

Absence of the liquid phase when the attraction is not pairwise additive

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Recent work on charged colloidal suspensions with very low levels of added salt has suggested that although pairs of the colloidal particles repel, clusters of the particles attract. Motivated by this, we study simple model particles which have many-body attractions. These attractions are generic many-body attractions and are not calculated for any specific colloidal suspension. We find that many-body attractions can stabilize solid phases at low pressures but that the liquid phase is either completely absent from the equilibrium phase diagram or present only within a small region of parameter space.

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I. INTRODUCTION

Although the behavior of suspensions of highly charged colloidal particles at very low added salt concentrations is highly controversial, accurate measurements on isolated pairs of the particles shows nothing but a pure repulsion [1] yet the particles form crystallites which appear to be metastable at close to zero osmotic pressure [2]. This is puzzling, particles interacting via a pairwise additive, purely repulsive interaction should only form a solid phase at high osmotic pressure, the spheres need to be pushed together against their repulsion. The solid phase of hard spheres is certainly not metastable at low pressure. Thus the observation of the repulsion of isolated pairs, and of the clustering of larger numbers of spheres is inconsistent with a description of the interaction of the colloidal particles via a pairwise additive potential of mean force. If we are to continue to describe these systems as particles interacting via some potential of mean force, then we must relax our restriction to a pairwise additive potential of mean force and consider a many-body potential [3]. We do this here. We consider simple, rather generic, many-body attractions and calculate the phase behavior they lead too. We find that if pairs of particles repel but triplets attract that the phase behavior is qualitatively similar to that found for a conventional pairwise additive attraction except that the region within which the liquid phase is found is much smaller. If pairs and triplets repel but four particles attract then there is no liquid phase at all; the attraction merely broadens the coexistence region between the fluid and solid phases. The experiments find metastable solid phases but no liquid phases, except for one, controversial, result [4].

Here, we do not address the question of what is the origin of a purely repulsive interaction between pairs of particles but an attraction between larger numbers of particles. We do *not* attempt to derive the many-body attraction from the electrostatic interactions between the charged colloids and the counter and coions. However, there has been some work in which the existence, or nonexistence, and origin of many-body interactions in suspensions of highly charged colloids has been considered [5,6]. Also, van Roij, Dijkstra, and Hansen [7] have found both fluid-solid and fluid-fluid coexistence within an approximate theory. A different theory, that of Levin, Barbosa, and Tamashiro [8] does not find a transi-

tion in the fluid state. We are simply interested in the consequences, particularly the phase behavior, of many body attractions. Because we have not derived our interaction potentials from the underlying electrostatic interactions we cannot say anything quantitative about the suspensions of highly charged colloidal particles. However, our results show that rather generally if pairs repel then a many-body attraction can still cause condensed phases to appear but that these condensed phases are much more likely to be solid rather than liquid phases. This conclusion only relies on the attractions being many-body, it does not rely on, for example, whether or not the particles are charged.

In order to keep our model of nonpairwise additive attractions as simple as possible, we generalize a simple van der Waals-type model. This model is that of particles interacting via a hard-sphere repulsion and a long-range pair attraction. It has been extensively studied, see Refs. [9–13]. We simply generalize the long-range pairwise additive attraction to a long-range attraction between n particles, i.e., an n -body attraction. This is done in Sec. II. In Sec. III we apply the standard perturbation theory to obtain the contribution of the attractions to the free energy. Then in Sec. IV we show and discuss the phase behavior before ending with a conclusion, Sec. V.

II. POTENTIAL

Our potential consists of a hard-core interaction which is pairwise additive—the hard-sphere potential—plus an n -body attraction. The energy of N particles is

$$V(\mathbf{r}^N, \epsilon_n) = V_{hs}(\mathbf{r}^N) + V_a(\mathbf{r}^N, \epsilon_n), \quad (1)$$

where \mathbf{r}^N denotes the N position vectors of the N spherical particles, and ϵ_n is a measure of the strength of the n -body attraction. It is the sum of two terms. V_{hs} is the potential energy of N hard spheres, given by

$$V_{hs}(\mathbf{r}^N) = \frac{1}{2} \sum_{i=1, N} \sum_{j=1, N}' \phi_{hs}(|\mathbf{r}_i - \mathbf{r}_j|), \quad (2)$$

where ϕ_{hs} is the hard-sphere pair potential,

$$\phi_{hs}(r) = \begin{cases} \infty, & r \leq \sigma \\ 0, & r > \sigma, \end{cases} \quad (3)$$

