Theory of Chain Association versus Liquid Condensation

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We combine the original van der Waals description for liquid condensation with the association theory of ideal particles into a simple association theory of nonideal chains. The theory shows that vapor-liquid coexistence becomes metastable if the tendency to form weakly interacting chains is sufficiently strong. Our findings qualitatively explain recent computer simulations on dipolar hard spheres. [S0031-9007(96)00039-7]

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In 1873 van der Waals argued that the existence of a dilute disordered phase, a vapor, and a condensed disordered phase, a liquid, can be explained by assuming long-range attraction and short-range repulsion between the constituent particles [1]. By now it is well established that the prototype *simple* fluid, described by a repulsive core and an attractive isotropic $1/r^6$ pair potential (r the particle separation), indeed gives rise to vapor-liquid coexistence below a critical temperature [2]. Also the prototype *ionic* fluid, consisting of charge carrying hard spheres, is now known to have a vapor-liquid critical point [3]. Here the attraction is provided by the Coulombic $1/r$ attractions (possibly screened) between oppositely charged particles.

The presence of a critical point in models of simple and ionic fluids strongly suggests similar phase behavior for the prototype *dipolar* fluid, consisting of permanent dipoles embedded in hard spheres, as may, for instance, be realized in ferromagnetic colloids. Indeed, all theoretical calculations of the phase diagram of the dipolar hard sphere system predict the presence of a critical point [4]. However, despite considerable effort, no vapor-liquid coexistence has been observed in recent extensive computer simulation studies of this system [5]. Instead, simulations reveal a completely different phenomenon: the formation of chains of locally head-to-tail aligned dipoles [6]. These chains resemble living polymers, in the sense that chains may form, break up, and reform again, etc. A similar conclusion was drawn from simulations of the modified Stockmayer fluid [7], where the long-range interactions are given by the sum of isotropic dispersive $1/r^6$ attractions and anisotropic dipolar $1/r^3$ interactions. By gradually decreasing the relative strength of the isotropic attraction, the critical temperature decreased as expected. However, below a specific value of this relative strength, no vapor-liquid coexistence could be observed, while snapshots revealed the presence of chains. These simulations thus suggest a competition between liquid condensation (primarily driven by the isotropic attraction) and chain formation (driven by anisotropic dipolar interactions).

Whereas the liquid condensation has been considered in great detail in the theoretical description of dipolar spheres so far, the association feature and its apparent competition with the liquid condensation has received less attention. This Letter describes a theoretical attempt to include both features simultaneously in the simplest possible fashion. That is, we do not follow the lines of previous theoretical studies, which are often focused on solving the Ornstein-Zernike equation within some closure approximation. Although we agree that it should be possible to describe chains in terms of a very anisotropic pair structure, we feel that a description in terms of a chemical equilibrium between monomers, dimers, trimers, and in general s-mers is more natural. We combine the simplest theories for the two phenomena under consideration: the original van der Waals theory for liquid condensation and the association theory of ideal particles. This results in a simple association theory of nonideal particles that describes how the vapor-liquid transition may become metastable due to the formation of weakly interacting chains.

First, we recall the van der Waals free energy F_{vdW} of a system of N particles in a volume V at temperature T:

$$F_{\text{vdW}}/V = nk_BT\left[\ln\left(\frac{n\mathcal{V}}{1-bn}\right) - 1\right] - an^2, \qquad (1)$$

with k_B the Boltzmann constant and $n = N/V$ the number density. The positive constants a and b parametrize the molecular long-range attractions and the short-range repulsions, respectively. The thermal volume $\mathcal{V}$, usually taken as the cube of the thermal wavelength, is irrelevant for the phase behavior. The critical temperature and density in terms of a and b follow readily from the conditions that the second and third derivatives of F_{vdW} with respect to V vanish.

