \; u(r_{ij}), \tag{1}$$

a sum of spherically symmetric pairwise-additive potentials $u(r)$. $\mathbf{r}^N$ denotes the coordinates of the N particles and r_{ij} is the scalar separation of particles i and j. But experiments are almost never on simple rigid particles. For example, the particles in a colloidal suspension are not simple rigid particles. Generally they are stabilized in the suspension either by being charged, in which case they are surrounded by a cloud of counterions, or by having short polymers grafted to their surface [1]. In either case we have not a rigid particle but a system with many degrees of freedom, e.g., the positions of the counterions, which fluctuate. Each particle is a system, with a free energy, susceptibilities, etc., in its own right. Here we will treat systems of particles, each of which is a weakly fluctuating statistical mechanical system in its own right. Each particle will have a Landau-like free energy which couples to that of neighboring particles. We will use the simplest possible form of this free energy, and show exactly and analytically that it leads to many-body attractions. These cannot be expressed as a Hamiltonian with the form of Eq. (1).

This work is partly inspired by recent experiments on highly charged colloidal particles under conditions of minimal amounts of added salt. The potential of mean force between an *isolated* pair of colloidal particles with minimal salt concentrations has been measured and is purely repulsive [2]. Yet the particles form crystallites which appear to be metastable at close to zero osmotic pressure [3]; this is very hard to explain unless there is some sort of cohesive attraction between the particles in the crystallites. It does not seem possible to explain these findings with a Hamiltonian which depends only on the coordinates of the colloidal particles and has the conventional form of Eq. (1). Here we develop a simple phenomenological theory for colloidal particles which treats each particle as a fluctuating statistical mechanical system. See Refs. [4–11] for recent theoretical work on understanding this behavior starting from a Hamiltonian which explicitly includes the counterions and the electrostatic interactions. The theory is phenomenological as we simply *assume* that the state of a particle can be described by a single coarse-grained scalar variable; we do not derive this. This scalar variable fluctuates and these fluctuations are perturbed by the presence of another particle nearby. The perturbations due to the particles which surround any given particle add up, meaning that the state of a particle changes with the number of its neighbors. Essentially, the more particles that surround any given particle, the more the particle's fluctuations are biased towards values that minimize the interaction free energy and so the more attractive is the interaction between the given particle and all the surrounding particles. It is possible for two of our model particles to repel each other but for particles in clusters of more than two particles to attract each other. This can lead to coexistence between a dilute fluid and a dense crystal phase even when a pair of particles repel each other. We will show that generally if the fluctuations can be described by a scalar variable, then the interaction between a pair of particles within a cluster of several particles is more attractive than between an isolated pair.

In the next section we define our model. In Sec. III we show that it exactly corresponds to a potential between structureless particle which contains both pair and triplet terms. Then in Sec. IV we apply a perturbation theory to obtain an approximation to the free energy of both the fluid and crystalline phases, which is accurate for long-ranged interactions between the fluctuating internal states. We show results for the phase behavior and for the zero-wave-vector structure factor in Sec. V. Section VI is the conclusion.

II. MODEL

Our model particles have an internal state specified by a single scalar variable s. The value of the s variable for a single isolated particle fluctuates weakly. Essentially, we view it as a coarse-grained variable [12] obtained by averaging over some large number of degrees of freedom associ-

---

*Email address: r.sear@surrey.ac.uk

ated with each particle. An outline of how our mesoscopic Hamiltonian may be derived from a microscopic one is given in the Appendix. The interaction between a pair of the particles depends on the value of this variable. Thus, when two particles interact the mean values of the s variables on the two particles will change; the particles ‘‘polarize’’ each other. The interaction between them biases both internal variables towards values for which their interaction free energy is low. We included polarize in quotation marks because our model is phenomenological not electrostatic; cf. Ref. [8] which considers the polarization of one charged colloidal particle by another.

The effective Hamiltonian H of the system of particles has two parts: one part independent of the s variables, U, and the other the free energy of the particles as a function of the N internal variables, F_N,

$$H(\mathbf{r}^N,s^N)=U(\mathbf{r}^N)+F_N(\mathbf{r}^N,s^N), \tag{2}$$

where $\mathbf{r}^N$ and s^N symbolize the center-of-mass and internal-variable coordinates, respectively, of all N particles.

We need not specify U beyond saying that it should be such that the system has a well-defined thermodynamic limit [13]. Later on we will set U to be the sum of hard-sphere repulsions between pairs of the particles,

$$U(\mathbf{r}^N)=\frac{1}{2}\sum_{i,j=1}^{N}{}' \, u_{hs}(r_{ij}), \tag{3}$$

where u_{hs} is the hard-sphere potential:

$$u_{hs}(r)=\begin{cases}0, & r\geqslant\sigma,\\ \infty, & r<\sigma.\end{cases} \tag{4}$$

r is the separation of the centers of the interacting particles. The prime to the sum in Eq. (3) means that the sum is only over those terms for which $j\neq i$. Note that not all the double and triple sums below will have a prime; in the unprimed ones terms with equal subscripts are summed over.