σ is the hard-sphere diameter. V_a is the energy of attraction coming from an n -body attractive potential ϕ_a ,

$$V_a(\mathbf{r}^N) = \frac{1}{n!} \sum_{i=1,N} \cdots \sum_{l=1,N}' \phi_a(\{|\mathbf{r}_j - \mathbf{r}_k|\}^n). \quad (4)$$

The n -fold sum is over the $N!/(N-n)!$ sets of n out of the N particles formed by choosing one of the N particles to be particle i , then one of the remaining $N-1$ particles to be particle j , \dots and then one of the $N-n+1$ particles as particle l . The dash on the sum over l indicates that the sum excludes terms in which $l=i, j, \dots$. This overcounts by a factor of $n!$ as it counts each interaction $n!$ times, each time with the n particles in a different order. For example, for $n=2$ it counts the interaction between particles numbers 11 and 103, for example, twice, once as $i=11, j=103$ and once as $i=103, j=11$. For general n , the number of ways a set of n particles can be assigned to the n indices i, j, \dots, l is $n!$. The n -body attractive potential ϕ_a is a nonpositive function of the set of $n(n-1)/2$ pair separations of the n particles. This set of scalar separations is denoted by $\{|\mathbf{r}_j - \mathbf{r}_k|\}^n$. The potential ϕ_a is symmetric with respect to exchanging any pair of the n particles. We write it as the product of a strength of attraction ϵ_n , and a function $\zeta(\{|\mathbf{r}_j - \mathbf{r}_k|\}^n)$ which determines the dependence of the energy on the particle coordinates

$$\phi_a(\{|\mathbf{r}_j - \mathbf{r}_k|\}^n) = -\epsilon_n \zeta(\{|\mathbf{r}_j - \mathbf{r}_k|\}^n), \quad (5)$$

where ζ is a non-negative function of the set of pair separations of the n particles which we need not specify explicitly but which must be long ranged, i.e., it decays to zero over some characteristic range much larger than the hard-sphere diameter σ . For a configuration in which all $n(n-1)/2$ separations $|\mathbf{r}_j - \mathbf{r}_k|$ are not much more than the hard-sphere diameter, $\zeta(\{|\mathbf{r}_j - \mathbf{r}_k|\}^n) \leq 1$. Then if one or more of the separations is increased ζ tends to zero over a range which is much larger than the hard-sphere diameter. The integral of ζ over the positions of all n particles is proportional to the volume V in the thermodynamic limit

$$\int \zeta(\{|\mathbf{r}_j - \mathbf{r}_k|\}^n) d\mathbf{r}^n = V \nu_n. \quad (6)$$

ν_n is finite and a constant; it has dimensions of length to the power of $3(n-1)$.

III. THERMODYNAMIC FUNCTIONS

As the attraction is assumed to be long-ranged, i.e., with a range much larger than the hard-sphere diameter σ , we may use the van der Waals approximation of approximating the free energy by the free energy of a system interacting only via the repulsive part of the potential plus the energy of interaction due to the attractive part of the potential. Here the system interacting only via the repulsions is that of hard spheres, whose free energy in the fluid and solid phases are accurately given by the approximations of Carnahan and

Starling [14], and of Hall [15], respectively. So, we approximate the Helmholtz free energy by that of hard spheres A_{hs} , plus the energy (not the free energy) evaluated by assuming that the configurations of the particles are unaffected by the attraction, U

$$A(N, V, T) = A_{hs}(N, V, T) + U(N, V). \quad (7)$$

A_{hs} is given by

$$A_{hs} = -kT \ln(Z_{hs}/(N! \Lambda^N)), \quad (8)$$

where

$$Z_{hs} = \int \exp[-\beta V_{hs}(\mathbf{r}^N)] d\mathbf{r}^N \quad (9)$$

is the configuration integral for N hard spheres in a volume V . Λ is the thermal volume of a particle. U is given by

$$U = \frac{\int V_a(\mathbf{r}^N) \exp[-\beta V_{hs}(\mathbf{r}^N)] d\mathbf{r}^N}{Z_{hs}}. \quad (10)$$