Next, we recall that the free energy F_{id} of an ideal mixture of $N_s = V\rho_s$ particles of type $s = 1, 2, \ldots$ is given by

$$F_{\text{id}}/V = \sum_s \rho_s k_BT(\ln \rho_s \mathcal{V}_s - 1), \qquad (2)$$

where $\mathcal{V}_s$ is the thermal volume of species s. If the composition of the mixture is fixed, the thermodynamics is independent of $\mathcal{V}_s$, which one then conventionally takes as the cube of the thermal wavelength of species s. However, if the composition of the system is not fixed, but is determined by a chemical equilibrium between monomers, dimers, trimers, etc. at fixed total number density $n = \sum_s s\rho_s$ and temperature T, the role of $\mathcal{V}_s$ is crucial, as we will show. Then, namely, we interpret $F_{\rm id}$ as a free energy functional that must be minimized with respect to ρ_s at fixed n and T. The minimizing ρ_s is then the equilibrium distribution of s-mers. The minimum free energy condition is equivalent to the chemical equilibrium condition $\mu_s = s\mu_1$, where $\mu_s = \partial F_{\rm id}/\partial N_s$ is the chemical potential of s-mers. Thus from Eq. (2) we obtain the law of mass action $\rho_s = q_s\rho_1^s$, where the chemical equilibrium constant q_s is defined by

$$\mathcal{V}_s = \frac{\mathcal{V}_1^s}{q_s}\,. \tag{3}$$

It can be shown that q_s is the internal configuration integral of an s-mer. This integral cannot be calculated analytically for complicated interaction potentials, so here we are satisfied with the following dimensionally correct simple estimate:

$$q_s = [\exp(\beta U)v]^{s-1} \equiv q^{s-1}, \tag{4}$$

with $\beta = 1/k_BT$, the phenomenological "bond energy" parameter $U > 0$ and the "configurational volume" v. This form for q_s, would be exact if the binding potential were a square-well potential of depth $-U$ localized in a volume v (small enough to prevent multiple binding), so that the internal energy of a chain like s-mer equals $-(s-1)U$. However, no unique mapping from a more complicated potential (e.g., the dipole-dipole potential) onto the parameters U and v is possible. Still, in such cases it seems reasonable to take $-U$ of the order of the minimum of the potential well. The choice for v is less clear, mainly because v depends on the temperature. At low temperatures ($k_BT \ll U$), v is of the order of the volume over which the binding potential deviates less than $\mathcal{O}(k_BT)$ from its minimum value, since other configurations hardly contribute to the configuration integral. At high temperatures ($k_BT \geq U$), we do not speak of a bond and set $v = 0$, leading to a monomeric state since then $q = 0$. In the intermediate temperature regime, we take v as the volume where the binding potential is more negative than $-k_BT$. The precise crossover from one regime to another remains of course arbitrary. For a given recipe to determine v and U, and hence q, the equilibrium distribution follows from Eq. (3) in terms of ρ_1. The value for ρ_1 then follows from the normalization condition $n = \rho_1\sum_s s(q\rho_1)^{s-1} = \rho_1/(1-q\rho_1)^2$, which can be worked out analytically to have only one physical root ρ_1, leading to a unique ideal equilibrium distribution ρ_s at a given n and T.

We now combine $F_{\rm vdW}$ and $F_{\rm id}$ to yield a free energy expression F that describes the liquid condensation and the chain association simultaneously. We adopted

$$F/V = \sum_s \rho_s k_BT\left[\ln\left(\frac{\rho_s\mathcal{V}_s}{1-bn}\right) - 1\right] - \sum_{s,s'} a_{ss'}\rho_s\rho_{s'}\,, \tag{5}$$

which is supposed to hold in combination with Eqs. (3) and (4) and the normalization condition $n = \sum_s s\rho_s$. We denoted the van der Waals attraction parameters by $a_{ss'}$ and assumed for simplicity that the free volume factor $(1-bn)$ is independent of the degree of association. Recognize that upon inserting Eqs. (3) and (4) into (5) the internal energy $-\sum_s \rho_s(s-1)U$, the internal configurational entropic term $k_BT\sum_s \rho_s(s-1)\ln v$, and the "kinetic" term $nk_BT\ln\mathcal{V}_1$ are recovered. The stationarity condition of F with respect to ρ_s yields the analog of the law of mass action as the nonlinear self-consistency relation

$$\rho_s = \left(\frac{q}{1-bn}\right)^{s-1}\exp\left(2\beta\sum_{s'}\Delta a_{ss'}\rho_{s'}\right)\rho_1^s\,, \tag{6}$$

where $\Delta a_{ss'} = a_{ss'} - sa_{1s'}$. Note that Eq. (6) is an identity for $s = 1$; ρ_1 must be chosen such that the normalization constraint $\sum_s s\rho_s = n$ is satisfied. For a particular choice of the parameters $a_{ss'}$, b, U, and $v = v(T)$, one can now solve the self-consistency equation numerically with an iterative scheme for a range of densities and temperatures, and infer the thermodynamics by resubstituting ρ_s into the free energy.