Each particle has a dimensionless internal variable s. Now, we assume that the coupling between these variables on different particles is pairwise additive and spherically symmetric. Then the free energy F_N is

$$F_N(\mathbf{r}^N,s^N)=\sum_{i=1}^{N} f^{(1)}(s_i)+\frac{1}{2}\sum_{i,j=1}^{N}{}' \, f^{(2)}(s_i,s_j,r_{ij}). \tag{5}$$

$f^{(1)}$ is the free energy of a single isolated particle and is a function only of its s variable. $f^{(2)}$ is the difference in free energy between an isolated pair of particles and two isolated particles, and is a function only of the two s variables and the magnitude of the separation of the two particles. An isolated particle is a particle far from any other particle; an isolated pair of particles is a pair of particles far from any other particle. For weak fluctuations s is small, so we Taylor expand $f^{(1)}$ and $f^{(2)}$,

$$f^{(1)}(s)=\alpha s^2+\alpha_3 s^3+\alpha_4 s^4+\cdots, \tag{6}$$

where the linear term is missing as the variable s is defined so that if a particle is isolated, its mean value is zero, and

$$f^{(2)}(s,s',r)=\phi_0(r)+\phi_1(r)(s+s')+\phi_2(r)(s^2+s'^2)+\phi_2^x(r)ss'+\cdots. \tag{7}$$

The coefficients α, α_3, etc., are derivatives of $f^{(1)}$,

$$\alpha=\frac{1}{2}\frac{d^2 f^{(1)}(s)}{ds^2}, \tag{8}$$

and α_3 is 1/6 times the third derivative, etc. Similarly, the coefficients $\phi_0(r)$, $\phi_1(r)$, etc., are derivatives of $f^{(2)}$ at a fixed separation of the particles. ϕ_0 is the zeroth derivative, ϕ_1 is the first derivative with respect to either of the two s variables,

$$\phi_1(r)=\left(\frac{\partial f^{(2)}(s,s',r)}{\partial s}\right)_{s',r}, \tag{9}$$

and similarly for the higher derivatives ϕ_2, etc.

Our Taylor expansions are quite general for particles which have a state which can be described by a single weakly fluctuating scalar variable and in which the interaction between two particles can be expressed in terms of this variable. If the variable is a vector or a tensor and not a scalar, then clearly there will be expressions analogous to that of Eq. (5) but vectorial or tensorial variables will in general lead to results very different from those found here.

We truncate the Taylor expansions, Eqs. (6) and (7), after their lowest nontrivial terms and substitute the resulting expansions into Eq. (5) to obtain

$$F_N(\mathbf{r}^N,s^N)=\sum_{i=1}^{N}\alpha s_i^2+\frac{1}{2}\sum_{i,j=1}^{N}{}' \,[\phi_0(r_{ij})+\phi_1(r_{ij})(s_i+s_j)]. \tag{10}$$

The inverse susceptibility α and the zeroth, ϕ_0, and first, ϕ_1, order coefficients all have the dimensions of energy. So for our Hamiltonian, Eqs. (2) and (10), to describe a system of particles accurately we require (1) that the fluctuations in s of an isolated particle be sufficiently small that the higher order terms in $f^{(1)}$ may be neglected, (2) that the interactions between the particles can be described as a sum over interactions of pairs, (3) that this interaction is spherically symmetric, (4) that this interaction can be accurately described by a function of this single scalar, coarse-grained, variable, and (5) that the interactions between fluctuations are sufficiently weak that the higher terms in $f^{(1)}$ and $f^{(2)}$ are small.

For noninteracting particles the second sum of Eq. (10) may be neglected and F_N is just a sum of independent quadratic terms. The distribution of the s's is then Gaussian, which is correct for small fluctuations of a coarse-grained variable [12,14]. α is the inverse susceptibility of an isolated particle; the smaller it is, the larger are the fluctuations. The interaction between a pair of particles is expressed as a Taylor expansion in the two s's truncated after the linear term. One particle feels an interaction due to another nearby particle, which couples to its order parameter s with a strength $\phi_1(r)$. The s dependence of the free energy of Eq. (10) is what we would expect if the particles were weakly interacting, weakly fluctuating thermodynamic systems.

III. EXACT THEORY

We start from the configurational integral Z_N for N particles in a volume V and at a temperature T,

$$Z_N=\int d\mathbf{r}^N ds^N \exp[-H(\mathbf{r}^N,s^N)/kT], \tag{11}$$

with the Hamiltonian given by Eqs. (2) and (10). The Helmholtz free energy A is then

$$A=-kT\ln(Z_N\Lambda^N/N!), \tag{12}$$

where Λ derives from the integration over the momenta. Using Eqs. (2) and (10) in Eq. (11),

$$\begin{aligned}Z_N&=\int d\mathbf{r}^N \exp[-U(\mathbf{r}^N)/kT]\int ds^N\\&\quad\times\exp\left(-\sum_{i=1}^{N}(\alpha/kT)s_i^2-\frac{1}{2}\sum_{i,j=1}^{N}{}'\,[\phi_0(r_{ij})/kT\right.\\&\quad\left.+\phi_1(r_{ij})(s_i+s_j)/kT]\right)\\&=\int d\mathbf{r}^N\exp\left(-\frac{U(\mathbf{r}^N)}{kT}-\frac{1}{2}\sum_{i,j=1}^{N}{}'\,\frac{\phi_0(r_{ij})}{kT}\right)\\&\quad\times\prod_{i=1}^{N}\left\{\int_{-\infty}^{\infty}\mathrm{d}s_i\exp\left(-\frac{\alpha}{kT}s_i^2-\sum_{j=1\ j\neq i}^{N}\frac{\phi_1(r_{ij})}{kT}s_i\right)\right\},\end{aligned} \tag{13}$$

where to obtain the second line we expressed the integral over the s variables as a product of integrations over each one and then grouped all the terms which depend on each s_i together. Each integration over an s variable is independent and can be done easily,