If we substitute our expression for V_a , Eq. (4), into Eq. (10) we note that it is the sum of $N!/(N-n)!$ equivalent terms [16]. So,

$$U = \frac{N!}{(N-n)! n!} \frac{\int \phi_a(\{|\mathbf{r}_j - \mathbf{r}_k|\}^n) \exp[-\beta V_{hs}(\mathbf{r}^N)] d\mathbf{r}^N}{Z_{hs}}, \quad (11)$$

but the n -particle density of hard spheres, $\rho_{hs}^{(n)}$, and their n -particle distribution function, $g_{hs}^{(n)}$, are defined as [10]

$$\begin{aligned} \rho_{hs}^{(n)}(\mathbf{r}^n) &= \left(\prod_{i=1,n} \rho_{hs}^{(1)}(\mathbf{r}_i) \right) g_{hs}^{(n)}(\mathbf{r}^n) \\ &= \frac{N!}{(N-n)!} \frac{\int \exp[-\beta V_{hs}(\mathbf{r}^N)] d\mathbf{r}^{N-n}}{Z_{hs}}. \end{aligned} \quad (12)$$

The one-particle density, $\rho_{hs}^{(1)}(\mathbf{r})$, is not assumed to be uniform so that the theory applies to solid as well as fluid phases. Using, Eq. (12) in Eq. (11), we obtain

$$U = \frac{1}{n!} \int \phi_a(\{|\mathbf{r}_j - \mathbf{r}_k|\}^n) \left(\prod_{i=1,n} \rho_{hs}^{(1)}(\mathbf{r}_i) \right) g_{hs}^{(n)}(\mathbf{r}^n) d\mathbf{r}^n. \quad (13)$$

We now use the long-range of the potential ϕ_a to simplify Eq. (13). As ϕ_a decays to zero only when the separations of the particles are much larger than σ , the integral for U is dominated by configurations when the spheres are far apart, i.e., when all $n(n-1)/2$ 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 one, $g_{hs}^{(n)} \approx 1$. Thus in the fluid phase the integrand of Eq. (13) is simply approximated by $\rho^n \phi_a$. In a solid 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 and so ϕ_a varies little across a unit cell and 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, we approximate $\rho_{hs}^{(n)}$ by ρ^n . Then the integrand of Eq. (13) is the same as in a fluid phase, $\rho^n \phi_a$. So, we approximate $g_{hs}^{(n)}$ by one, and $\rho_{hs}^{(1)}$ by ρ in Eq. (13) for both fluid and solid phases,

$$U = \frac{\rho^n}{n!} \int \phi_a(\{|\mathbf{r}_j - \mathbf{r}_k|\}^n) d\mathbf{r}^n, \quad (14)$$

then using Eqs. (5) and (6) we obtain our final expression for the energy

$$U = -\frac{N\rho^{n-1}\epsilon_n\nu_n}{n!} = -N\alpha_n\rho_r^{n-1}kT, \quad (15)$$

where $\rho_r = \rho\sigma^3$ is a reduced density and

$$\alpha_n = \frac{\epsilon_n\nu_n}{n!\sigma^3(n-1)kT}, \quad (16)$$

is inversely proportional to the temperature.

Using our expression for the energy, Eq. (15), in the van der Waals approximation for the Helmholtz free energy, Eq. (7) yields

$$\beta a(\rho, T) = \beta a_{hs}(\rho) - \alpha_n \rho_r^{n-1}, \quad (17)$$

where $a = A/N$ and $a_{hs} = A_{hs}/N$. The pressure times σ^3 , p , is easily obtained by differentiating the free energy, Eq. (17),

$$\beta p(\rho, T) = \beta p_{hs}(\rho) - (n-1)\alpha_n \rho_r^n. \quad (18)$$

p_{hs} is the pressure of hard spheres times σ^3 . The chemical potential μ is then obtained from $\mu = a + p/\rho_r$. Knowledge of the pressure and chemical potential is enough to determine the phase diagram.

For $n=2$, Eq. (17) reduces to a corrected version of the free energy derived by van der Waals 120 years ago [9,10,12]. By corrected we mean that van der Waals' crude approximation for the free energy of particles interacting via a strong repulsion has been replaced by the free energy of hard spheres. Van Kampen [11], and Lebowitz and Penrose [12] were able to show that if a_{hs} is exact, then Eq. (17) for $n=2$ is exact in the limit that the range of the attractive potential tends to infinity. For finite range it is a reliable and very widely used approximation.