At first sight it *seems* reasonable to take $a_{ss'} = ss'a$ for the dipolar hard sphere system. The reason is that the total dipole moment of a linear chain of s aligned point dipoles of strength μ equals $s\mu$, so that the *long-range* interaction between a single s-mer and s'-mer is that of two point dipoles of strength $s\mu$ and $s'\mu$. In a fluid, however, we expect that the long-range dipolar interactions are screened by other dipolar particles, so that $a_{ss'}$ is mainly determined by the *shorter-range* character of the chain-chain interaction, which differs from that of point dipoles. The internal geometry of a chain and the anisotropy of the point dipole of its constituent monomers lead to cancellations, and hence to relatively weak chain-chain interactions, characterized by $a_{ss'} < ss'a$. A convenient simplification, which retains the essential ingredient of weak chain-chain interactions, is provided by the Bjerrum-like approximation $a_{ss'} = a\delta_{s1}\delta_{s'1}$ [8]. This choice, which we adopt from now on, has the technical advantage that $\sum_{s'}\Delta a_{ss'}\rho_{s'} = -sa\rho_1$ for $s \geq 2$, so that the right hand side of Eq. (6) is dependent only on ρ_1. Inserting this into Eq. (6) and using elementary sums yields the normalization condition as a nonlinear relation between n, T, and ρ_1, given by

$$n = \rho_1 + \rho_1\exp[-2\beta a\rho_1] \times\left[\frac{1}{\{1 - q\rho_1\exp[-2\beta a\rho_1]/(1-bn)\}^2} - 1\right]. \tag{7}$$

The roots ρ_1 of this equation are readily found numerically for a given n and T. The key difference with the case of ideal association is the possibility of more than one physical root ρ_1, corresponding to different chain distributions

ρ_s, and therefore to different free energies $f = \beta F/N$. Obviously, the distribution with the lowest f for given n and T is a candidate for the thermodynamic equilibrium distribution. The full thermodynamics is conveniently analyzed in terms of f as a function of $1/n$ at fixed T; this representation allows for common tangent constructions and is therefore well suited to analyze both local and global stability of the phases under consideration.

We introduce the dimensionless temperature $T^* = k_B T/U$ and density $n^* = nD^3$ where D is the hard sphere diameter. Throughout we take $b = 2\pi D^3/3 = b^* D^3$. This leaves the dimensionless van der Waals parameter $a^* = a/UD^3$, which is a measure for the relative tendency for liquid condensation versus chain association, as the only externally imposed parameter. For a given value of a^* and b^*, the dimensionless bare van der Waals critical liquid-vapor temperature is given by $T^*_{c,\mathrm{vdW}} = 8a^*/27b^*$, which gives rise to a convenient relative temperature scale $t^* = T^*/T^*_{c,\mathrm{vdW}}$. In the following we characterize the distributions by the parameter $\ell = \sum_s \rho_s s^2/n$, which is a measure for the typical length of the chains in units of D.

We have determined the equilibrium distributions ρ_s of F, and hence the phase behavior of the associating van der Waals system, for several values of a^*. For $a^* > 1.5$, we found a vapor-liquid critical point, as determined from the vanishing second and third derivative of f with respect to $1/n$. The critical temperature is found to be at most a few percent lower than the bare van der Waals critical temperature $t^* = 1$. For $a^* < 1.5$ there is *no* critical point, since f is convex with respect to $1/n$ for all temperatures t^*. This result is to be compared with the simulations of Ref. [7], where the critical point also disappeared when the isotropic attraction between the particles was sufficiently weak. From Fig. 1 we get an idea of the distributions ρ_s by considering the chain length parameter ℓ as a function of n^* at several values of t^* for $a^* = 1.7$. Far above the critical temperature, at $t^* = 2$, we find a unique distribution for every n^*. When the temperature is lowered slightly to $t^* = 1.7$, we find a density regime with three solutions to the stationarity condition. The smallest and largest values of ℓ characterize distributions that minimize F, whereas the intermediate one maximizes F, and is hence unphysical. At even lower temperatures we see that the density regime with multiple solutions increases, leaving unique distributions only at low densities. Note that the low density distribution is "connected" to the monomeric ($\ell \approx 1$) high density distribution at $t^* = 0.9$, and to the chain distribution ($\ell \gg 1$) at $t^* = 0.85$. This "reconnection" hardly has thermodynamic consequences, since the chain distributions become more and more monomerlike as the density decreases. In Fig. 2, we plot the minimized free energy f as a function of $1/n^*$ for the cases $a^* = 1.7$ and 1.4, for both $t^* = 1.25$ and 0.90. For $a^* = 1.7$ we see that in the density regime of multiple solutions, the monomeric branch m (with $\ell \approx 1$) has the lowest free energy, except at high densities $n^* b^* \approx 1$, where the chain branch (labeled c) is stable. The m branch develops a vapor-liquid instability when decreasing the temperature, while the c branch remains metastable. For $a^* = 1.4$ we again see that the