$$\begin{aligned}Z_N&=\int d\mathbf{r}^N\exp\left(-\frac{U(\mathbf{r}^N)}{kT}-\frac{1}{2}\sum_{i,j=1}^{N}{}'\,\frac{\phi_0(r_{ij})}{kT}\right)\prod_{i=1}^{N}\left\{\left(\frac{\pi kT}{\alpha}\right)^{1/2}\exp\left(\frac{1}{4\alpha kT}\left[\sum_{j=1\ j\neq i}^{N}\phi_1(r_{ij})\right]^2\right)\right\}\\&=\left(\frac{\pi kT}{\alpha}\right)^{N/2}\int d\mathbf{r}^N\exp\left(-\frac{U(\mathbf{r}^N)}{kT}-\frac{1}{2}\sum_{i,j=1}^{N}{}'\,\frac{\phi_0(r_{ij})}{kT}\right)\prod_{i=1}^{N}\left\{\exp\left(\frac{1}{4\alpha kT}\sum_{j=1\ j\neq i}^{N}\sum_{k=1\ k\neq i}^{N}\phi_1(r_{ij})\phi_1(r_{ik})\right)\right\}\\&=\left(\frac{\pi kT}{\alpha}\right)^{N/2}\int d\mathbf{r}^N\exp\left(-\frac{U(\mathbf{r}^N)}{kT}-\frac{1}{2}\sum_{i,j=1}^{N}{}'\,\frac{\phi_0(r_{ij})}{kT}+\frac{1}{4\alpha kT}\sum_{i,j,k=1\ j\neq i k\neq i}^{N}\phi_1(r_{ij})\phi_1(r_{ik})\right),\end{aligned} \tag{14}$$

where to obtain the second from the first line we expressed the square of the sum as a double sum. To obtain the third line we converted the product of exponentials to the exponential of a sum. The factor in front of the integration is of course very familiar: it is just the partition function of N independent simple harmonic oscillators. It does not depend on density and so has no effect on the phase behavior. Note that in the triple sum, although neither j nor k can be equal to i, j can be equal to k. The restrictions on j and k derive from the fact that a particle cannot interact with itself, which would correspond to $j,k=i$, but as both j and k in the triple sum come from the square of a single sum they are in effect from the same interaction and therefore are allowed to be equal. We can rewrite Eq. (14) by extracting the $j=k$ terms from the triple sum,

$$\begin{aligned}Z_N=\left(\frac{\pi kT}{\alpha}\right)^{N/2}\int \mathrm{d}\mathbf{r}^N\exp&\left(-\frac{U(\mathbf{r}^N)}{kT}\right.\\&-\frac{1}{2}\sum_{i,j=1}^{N}{}'\left[\frac{\phi_0(r_{ij})}{kT}-\frac{\phi_1(r_{ij})^2}{2\alpha kT}\right]\\&\left.+\frac{1}{4\alpha kT}\sum_{i,j,k=1}^{N}{}'\,\phi_1(r_{ij})\phi_1(r_{ik})\right),\end{aligned} \tag{15}$$

where the triple sum has a prime to indicate that terms in which any of the three subscripts are the same are excluded. The configurational integral, Eq. (15), is an integral only over the positions of the N particles. Neglecting the irrelevant (for the phase behavior) prefactor it is nothing but the configurational integral of the Hamiltonian H_{eff},

$$H_{eff}(\mathbf{r}^N)=U(\mathbf{r}^N)+\frac{1}{2}\sum_{i,j=1}^{N}{}'\left[\phi_0(r_{ij})-\frac{\phi_1(r_{ij})^2}{2\alpha}\right]-\frac{1}{6}\sum_{i,j,k=1}^{N}{}'\,\frac{[\phi_1(r_{ij})\phi_1(r_{ik})+\phi_1(r_{ij})\phi_1(r_{jk})+\phi_1(r_{ik})\phi_1(r_{jk})]}{2\alpha}, \tag{16}$$

where we have rewritten the summand of the triple sum to make it symmetric with respect to the three indices. The phase behavior of our model particles will be identical to that of structureless, spherically symmetric particles with interactions described by the Hamiltonian H_{eff} of Eq. (16). The Hamiltonian is that of a triplet or three-body potential; the first two sums are conventional sums over pair potentials but the last sum is over a three-body potential. We started with a pair potential which depended on the s variables as well as the positions; integration over the s variables resulted in a potential which depends only on the positions but is no longer a simple pair potential.

The effective Hamiltonian H_{eff} can lead to behavior qualitatively different from that of a Hamiltonian which is a simple sum over a pair potential. To see this we will compare the interaction between a pair of particles to that between a triplet of particles. For a pair of particles 1 and 2, a distance r apart, the interaction is from Eq. (16),

$$H_{eff}(\mathbf{r}^2)=U(\mathbf{r}^2)+\phi_0(r)-\frac{1}{2}\frac{\phi_1(r)^2}{\alpha}. \tag{17}$$

Note that the contribution due to the fluctuations, the part inversely proportional to α is always negative regardless of the sign of ϕ_1; fluctuations always produce an effective attraction. Now, consider three particles, at the corners of an equilateral triangle of side r for simplicity. We denote the set of three coordinates marking the corners of an equilateral triangle by $\mathbf{r}_e^3$. The interaction is, from Eq. (16),

$$H_{eff}(\mathbf{r}_e^3)=U(\mathbf{r}_e^3)+3\phi_0(r)-3\frac{\phi_1(r)^2}{\alpha}. \tag{18}$$

If we compare this with the interaction of a pair, Eq. (17), we see that the ratio of the ϕ_1^2/α to ϕ_0 term has doubled. For a pairwise additive potential, the interaction free energy would be simply 3 times Eq. (17): $3\phi_0-(3/2)\phi_1^2/\alpha$. The relative contribution from the fluctuations in the s variables has doubled. This contribution is always attractive, so the free energy of attraction is always more negative than for a pairwise additive potential. This is a general result for a weakly fluctuating scalar variable. Our result for the interaction between three particles may be compared with the more microscopic work on the interaction between three particles of Löwen and co-workers. They considered triplet interactions between charged colloidal particles [15] and between star polymers [16].