IV. PHASE BEHAVIOR

Hard spheres freeze at high densities, i.e., they undergo a first-order transition to the solid phase [10]. The transition occurs between a fluid phase at a volume fraction $\eta = (\pi/6)\rho\sigma^3 = 0.49$ and a solid phase at the higher volume fraction $\eta = 0.55$ [17–19]. This is the only transition in the $\alpha_n = 0$ limit. The α_n are integrated strengths of attraction divided by temperature and so $1/\alpha_n$ is a reduced temperature.

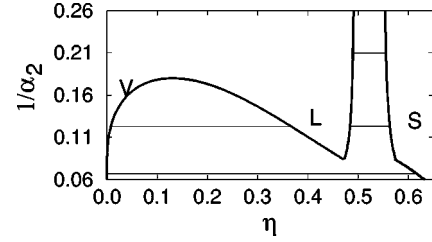


FIG. 1. The phase diagram of hard spheres plus a long-range pairwise additive attraction, $n=2$. The x axis is a reduced density, the volume fraction η , and the y axis is a reduced temperature, $1/\alpha_2$. The thick solid curves separate the one- and two-phase regions. The letters V, L, and S denote the regions of the phase space occupied by the vapor, liquid, and solid phases, respectively. The horizontal thin lines are tie lines connecting coexisting densities.

Thus, the $\alpha_n = 0$ limit is equivalent to the $T \rightarrow \infty$ limit. However, as the temperature decreases α_n increases. The first effect this has is to widen the fluid-solid coexistence region due to the fact that the denser solid phase has its chemical potential and pressure lowered more than the less dense fluid. But at sufficiently low temperature the pressure in a single phase can become a nonmonotonic function of density—the negative term due to attractions in the pressure, Eq. (18), creates a dip in the pressure—this is a van der Waals loop and it indicates that there is phase separation into dilute and dense phases of the same symmetry. The signature of phase coexistence is a van der Waals loop as our theory is a mean-field theory; it will therefore predict incorrect critical exponents.

For $n=2$, we have particles interacting via a hard-sphere repulsion and a long-range pairwise additive attraction: essentially the model postulated by van der Waals in the last century to describe the vapor-liquid transition. It, of course, has a vapor-liquid transition, as can be seen in Fig. 1 which shows its phase behavior in the density-temperature plane. There is a large temperature range over which there are coexisting dilute (vapor) and dense (liquid) fluid phases: the temperature at the critical point is more than twice its value at the triple point. The critical point is the maximum in the vapor-liquid coexistence curve and occurs at $1/\alpha_2 = 0.18$, and the triple point temperature is the temperature at which vapor, liquid, and solid phases coexist. It marks the lower limit of equilibrium vapor-liquid coexistence and occurs at $1/\alpha_2 = 0.084$.

For $n=3$, although there is still equilibrium vapor-liquid coexistence, see Fig. 2, the temperature range over which it occurs is much reduced. At the critical and triple point temperatures, $1/\alpha_3 = 0.20$ and 0.17 , respectively. The ratio be-

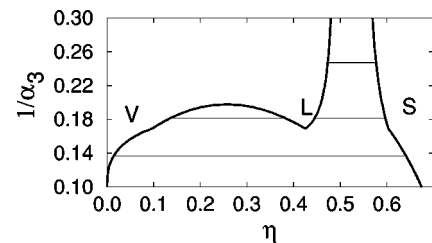


FIG. 2. The phase diagram of hard spheres plus a long-range three-body attraction, $n=3$. See the caption of Fig. 1 for details.

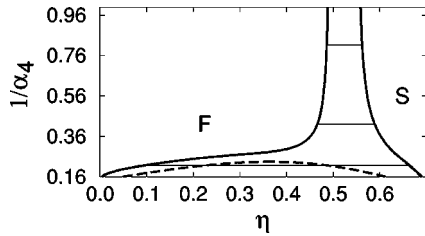


FIG. 3. The phase diagram of hard spheres plus a long-range four-body attraction. The letters F and S denote the regions of the phase space occupied by the fluid and solid phases. The dashed curve is the coexistence curve for a vapor-liquid transition within the fluid-solid coexistence region. See the caption of Fig. 1 for further details.

tween the two temperatures is only 1.2. The density at the critical point is also considerably higher than for a pairwise additive attraction.