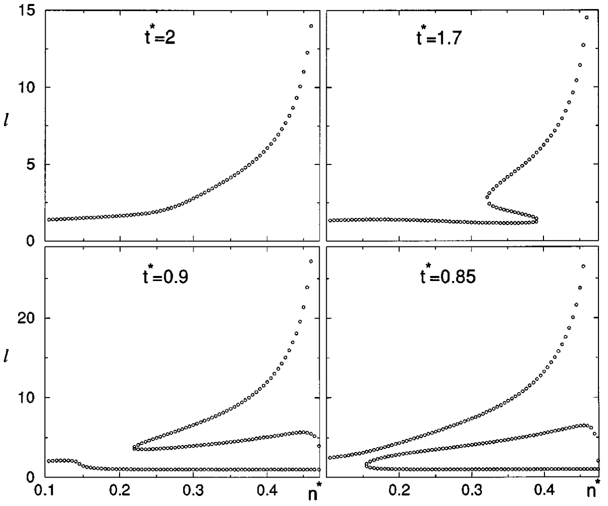

FIG. 1. ℓ vs n^* for $a^* = 1.7$ at several relative temperatures t^* (see text for symbols). At $t^* = 2$ there is only one distribution that optimizes the free energy for given n^*. At $t^* = 1.7$ and below multiple solutions are possible. In the case of three solutions at fixed density, the middle one corresponds to a local maximum of the free energy, the other two to a minimum.

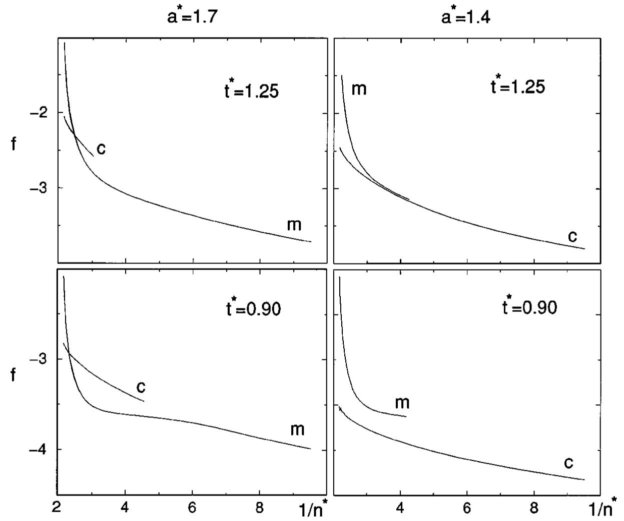

FIG. 2. Free energy per particle per $k_B T$ as a function of $1/n^*$ at relative temperatures $t^* = 1.25$ and 0.90 for $a^* = 1.7$ (left column) and $a^* = 1.4$ (right column). This representation allows a common tangent construction. For $a^* = 1.7$, the monomeric branch (m) has a lower free energy than the chain branch (c), both above and below the critical temperature, except in the high density regime $n^* b^* \approx 1$. The vapor-liquid instability of the m branch is clearly visible at $t^* = 0.90$. For $a^* = 1.4$ the m branch is metastable with respect to the (convex) c branch at both temperatures. The instability of the m branch at $t^* = 0.90$ does, therefore, not lead to vapor-liquid coexistence for $a^* = 1.4$.

m branch (which is disconnected from the low density branch as in Fig. 1 at $t^* = 0.85$) develops the vapor-liquid instability upon lowering the temperature, but now this branch is metastable with respect to the *c* branch (which is convex), so that *no* phase separation will occur. These results indicate that the vapor-liquid transition is metastable with respect to chain formation if $a^* < 1.5$, whereas it is stable if $a^* > 1.5$.