When $\phi_0(r)>0$ and $\phi_0(r)<\phi_1(r)^2/\alpha<2\phi_0(r)$, the interaction minus the part from U is repulsive, i.e., greater than zero, for a pair r apart but attractive for a triplet at the corners of an equilateral triangle of side r. If U is some short-range repulsion, e.g., a hard-sphere repulsion, which is zero at some sufficiently large value of r, then it is possible for a pair of our model colloidal particles to repel each other, but for a triplet of them to attract. For other arrangements of three particles the sign of the interaction free energy will depend on the values of the three separations of the centers of the particles and on the distance dependence of ϕ_0 and ϕ_1. However, this should not obscure the basic fact that the interaction free energy of three particles can be negative when the interaction of two particles is positive. For four particles at the corners of a tetrahedron the interaction minus the part from U is $6\phi_0-9\phi_1^2/\alpha$. Again, it is possible to obtain negative interaction free energies even when the interaction free energy of a pair is always positive. Indeed it is possible to obtain negative free energies even when they are positive for three particles at the corners of an equilateral triangle.

IV. MEAN-FIELD FREE ENERGY

In order to able to keep the theory simple we now specialize to an interaction between the internal variables which is both weak and long ranged. Weak in the sense that $|\phi_0(r)|,|\phi_1(r)\phi_1(r')/\alpha|\ll kT$ for all values of r, r', and long ranged as both $\phi_0(r)$ and $\phi_1(r)$ decay to zero over a characteristic length scale which is much longer than the hard-sphere diameter σ. We also set U to be the hard-sphere interaction. So the interaction Hamiltonian, Eq. (16), which is a function of the positions only, consists of a hard-sphere interaction U and a weak long-ranged interaction which has two parts: a pair potential and a triplet potential. Weak but long-range many-body interactions have been considered by the author in Ref. [17].

We view the long-range part of the interactions as a perturbation [18]. The free energy is expressed as that of hard spheres, A_{hs}, plus the difference in free energy between a system of our particles and that of hard spheres, ΔA,

$$A=A_{hs}+\Delta A. \tag{19}$$

For the hard-sphere free energy we use the expression of Carnahan and Starling [19] for the fluid phase and the fit to simulation data of Hall [20] for the solid phase. We approximate ΔA by an average of the perturbing part of the Hamiltonian, $H_{eff}-U$,

$$\Delta A=\frac{\int d\mathbf{r}^N[H_{eff}(\mathbf{r}^N)-U(\mathbf{r}^N)]\exp[-U(\mathbf{r}^N)/kT]}{Z_{hs}}, \tag{20}$$

where Z_{hs} is the configurational integral for N hard spheres.

Substituting Eq. (16) into Eq. (20),

$$\Delta A=Z_{hs}^{-1}\int d\mathbf{r}^N\exp[-U(\mathbf{r}^N)/kT]\times\left\{\frac{1}{2}N(N-1)\left(\phi_0(r_{12})-\frac{\phi_1(r_{12})^2}{2\alpha}\right)-\frac{1}{6}(N-1)(N-2)\frac{3\phi_1(r_{12})\phi_1(r_{13})}{2\alpha}\right\}. \tag{21}$$

The n-particle density of hard spheres, $\rho_{hs}^{(n)}$, and their n-particle distribution function $g_{hs}^{(n)}$ are defined as [18]

$$\rho_{hs}^{(n)}(\mathbf{r}^n)=\left(\prod_{i=1}^{n}\rho_{hs}^{(1)}(\mathbf{r}_i)\right)g_{hs}^{(n)}(\mathbf{r}^n)$$
$$=\frac{N!}{(N-n)!}\frac{\int\exp[-\beta U(\mathbf{r}^N)]d\mathbf{r}^{N-n}}{Z_{hs}}. \tag{22}$$

The one-particle density $\rho_{hs}^{(1)}(\mathbf{r})$ is not assumed to be uniform so that the theory applies to crystalline as well as fluid phases. Using, Eq. (22) in Eq. (21), we obtain

$$\Delta A=\frac{1}{2}\int d\mathbf{r}^2\rho_{hs}^{(2)}(\mathbf{r}_1,\mathbf{r}_2)\left(\phi_0(r_{12})-\frac{\phi_1(r_{12})^2}{2\alpha}\right)$$
$$-\frac{1}{4\alpha}\int d\mathbf{r}^3\rho_{hs}^{(3)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)\phi_1(r_{12})\phi_1(r_{13}). \tag{23}$$

As ϕ_0,ϕ_1 decay to zero only when the separations of the particles are much larger than σ, the integrals in Eq. (23) are dominated by configurations when the spheres are far apart, i.e., where the pair separations are much larger than σ. In a fluid the one-particle density is a constant, $\rho^{(1)}=\rho$, and at separations large with respect to σ the distribution function is close to 1, $g_{hs}^{(n)}\simeq 1$. Thus in the fluid phase the integrands of Eq. (23) can be simply approximated by $\rho^2[\phi_0(r_{12})-\phi_1(r_{12})^2/2\alpha]$ and $\rho^3\phi_1(r_{12})\phi_1(r_{13})$. In a crystalline phase, although there are long-range correlations in $\rho_{hs}^{(n)}$, the one-particle density $\rho_{hs}^{(1)}$ averaged over a unit cell is just ρ. The attractive interaction between particles has a range much larger than the lattice constant of the lattice (a little larger than σ) and so as ϕ_0 and ϕ_1 vary little across a unit cell we can regard $\rho_{hs}^{(1)}(\mathbf{r})$ as approximately constant at its average value, ρ. Similarly, as we change any one of the n position vectors upon which the n-body distribution function $\rho_{hs}^{(n)}$ depends, the density oscillates rapidly over each unit cell but averages to ρ. So in the crystalline phase as well as in the fluid phase we approximate $\rho_{hs}^{(n)}$ by ρ^n. Then the integrands are the same as in a fluid phase. We have

$$\Delta A=\frac{1}{2}V\rho^2\int_\sigma^\infty d\mathbf{r}\left(\phi_0(r)-\frac{\phi_1(r)^2}{2\alpha}\right)$$
$$-\frac{1}{4\alpha}V\rho^3\left(\int_\sigma^\infty d\mathbf{r}\phi_1(r)\right)^2. \tag{24}$$