For $n=4$ there is no equilibrium vapor-liquid coexistence, see Fig. 3. At equilibrium there is only one phase transition: the fluid-solid transition. The vapor-liquid transition has not disappeared without trace, however. Our mean-field pressure in the fluid phase does develop a van der Waals loop at low temperature and we can construct a vapor-liquid coexistence curve *within* the fluid-solid coexistence region. This is plotted as a dashed curve in Fig. 3. Note that the critical density is even higher than for a three-body attraction. The disappearance of the equilibrium vapor-liquid coexistence is just what is observed when the range of a pairwise additive attraction is reduced so that it is only about 10% or less of the hard-sphere diameter, see Refs. [20–25].

For n larger than 4, the vapor-liquid transition moves deeper into the fluid-solid coexistence region, the density at the critical point increases with increasing n . If n is made extremely large then a van der Waals loop appears in the pressure of the *solid* phase. By $n=15$ there is equilibrium coexistence between two solid phases of the same symmetry but different densities. This is just as has been found with a very short-range attraction, a few % of the hard-sphere diameter [23].

The physical interpretation of the phase behavior is straightforward. The energy per unit volume due to an n -body attraction is proportional to the number of clusters of n particles where all n particles are close enough to each other to be within range of the attraction. It is this dependence which leads directly to the ρ^n dependence of the energy per unit volume. So, the larger the n is, the smaller the number of clusters of n particles at low density and the more rapidly the number of clusters grows as density increases. When n is small, $n=2$, the energy starts to become significant at a relatively low density and it decreases gently, as density squared. This creates a van der Waals loop in the pressure at low density. The slow decrease in energy as density increases allows the hard-sphere part of the free energy to dominate at densities which are not too high. This means that the pressure turns up at densities below freezing, so allowing a stable liquid to coexist with the vapor. For $n=2$ the van der Waals loop is below the density at which hard-

spheres solidify and we see equilibrium fluid-fluid coexistence. However, for $n>2$, the energy only becomes significant at higher densities and it decreases rapidly with increasing density. The more rapid decrease with density of many-body attractions directly favors the solid phase simply because it is more dense. This then broadens the fluid-solid coexistence region to such an extent that the fluid-fluid transition becomes metastable. Also, as the energy only decreases at relatively high density for large n , the van der Waals loop is shifted to higher density; ultimately for $n=6$ the critical point is at such high density, a volume fraction $\eta=0.51$, that it is above the density at which the particles freeze. It is, therefore, not observable.

To summarize: a combination of the increased stability of the denser solid phase with respect to the less dense fluid phase, and the increasing density of the critical point drive the fluid-fluid transition metastable, then, as we continue to increase n , the critical density becomes so large that it exceeds the density at which hard spheres crystallize. Beyond this point it is not possible to observe fluid-fluid coexistence.

V. CONCLUSION

We have shown that many-body attractions have a much weaker tendency to induce separation of the fluid phase into dilute (vapor) and dense (liquid) phases than do pairwise additive attractions. Indeed when not only pairs but triplets of particles interact via a pure repulsion and with only four or more particles is there attraction, we found no equilibrium coexistence between dilute and dense fluid phases. Therefore, we expect that the findings for highly charged colloidal particles are general in the following sense: if pairs of particles repel then some systems may still have an attraction between larger numbers of particles. This may cause the fluid-solid transition to broaden greatly and produce a solid phase at much lower (osmotic) pressures than in a purely repulsive system, however, there will either be only a small range of parameters over which there is equilibrium fluid-fluid coexistence or no equilibrium fluid-fluid coexistence at all. Of course, there are an infinity of possible n -body attractions and they will lead to different behavior in the same way that different forms of pairwise attraction leads to different behavior. However, our results should apply to potentials which are reasonably smooth and long ranged, i.e., with a range of roughly the hard-sphere diameter or more. We are also assuming that the particles are spherical.

Finally, there has been a great deal of interest in the disappearance of the liquid phase as the potential is varied; attention has focused on particles in which the range of a pairwise additive attraction is very short [20–25]. But for other examples of liquid phases disappearing, see Ref. [26]. The behavior we have found as we went from two to three to four-body attractions is qualitatively exactly the same as has been found as the range of a pairwise additive attraction is made very short.

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