Can these results "explain" the phase behavior of dipolar hard spheres? Obviously, the theory does not include explicitly the magnetic degrees of freedom, so that possible ferromagnetic phases cannot be described. Moreover, the theory is essentially a fluid theory, so that the high density solid phase is not included, either. It is for these reasons that we did not pay much attention to the fact that the chain phase is the stable one at high densities ($n^*b^* \approx 1$), even for $a^* > 1.5$. Besides the fact that the notion of a chain is ill defined at such densities, we also expect the ferromagnetic fluid or the solid phase to take over. Still, we expect that the theory is capable of describing the competition between chain formation and liquid condensation qualitatively correctly. But what is the value of a/D^3 and U (and thus that of a^*) for dipolar hard spheres? As mentioned above, there is no unique way to characterize the potential energy $U_{dd}(\boldsymbol{r}, \hat{\mu}_1, \hat{\mu}_2)$ of two dipoles with orientations $\hat{\mu}_1$ and $\hat{\mu}_2$ at separation $\boldsymbol{r}$ in terms of two semiphenomenological parameters, but one can perform an estimate as follows. First we rewrite $U_{dd} = \langle U_{dd} \rangle + (U_{dd} - \langle U_{dd} \rangle)$, where $\langle \cdots \rangle$ denotes the statistical average over the orientations of the two dipoles and the interparticle direction. We now argue that the orientationally averaged potential energy, which is attractive and isotropic, drives the liquid condensation, whereas the anisotropic deviation from this average drives the chain formation. Since the deepest minimum of the dipolar hard sphere potential, obtained by the touching aligned head-to-tail configuration, is twice as deep as the potential of the antiparallel side-side configuration (which gives an important contribution to the orientational average), we argue heuristically that a/D^3 and U are of the same order, so that $\mathcal{O}(a^*) = 1$. This may well be in the regime where chain formation dominates over liquid condensation.

The crossover from the chain dominated to the condensation dominated regime may be studied explicitly in the dipolar hard spherocylinder fluid (length $L + D$ and diameter D) with the dipole moment parallel to the long axes. For $L/D > 2^{1/3} - 1 \approx 0.26$, namely, the touching aligned parallel head-to-tail configuration is energetically unfavorable with respect to the touching antiparallel side-side configuration. Therefore the tendency for chain formation is destroyed by the anisotropic hard core, and the condensation mechanism is probably dominant. Entropic considerations suggest that we should expect the crossover to take place at even smaller elongations of the rods. Simulations of this system are in progress [9].

In conclusion, we have combined the van der Waals theory for liquid condensation with the association theory for ideal particles to yield a simple theory of association of nonideal chains. The theory is capable of describing the disappearance of liquid condensation due to chain formation, as observed in simulations of dipolar hard spheres.

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[1] J. S. Rowlinson, *Studies in Statistical Mechanics*, edited by J. L. Lebowitz (North-Holland, Amsterdam, 1988), Vol. XIV.

[2] J.-P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic Press Limited, London, 1990).

[3] M. E. Fisher and Y. Levin, Phys. Rev. Lett. **71**, 3826 (1993), and references therein.

[4] P. G. de Gennes and P. A. Pincus, Phys. Kondens. Mater. **11**, 189 (1970); V. Kalikmanov, Physica (Amsterdam) **183A**, 25 (1992); M. Wertheim, J. Chem. Phys. **55**, 4291 (1971); G. Rushbrooke, G. Stell, and J. Hoye, Mol. Phys. **26**, 1199 (1973).

[5] J.-M. Caillol, J. Chem. Phys. **98**, 9835 (1993).

[6] J. J. Weis and D. Levesque, Phys. Rev. Lett. **71**, 2729 (1993); D. Levesque and J. J. Weis, Phys. Rev. E **49**, 5131 (1994).

[7] M. E. van Leeuwen and B. Smit, Phys. Rev. Lett. **71**, 3991 (1993).

[8] N. Bjerrum, K. Dan. Vidensk. Selsk. Mat. Fys. Medd. **7**, 1 (1926).

[9] J. J. Weis and D. Levesque (private communication).