What Happened to the Gas-Liquid Transition in the System of Dipolar Hard Spheres?

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We explore the equilibrium properties of a system composed of dipolar hard spheres. A new theory based on the ideas derived from the work of Debye and Hückel, Bjerrum, and Onsager is proposed to explain the absence of the anticipated critical point in this system.

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A representation of polar liquid in terms of dipolar hard spheres (DHS), N rigid spheres of diameter a, and dipole moment $\boldsymbol{p}$ inside a uniform medium of dielectric constant ϵ_0 is, probably, one of the most basic statistical mechanical models. Yet, our understanding of this seemingly simple system is far from complete. A naive argument based partially on intuition and partially on oversimplified approximations suggests that, as the temperature is lowered, a fluid composed of DHS will phase separate into a coexisting liquid and gas phases. This conclusion seems to be quite intuitive, after all, if the potential between two dipoles,

$$U^{dd}(\boldsymbol{r}) = \frac{1}{\epsilon_0 r^3}\left(\boldsymbol{p}_1 \cdot \boldsymbol{p}_2 - \frac{3(\boldsymbol{p}_1 \cdot \boldsymbol{r})(\boldsymbol{p}_2 \cdot \boldsymbol{r})}{r^2}\right), \quad (1)$$

is Boltzmann averaged over the relative orientations, one finds the familiar $1/r^6$ potential of van der Waals [1] which, of course, leads to phase separation. This argument, however, does not withstand the test of computer simulations which, until now, have failed to locate any vestige of phase transition [2–5]. Instead, the simulations find that, as the temperature is lowered, the dipolar spheres associate forming polymerlike chains [3]. Can the formation of chains explain the disappearance of the liquid-gas transition?

To respond to this question is not easy. In searching for the answer, it is interesting to recall the mechanism of phase separation in a different, but very related, system—the restricted primitive model (RPM) of electrolyte [6]. In that case, ions are idealized as hard spheres half of which carry a positive charge, while the other half carry a negative charge. At low temperatures, formation of clusters composed of positive and negative ions is energetically favored. First appear dimers made of $+-$ pairs, then trimers $+\ -\ +$, etc. [7]. This looks very similar to the formation of chains in DHS, and yet the RPM does phase separate, while the DHS do not. What is responsible for this fundamental difference? At first, one might try to appeal to purely electrostatic considerations. Thus, it is tempting to attribute the phase transition in the RPM to the fact that, by the time a cluster grows to contain four ions, the linear configuration becomes energetically unfavorable, and ions tend to arrange themselves in a square. These compact configurations could, in principle, provide the nuclei for the start of condensation. It is tantalizing to think that this is the essential difference between the ions and the dipoles; ions energetically prefer compact clusters, while dipoles prefer linear chains. As appealing as this argument might sound, it is, nevertheless, incorrect. A careful analysis of energies clearly demonstrates that the compact configurations also become energetically favored for DHS by the time the clusters grow to contain four or more dipoles [8]. Thus, a square cluster, in which the dipolar vectors are arranged circularly (head-to-tail) at 45° to the lines connecting the centers of the nearest neighbors, has electrostatic energy *smaller* than a linear chain of dipoles. The fact that the simulations observe polymerlike chains of dipoles, instead of compact configurations favored by electrostatics, implies that the entropy plays an essential role in the formation of clusters. The energetics alone is insufficient to explain the distinct thermodynamic behavior exhibited by the RPM and the DHS.

The analogy between the RPM and the DHS suggests that the methods developed to study the RPM might also be applicable to the exploration of DHS. In this respect the Debye-Hückel-Bjerrum theory DHBj of electrolyte has proven particularly illuminating [9,10]. This theory augments the idea of screening, introduced by Debye and Hückel [11], to explicitly take into account the formation of clusters composed of oppositely charged ions [12]. The estimates of critical parameters based on DHBj theory are, thus far, the closest to Monte Carlo simulations [13]. While the idea of cluster formation is directly applicable to DHS and has already been exploited by various authors [14–17], dipoles, unlike ions, do not produce any screening. Instead, the thermodynamic effect of dipolar motion translates into renormalization of the effective dielectric constant of the medium. The question that we would like to answer is whether this residual interaction is sufficient to produce phase separation.