Now the term coming from the square of ϕ_1 is negligible if ϕ_1 is long ranged. To see this consider an explicit functional form for ϕ_1. We choose a Kac potential

$$\phi_1(r)=\epsilon\gamma^3\exp(-\gamma r/\sigma). \tag{25}$$

The range of this function is σ/γ; i.e., γ^{-1} is a range in units of σ. Now the integral of Eq. (25) over three-dimensional space is $\mathcal{O}(\epsilon\sigma^3)$; essentially the integrand is of order $\epsilon\gamma^3$ within a volume of order $(\sigma/\gamma)^3$, and negligible outside of this volume. However, the integral of the square of Eq. (25) over three-dimensional space is $\mathcal{O}(\epsilon^2\sigma^3\gamma^3)$. For a long-range ϕ_1, the inverse range $\gamma\ll 1$ and so the integral of the square is negligible. We chose a specific functional form for ϕ_1 simply for clarity; our conclusion that the integral of the square is negligible holds for any long-range slowly decaying function.

So, in Eq. (24), we neglect the ϕ_1^2 term, integrate over the remaining terms in Eq. (24), and obtain

$$\frac{\Delta A}{N}=\frac{1}{2}\rho\nu_0-\frac{1}{4}\frac{(\rho\nu_1)^2}{\alpha}, \tag{26}$$

where ν_0 and ν_1 are the integrals

$$\int_\sigma^\infty d\mathbf{r}\phi_i(r)=\nu_i,\quad i=0,1. \tag{27}$$

The pressure p can be easily derived from the free energy, Eq. (26),

$$p=p_{hs}+\frac{1}{2}\rho^2\nu_0-\frac{1}{2}\frac{\rho^3\nu_1^2}{\alpha}, \tag{28}$$

where p_{hs} is the pressure of hard spheres. The contribution from the fluctuations in the s variables to the pressure is cubic in the density as it must be; it is equivalent to a long-range three-body attraction [17]. The chemical potential μ is then simply given by $\mu=A/N+p/\rho$. The pressure and chemical potential as functions of the temperature and density allow us to calculate phase diagrams.

V. RESULTS

The free energy, Eq. (26), depends on a single parameter, the dimensionless ratio $R=\nu_0\alpha\sigma^3/\nu_1^2$. R ranges from $-\infty$ to $+\infty$; the sign of R is determined by the sign of ν_0 as α must be positive. The larger the magnitude of R, the more dominant is the part of the interaction potential which does not depend on s and so the closer the interaction is to a pairwise additive potential. In the $R\rightarrow-\infty$ limit the interaction is a simple pairwise additive attractive potential. Then the free energy is just a modification of the free energy of van der Waals [18,21–23], the modification being the replacement of his approximate free energy of hard spheres by that of Carnahan and Starling [19] in the fluid and that of Hall [20] in the crystal. In the $R\rightarrow+\infty$ limit the potential is again pairwise additive but it is repulsive. A long-range repulsion tends to cause not bulk vapor-liquid separation but microphase separation; see Refs. [22,24]. The $R\rightarrow\pm\infty$ limits result from either the interaction between particles not depending on the value of the s variables, $\nu_1\rightarrow 0$, or the fluctuations of the s variables tending to zero, $\alpha\rightarrow\infty$.

When R is finite then the interactions depend on the fluctuations in s and are no longer pairwise additive. For $R<0$ the interactions are attractive even in the absence of fluctuations in s; the fluctuations in s merely make the attractions stronger and not pairwise additive. For $R>0$ the pairwise interactions are repulsive while the three-body interactions from the fluctuations are, as always, attractive. The part of the free energy due to fluctuations, the last term in Eq. (26), is one power higher in the density than the part independent of the fluctuations, the second in Eq. (26). Thus, if $\nu_0>0$, the interactions are always repulsive at sufficiently low densities but become attractive, i.e., contribute a negative

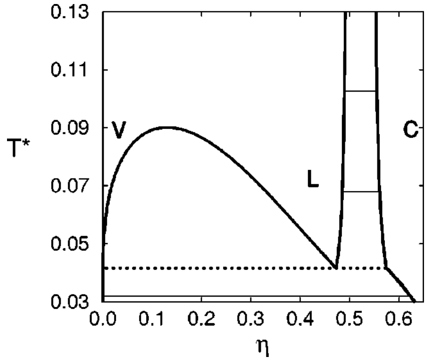

FIG. 1. The phase diagram of hard spheres plus a long-range pairwise additive attraction, a van der Waals fluid. $\nu_1=0$, $\nu_0<0$ and the reduced temperature $T^*=kT\sigma^3/|\nu_0|$. The thick solid curves separate the one- and two-phase regions. The letters V, L, and C denote the regions of the phase space occupied by the vapor, liquid, and crystalline phases, respectively. The horizontal thin lines are tie lines connecting coexisting densities, and the dotted line connects the three coexisting densities at the triple point.

amount to the free energy of the system, at a density $2R/\sigma^3$.

We now discuss some example phase diagrams. The diagrams are in the density-temperature plane. We use the reduced density $\eta=(\pi/6)\rho\sigma^3$, which is equal to the fraction of the volume occupied by the hard cores, and a reduced temperature T^* which is either $kT\sigma^3/|\nu_0|$ or $kT\alpha\sigma^6/\nu_1^2$. For reference we plot the familiar phase diagram of hard spheres with a long-range attraction, often called the van der Waals fluid [21–23], the $R\rightarrow-\infty$ limit. This has a free energy given by Eqs. (19) and (26) with $\nu_1=0$ and $\nu_0<0$. The first condition means that the internal variables on different particles do not couple and so the attraction is a simple pair potential and the second condition makes the long-range interaction attractive so that there is a vapor-liquid transition, i.e., phase separation into two fluid phases of different densities. The phase diagram is shown in Fig. 1; there is a large temperature range over which there is stable vapor-liquid coexistence. This is, of course, not new; in the $\nu_1=0$ limit our model reduces to the most basic model of particles which form a liquid.

In Fig. 2 we show the phase diagram of particles with $R=0$. The long-range interaction is purely proportional to the internal variable s, i.e., $\nu_0=0$. There is vapor-liquid coexistence over a range of temperatures but this range is much smaller than for the simple pair potential of Fig. 1. The ratio of the temperature at the critical point to that at the triple point is smaller in Fig. 2 than in Fig. 1. Also, the density at the critical point is higher; it is almost double that in Fig. 1 and so the density range of the liquid phase is small. The interaction between s variables is effectively a long-range three-body attraction, i.e., an attraction which is van der Waals like except for the fact that it is between triplets not pair of particles [17]. The phase diagram, Fig. 2, differs from Fig. 2 of Ref. [17] only in that the temperature scale is different.

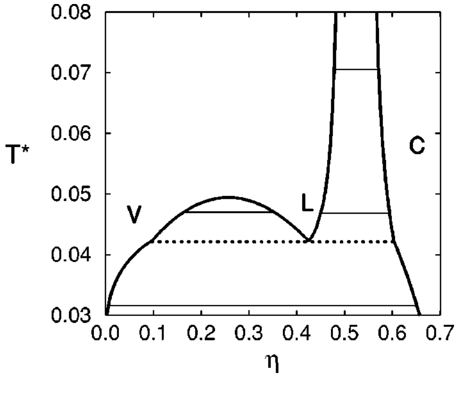

FIG. 2. The phase diagram of hard spheres plus a long-range interaction proportional to the fluctuating internal variable s. $\nu_0=0$, and the reduced temperature $T^*=kT\alpha\sigma^6/\nu_1^2$. See caption to Fig. 1 for the meaning of the letters, curves, and horizontal lines.

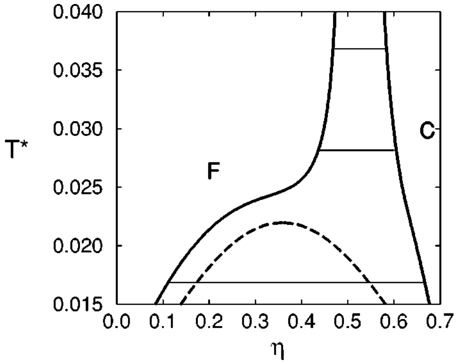

FIG. 3. The phase diagram of hard spheres plus a long-range repulsion and a long-range attraction proportional to the fluctuating internal variable s. $R=0.5$, and the reduced temperature $T^*=kT\alpha\sigma^6/\nu_1^2$. The letters F and C denote the regions of the phase space occupied by the fluid and crystalline phases, respectively. The dotted curve is the bulk free energy prediction of a vapor-liquid-like transition within the fluid-crystal coexistence region. See caption to Fig. 1 for the meaning of the other curves and the horizontal lines.

In Fig. 3 we show the phase diagram of particles with $R=0.5$. There is no vapor-liquid coexistence at equilibrium, only a fluid-crystal coexistence region which broadens dramatically at low temperatures. The liquid phase has disappeared. For other examples of liquid phases disappearing see Ref. [25]; the most studied system in which the liquid disappears is that of particles with a short-range, pairwise additive attraction [26–29]. Within the fluid-crystal coexistence region the pressure and chemical potential have van der Waals loops, so our bulk free energy predicts vapor-liquid coexistence within the fluid-crystal coexistence region. Note that the density at the critical point is even higher than in Fig. 2.

We have only considered fluid phases and crystalline phases. However, sufficiently strong long-range repulsions can transform a bulk phase separation into a microphase separation [22,24]. Essentially, microphase separation occurs when the interaction between particles is repulsive at the largest separations at which they interact separately and the repulsion is sufficiently strong and long ranged. Thus our present theory, which neglects the possibility of microphase separation, should not be used if the long-range interaction is predominantly repulsive, i.e., if $\nu_0>0$, and either ϕ_0 is longer ranged than ϕ_1, or $R\gg1$.

Structure of the fluid phase

We have shown that the phase behavior of our particles can be very different from that of a simple pair potential but what about the structure? Of course the pair distribution function or equivalently the structure factor [18] depends on the functional form of the interactions, i.e., on the precise forms of the functions $\phi_0(r)$ and $\phi_1(r)$. However, we have only considered long-range interactions and there the bulk phase behavior is insensitive to the precise details of $\phi_0(r)$ and $\phi_1(r)$; it only depends on their integrals ν_0 and ν_1. Also, long-range interactions only affect the structure factor $S(q)$ at small wave vectors q, small meaning of order of the reciprocal of their range or less. Thus, we will consider only the zero-wave-vector limit $S(0)$ of the structure factor. This is simply related to a thermodynamic quantity, the isothermal compressibility χ_T, by [18]

$$S(0)=\rho kT\chi_T, \tag{29}$$

where

$$\chi_T^{-1}=\rho\left(\frac{\partial p}{\partial \rho}\right)_T. \tag{30}$$

Using Eq. (28) for the pressure,

$$\chi_T^{-1}=\rho\left(\frac{\partial p_{hs}}{\partial \rho}\right)_T+\rho^2\nu_0-\frac{3}{2}\frac{\rho^3\nu_1^2}{\alpha}. \tag{31}$$