We shall proceed in the spirit of DHBj theory [10]. The reduced free energy density, $f = \beta F/V$, of solution will be constructed as a sum of terms embodying the most relevant physical features of the system, starting with the entropic ideal gas contribution $f^{\mathrm{id}} = \rho \ln(\rho\Lambda^3) - \rho$. Here, $\rho = N/V$ is the density of dipoles, $\beta = 1/k_B T$, and

Λ is the thermal wavelength. To obtain the electrostatic free energy, let us fix one particle at the origin and calculate the electrostatic potential that this dipole feels due to the presence of other molecules. The electrostatic potential can be found from the solution of the Laplace equation, $\nabla^2\phi = 0$, supplemented by the appropriate boundary conditions. We shall separate this potential into two parts, $\phi_{\rm in}$ for $r < a$, and $\phi_{\rm out}$ for $r \geq a$. Clearly, $r < a$ corresponds to the excluded volume region into which, due to the hard-core repulsion, no other particles can penetrate. The boundary conditions require continuity of the potential, $\phi_{\rm in}(a) = \phi_{\rm out}(a)$, and the displacement field, $\epsilon_0\phi'_{\rm in}(a) = \epsilon\,\phi'_{\rm out}(a)$, across the surface $r = a$. We have introduced the renormalized dielectric constant of the bulk ϵ, the expression for which can be obtained from the Onsager's reaction field theory [18],

$$\frac{(\epsilon - \epsilon_0)(\epsilon_0 + 2\epsilon)}{\epsilon} = 4\pi\beta p^2\rho\,. \tag{2}$$

The Laplace equation can now be integrated to yield the potential of the central dipole due to other particles. The electrostatic *free energy* of the whole system is obtained through the Debye charging process [10,11] in which all the particles in the system are charged simultaneously from zero to their final dipolar strength,

$$F^{dd} = -\frac{2Np^2}{\epsilon_0 a^3}\int_0^1 \lambda\mathrm{d}\lambda\,\frac{\epsilon(\lambda p) - \epsilon_0}{2\epsilon(\lambda p) + \epsilon_0}\,. \tag{3}$$

The integration can be done explicitly yielding the electrostatic free energy density [19],

$$f^{dd} = \frac{\beta F_{dd}}{V} = -\frac{1}{4\pi a^3}\Big\{-2 + \frac{1}{\psi(u)} + \psi(u) + \frac{9}{2}\ln\Big(\frac{3}{2\psi(u)+1}\Big) + 3\ln\psi(u)\Big\}, \tag{4}$$

with

$$\psi(u) \equiv \epsilon(u)/\epsilon_0 = \frac{1}{4}(1+u) + \frac{1}{4}\sqrt{9+2u+u^2}\,, \tag{5}$$

and $u = 4\pi\rho^*/T^*$, where we have introduced the reduced density $\rho^* = \rho a^3$ and the reduced temperature $T^* = k_B T\epsilon_0 a^3/p^2$. Combining Eq. (4) with the entropic contribution mentioned earlier, the total free energy density of the system becomes $f = f^{\rm id} + f^{dd}$. It is a simple matter to see that as the temperature is lowered this free energy violates the thermodynamic convexity requirement, which results in a phase separation into coexisting high and low density phases [19,20]. Specifically, we find the critical parameters to be $\rho_c^* = 0.039\,080\,7\ldots$ and $T_c^* = 0.138\,904\ldots$. In principle, we could have also included the excluded volume contribution to the total free energy, expressed through the free volume or Carnahan-Starling approximation, but this would not significantly affect the location of the critical point [21]. The fundamental conclusion of this Debye-Hückel-Onsager theory (DHO) is that the system of dipolar hard spheres separates into a coexisting liquid and gas phases. Can this result be trusted? Clearly, based on our experience with the RPM [10], this conclusion must be taken with a grain of salt. Just like pure DH, the DHO theory is linear. This means that, although the DHO is quite adequate for capturing physics of large length scales, it fails for short distances. In particular, the DHO theory does not take into account the low temperature propensity to form clusters. It is precisely the importance of these configurations which is lost in the process of linearizations [18] leading to the Onsager relation (2). This conclusion is very similar to the one reached for RPM [10]. A solution, in that case, had been proposed more than seventy years ago by Bjerrum, who suggested that the nonlinearities, in the form of clusters, can be reintroduced into the DH theory through the allowance of "chemical" association between particles [12]. A theory based on Bjerrum's concept of chemical equilibrium has proven quite successful at treating the phase separation in RPM [10]. This suggests that the same kind of methodology might also be useful for studying DHS. We, thus, suppose that at low temperatures the system consists of some free unassociated dipoles of density ρ_1, as well as clusters containing $2 \leq n < \infty$ hard spheres. The density of an n cluster is ρ_n. The particle conservation requires that

$$\rho = \sum_{n=1}^{\infty} n\rho_n\,. \tag{6}$$

Following Bjerrum, we shall first treat clusters as noninteracting ideal species. The interactions, therefore, are restricted to *unassociated* dipoles, and their contribution to the total free energy density is given by Eqs. (4) and (5), with $u = 4\pi\rho_1^*/T^*$. In the case of the RPM model, this approximation has proven to be sufficient to locate the critical point [10]. The free energy density of an n cluster reduces to the ideal gas form,

$$f_n^{\rm id} = \rho_n\ln(\rho_n\Lambda^{3n}/\zeta_n) - \rho_n\,, \tag{7}$$

where we have introduced the internal partition function of an n cluster,

$$\zeta_n = \frac{1}{Vn!}\int\prod_{i=1}^{n}\mathrm{d}^3\boldsymbol{r}_i\,\frac{\mathrm{d}\Omega_i}{4\pi}\,e^{-\beta U_n^{dd}}. \tag{8}$$

Here, U_n^{dd} is the pairwise interaction potential obtained from (1), and Ω's are the relative angular orientations of dipoles forming a cluster. In the limit of low temperatures, where the DHO predicts the location of the critical point, the integrals in (8) can be evaluated for chainlike configurations to yield [10,14]

$$\zeta_n = \Big\{\frac{\pi T^{*3}a^3}{18}\Big\}^{n-1}\exp\Big\{\frac{n}{T^*}[\psi^{(2)}(n) - \psi^{(2)}(1)] + \frac{2}{T^*}[\psi^{(1)}(n) - \psi^{(1)}(1)]\Big\}, \tag{9}$$

where $\psi^{(1)}(n)$ and $\psi^{(2)}(n)$ are the polygamma functions of the first and second order, respectively. The condition for chemical equilibrium between dipoles and clusters is expressed through the law of mass action, $\mu_n = n\mu_1$, where the reduced chemical potential of a species s is $\mu_s = \partial f/\partial\rho_s$. Substituting the total free energy density, $f = \sum_{n=1}^{\infty} f_n^{\mathrm{id}} + f^{dd}$, we find the distribution of cluster densities to be

$$\rho_n = \zeta_n \rho_1^n e^{n\mu_1^{\mathrm{ex}}}, \tag{10}$$

where the excess chemical potential is defined in terms of the excess over the ideal gas contribution, in this case, $\mu_s^{\mathrm{ex}} = \partial f^{dd}/\partial\rho_s$. It is important to note that within the Bjerrum approximation the excess chemical potential depends only on the density of *free* dipoles, and the expression (10) reduces to an infinite set of *decoupled* algebraic equations.

We now make the following fundamental observation: Since the clusters are ideal, their presence can only shift the critical density, while leaving the critical temperature unaffected [10]. Thus, the critical point must *still* be located at $T_c^* = 0.138\,904\ldots$ and must *still* have the density of *free* dipoles $\rho_{1c}^* = 0.039\,080\,7\ldots$! The distribution of clusters at criticality is obtained by substituting these parameters into Eq. (10). In order for the sum in (6) to converge, the Cauchy-Hadamard theorem requires that $\Delta \equiv \lim_{n\to\infty} \rho_n^{1/n} < 1$. Inserting the critical parameters into Eq. (10), we find that at criticality $\Delta_c \approx 100$ and the theorem is *strongly* violated. The critical density ρ_{1c}^* lies far outside the radius of convergence of (6). This means that for *any* finite total density ρ the density of *free* dipoles remains insufficiently small to reach phase separation. Clearly, the argument presented above assumes that only free particles interact while the clusters are treated as noninteracting ideal species. This certainly is a very strong approximation which must be considered in more detail; nevertheless, we note that a similar argument has proven to be sufficient to locate the critical point of the RPM [10]. In that case, it was found that, in the vicinity of the critical point, the series (6) was very quickly convergent with most of the ions belonging to dipolar pairs [7,10].

To explore the role played by dipole-cluster and cluster-cluster interactions, it is necessary to account for their contribution to the overall free energy. This is far from simple. Some progress, however, can be made if we make the following observation. The electrostatic potential produced by a rigid line of dipolar density $\boldsymbol{p}/a$ is *exactly* the same as the potential due to two fictitious monopoles of charge $\pm p/a$ located at the line's extremities. This can be shown explicitly by integrating Eq. (1). The isomorphism between the line of dipoles and two discrete monopoles suggests that, for low temperatures, when the dipolar chains are quite rigid, the dipole-cluster and cluster-cluster contribution to the total free energy can be approximated by the energy that is required to solvate $N_c = 2V\sum_{n=2}^{\infty}\rho_n$ monopoles in the sea of dipoles, and by the energy of their mutual interaction. The solvation energy of an ion can be obtained following the same method presented earlier for calculating the dipole-dipole contribution. We find

$$F^{dc} = \frac{N_c p^2}{\epsilon_0 a^3}\int_0^1 \lambda\mathrm{d}\lambda\left[\frac{\epsilon_0}{\epsilon(\lambda p)} - 1\right]. \tag{11}$$