Equations (29) and (31) give us the zero-wave-vector structure factor of our particles. Below we will consider the density dependence of $S(0)$. It will therefore be useful to obtain $S(0)$ as a density expansion. To do this we start by inserting the virial expansion for the pressure into the definition of the isothermal compressibility χ_T, Eq. (30). Inserting this expansion into Eq. (29) for $S(0)$ yields

$$S(0)=1-2B_2\rho+O(\rho^2); \tag{32}$$

the initial slope of $S(0)$ is equal to minus twice the second virial coefficient B_2. For our particles,

$$B_2=\frac{2}{3}\pi\sigma^3+\frac{1}{2}\frac{\nu_0}{kT}, \tag{33}$$

where the first term on the right hand side is the second virial coefficient of hard spheres. Note that the fluctuations in the s variables do not contribute to the second virial coefficient. This is only the case in the long-range interaction limit. In Sec. III and in Eq. (24) we found that in general the fluctuations did contribute to the interaction between pairs and hence to the second virial coefficient but that this contribution was weaker than its contribution to the interaction between larger numbers of particles and to the third virial coefficient. The term in the free energy per unit volume proportional to ν_1^2/α which comes from the fluctuations varies with density as ρ^3 and so it contributes (only) to the third virial coefficient.

In Fig. 4 we have plotted the zero-wave-vector structure factor for a van der Waals fluid (hard spheres plus a long-range pairwise additive attraction) (the solid curve), and for an attraction which is proportional to s (the dashed curve). They are both at temperatures just above the critical temperature. The peaks in $S(0)$ are due to the nearby critical points, where $S(0)$ diverges, of course. The striking difference between the curves is their opposite slopes at low densities. The limiting slope at vanishing densities is equal to $-2B_2$, Eq. (32). For a van der Waals fluid the second virial coefficient is negative at the critical temperature, so the slope of $S(0)$ is positive until above the critical density. However, interactions between fluctuations do not contribute to the second virial coefficient and so it is equal to that of hard spheres which is positive. Thus the slope of $S(0)$ is negative at low densities and $S(0)$ goes through a minimum below the critical density.

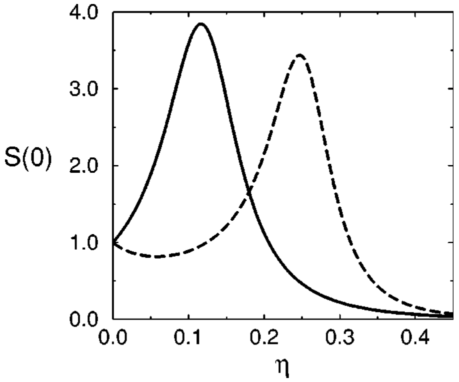

FIG. 4. The zero-wave-vector structure factor of our particles in the fluid phase, $S(0)$, as a function of the volume fraction η. The solid curve is for an attraction which does not depend on s, the potential with the phase diagram of Fig. 1. $\nu_0/(\sigma^3kT)=-10$, which is just above the critical temperature. The dashed curve is for an attraction which is proportional to the fluctuating internal variable s, the potential with the phase diagram of Fig. 2. $\nu_1^2/(\sigma^6kT\alpha)=19.4$, which is again just above the critical temperature.

VI. CONCLUSION

Particles which have a fluctuating internal state interact in a way which is different from structureless particles. The interaction is intrinsically many body and cannot be described using a pair potential. It is even possible for pairs of particles with a fluctuating state to repel but larger clusters of particles to attract each other. We have studied a rather generic model of a particle with a fluctuating state. Remarkably, because of the very simple form of our Hamiltonian's dependence on the variables which describe the states of the particles [see Eq. (10)], we have been able to integrate over these variables exactly and analytically. The result is an interaction between the particles which has both pair and triplet interactions, Eq. (16). Our model only included the leading order terms in Taylor expansions for the free energy associated with the internal states of the particles. It is possible to include higher order terms although then the s variables will have to integrated over approximately or numerically; alternatively computer simulation could be used. In any case the effective potential will then contain not only pair and triplet terms but terms of all orders, four-body, five-body, etc.

It is perhaps of interest to contrast the particles with mesoscopic fluctuations studied here to the rods with microscopic fluctuations studied by Ha and Liu [30]; see also Refs. [31–33]. They studied the interactions between parallel rods and allowed the charge density along each rod to fluctuate; if a rod is along the z axis then we can define a one-dimensional charge density $\rho(z)$, which will fluctuate. The Coulomb interaction between charges will then couple the fluctuations in $\rho(z)$ in nearby rods. Ha and Liu found that not only can this coupling generate an attraction but that it is strongly nonpairwise additive. In contrast with their model our is rather general and simpler. The results for our rather nonspecific model show clearly that these findings of Ha and Liu are rather generic. The disadvantage of our model with respect to that of Ha and Liu is that to relate it to experiment requires determining or at least guessing the appropriate values of the parameters of our phenomenological interaction.

We hope that our model will be useful for determining generic differences in the behavior between rigid particles interacting via a pair potential and particles with a fluctuating state. For example, although all our calculations have been for a single component, they are easily generalized to mixtures. When this is done, it is straightforward to see that, if the fluctuations between the internal states of particles of different components are only weakly coupled, then this will tend to drive phase separation of these components. However, differences between the inverse susceptibility α cannot drive phase separation. At least within our theory which includes only leading order terms.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge discussions with B.-Y. Ha, Y. Levin, R. van Roij, and P. B. Warren.

APPENDIX

Rather generally, when we are evaluating a configurational integral, with the aim of calculating the free energy, we can split the variables over which we are integrating into two sets. Then integrating over one set is always possible in principle, and it results in an effective Hamiltonian which is a function only of the remaining set of variables. However, this effective Hamiltonian is not in general pairwise additive, simply because there is no reason for it to be. If we denote the set of all variables by v^{N+M} and the two subsets by v^N and v^M, then the configurational integral is

$$Z=\int dv^{N+M}\exp[-H(v^{N+M})/kT] = \int dv^{N}\exp[-H'(v^{N})/kT], \tag{A1}$$

where

$$\exp[-H'(v^N)/kT]=\int dv^M\exp[-H(v^{N+M})/kT]. \tag{A2}$$

H' will not in general be expressible as a sum over a pair potential even if H can be. Physically, this is most often useful when the two sets of coordinates v^N and v^M are very different. We consider a model in which the set of coordinates v^M is coarse grained [12]; i.e., the integration over v^M is left as a function of a set of coarse-grained variables, so instead of Eq. (A2) we have

$$\exp[-H'(v^N,c^L)/kT] = \int dv^M\exp[-H(v^{N+M})/kT]\prod_{a=1}^{L}\delta(c_a(v^M)-c_a), \tag{A3}$$

where c^L is a set of $L\ll M$ coarse-grained variables. c_a is the ath coarse-grained variable and $c_a(v^M)$ is the definition of the ath coarse-grained variable in terms of the microscopic coordinates v^M. The configurational integral is then

$$Z=\int dv^N dc^L\exp[-H'(v^N,c^L)/kT]. \tag{A4}$$

Our model has a configurational integral, Eq. (11), of this form, with $L=N$ as there is one coarse-grained variable per particle. The v^N and c^N coordinates are the positions and s variables of the particles.

[1] W. B. Russel, D. A. Saville, and W. R. Schowalter, *Colloidal Dispersions* (Cambridge University Press, Cambridge, England, 1989).

[2] G. M. Kepler and S. Fraden, Phys. Rev. Lett. **72**, 356 (1996); J. C. Crocker and D. G. Grier, *ibid.* **72**, 352 (1996); **77**, 1897 (1996); T. Sugimoto, T. Takahashi, H. Itoh, S. Sato, and A. Muramatsu, Langmuir **13**, 5528 (1997).

[3] K. Ito, H. Yoshida, and N. Ise, Science **263**, 66 (1994); A. E. Larsen and D. G. Grier, Nature (London) **385**, 230 (1997); H. Yoshida, J. Yamanaka, T. Koga, N. Ise, and T. Hashimoto, Langmuir **15**, 2684 (1999); N. Ise, T. Konishi, and B. V. R. Tata, *ibid.* **15**, 4176 (1999).

[4] R. van Roij, M. Dijkstra, and J. P. Hansen, Phys. Rev. E **59**, 2010 (1998).

[5] R. van Roij and R. Evans, J. Phys.: Condens. Matter **11**, 10 047 (1999).

[6] A. R. Denton, J. Phys.: Condens. Matter **11**, 10 061 (1999).

[7] Y. Levin, M. C. Barbosa, and M. N. Tamashiro, Europhys. Lett. **41**, 123 (1998).

[8] Y. Levin, Physica A **265**, 432 (1999).

[9] P. B. Warren, J. Chem. Phys. **112**, 4683 (2000).

[10] K. S. Schmitz, Phys. Chem. Chem. Phys. **1**, 2109 (1999).

[11] R. Tehver, F. Ancilotto, F. Toigo, J. Koplik, and J. R. Banavar, Phys. Rev. E **59**, R1335 (1999).

[12] P. M. Chaikin and T. C. Lubensky, *Principles of Condensed Matter Physics* (Cambridge University Press, Cambridge, England, 1995).

[13] D. Ruelle, in *The Equilibrium Theory of Classical Fluids*, edited by H. Frisch and J. L. Lebowitz (Benjamin, New York, 1964).

[14] E. M. Lifshitz and L. P. Pitaevskii, *Statistical Physics*, 3rd ed. (Pergamon, Oxford, 1980).

[15] H. Löwen and E. Allahyraov, J. Phys.: Condens. Matter **10**, 4147 (1998).

[16] C. von Ferber, A. Jusufi, C. N. Likos, H. Löwen, and M. Watzlawek, e-print cond-mat/0001270.

[17] R. P. Sear, Phys. Rev. E **61**, 651 (2000).

[18] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, 2nd ed. (Academic Press, London, 1986).

[19] N. E. Carnahan and K. E. Starling, J. Chem. Phys. **51**, 635 (1969).

[20] K. R. Hall, J. Chem. Phys. **57**, 2252 (1972).

[21] N. van Kampen, Phys. Rev. **135**, 362 (1964).

[22] J. L. Lebowitz and O. Penrose, J. Math. Phys. **7**, 98 (1966).

[23] H. C. Longuet-Higgins and B. Widom, Mol. Phys. **8**, 549 (1964).

[24] R. P. Sear and W. M. Gelbart, J. Chem. Phys. **110**, 4582 (1999).

[25] R. P. Sear, Faraday Discuss. **112**, 355 (1999).

[26] A. P. Gast, C. K. Hall, and W. B. Russel, J. Colloid Interface Sci. **96**, 251 (1983).

[27] M. H. J. Hagen and D. Frenkel, J. Chem. Phys. **101**, 4093 (1994).

[28] A. Daanoun, C. F. Tejero, and M. Baus, Phys. Rev. E **50**, 2912 (1994).

[29] M. Dijkstra, R. van Roij, and R. Evans, Phys. Rev. E **59**, 5744 (1999).

[30] B.-Y. Ha and A. Liu, Phys. Rev. Lett. **79**, 1289 (1997); Phys. Rev. E **60**, 803 (1999).

[31] J. G. Kirkwood and J. B. Schumaker, Proc. Natl. Acad. Sci. USA **38**, 863 (1952).

[32] N. Gronbech-Jensen, R. J. Mashl, R. F. Bruinsma, and W. M. Gelbart, Phys. Rev. Lett. **78**, 2477 (1997).

[33] R. Podgornik and V. A. Parsegian, Phys. Rev. Lett. **80**, 1560 (1998).