Performing the integration, the reduced free energy density due to dipole-cluster interactions is found to be

$$f^{dc} = \sum_{n=2}^{\infty}\frac{\rho_n}{4\pi\rho_1^*}\left\{\frac{3}{2} - \frac{1}{2\psi^2(u)} + \frac{1}{\psi(u)} - 2\psi(u) + 2\ln\psi(u)\right\}. \tag{12}$$

Finally, the cluster-cluster contribution can now be estimated as the energy of a plasma composed of N_c ions inside a medium of dielectric constant ϵ. We find the familiar Debye-Hückel expression [10,11],

$$f^{cc} = \frac{-1}{4\pi a^3}\left[\ln(1+\kappa a) - \kappa a + \frac{(\kappa a)^2}{2}\right], \tag{13}$$

where now

$$(\kappa a)^2 = \frac{8\pi\sum_{n=2}^{\infty}\rho_n^*}{T^*\psi(u)}. \tag{14}$$

It is easy to check that at low temperatures both dipole-cluster and cluster-cluster contributions are quite small, and are unlikely to modify the previous conclusion of the absence of criticality in DHS. The exact calculation is rather difficult to perform since the law of mass action, when the dipole-cluster and cluster-cluster interactions are included into the total free energy, reduces to an infinite set of *coupled* algebraic equations. The preliminary analysis of these, based on a variational approximation for the distribution of clusters, does not, however, find any indication of phase separation. The details of these calculations will be presented elsewhere.

We conclude that the low temperature propensity to form weakly interacting clusters absorbs most of the dipoles, preventing the density of free unassociated particles from reaching the minimum necessary for phase separation.

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[1] P. G. de Gennes and P. A. Pincus, Phys. Kondens. Mater. **11**, 189 (1970).

[2] J. J. Weis and D. Levesque, Phys. Rev. Lett. **71**, 2729 (1993).
[3] M. E. Leeuwen and B. Smit, Phys. Rev. Lett. **71**, 3991 (1993).
[4] M. J. Stevens and G. S. Grest, Phys. Rev. Lett. **72**, 3686 (1994).
[5] J.-M. Caillol, J. Chem. Phys. **98**, 9835 (1993).
[6] G. R. Stell, K. C. Wu, and B. Larsen, Phys. Rev. Lett. **37**, 1369 (1976).
[7] M. J. Gillan, Mol. Phys. **49**, 421 (1983).
[8] I. S. Jacobs and C. P. Bean, Phys. Rev. **100**, 1060 (1955).
[9] W. Ebeling, Z. Phys. Chem. (Leipzig) **238**, 400 (1968).
[10] M. E. Fisher and Y. Levin, Phys. Rev. Lett. **71**, 3826 (1993); Y. Levin and M. E. Fisher, Physica (Amsterdam) **255A**, 164 (1996).
[11] P. W. Debye and E. Hückel, Phys. Z. **24**, 185 (1923).
[12] N. Bjerrum, K. Dan. Vidensk. Selsk. Mat. Fys. Medd. **7**, 1 (1926).
[13] J. P. Valleau, J. Chem. Phys. **95**, 584 (1991); A. Z. Panagiotopoulos, Fluid Phase Equilib. **76**, 92 (1993).
[14] P. C. Jordan, Mol. Phys. **25**, 961 (1973).
[15] R. P. Sear, Phys. Rev. Lett. **76**, 3348 (1996).
[16] R. van Roij, Phys. Rev. Lett. **76**, 3348 (1996).
[17] J. M. Tavares, M. M. Telo da Gama, and M. A. Osipov, Phys. Rev. E **56**, R6252 (1997); Phys. Rev. E **57**, 7367(E) (1998); M. A. Osipov, P. I. C. Teixeira, and M. M. Telo da Gama, Phys. Rev. E **54**, 2597 (1996).
[18] L. Onsager, J. Am. Chem. Soc. **58**, 1486 (1936).
[19] See also G. Nienhuis and J. M. Deutch, J. Chem. Phys. **55**, 4213 (1971); J. W. Sutherland, G. Nienhuis, and J. M. Deuthch, Mol. Phys. **27**, 721 (1974).
[20] G. S. Rushbrooke, G. Stell, and J. S. Høye, Mol. Phys. **26**, 1199 (1973).
[21] V. C. Weiss and W. Schröer, J. Chem. Phys. **108**, 7747 (1998).