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## Criticality in strongly correlated fluids

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### Abstract

In this brief review I will discuss criticality in strongly correlated fluids. Unlike the molecules of simple fluids, which interact through short-ranged isotropic potentials, particles of strongly correlated fluids usually interact through long-ranged forces of Coulomb or dipolar form. While for simple fluids the mechanism of phase separation into liquid and gas was elucidated by van der Waals more than a century ago, the universality class of strongly correlated fluids, or in some cases even the existence of liquid–gas phase separation, remains uncertain.

Over a century ago, van der Waals (vdW) provided a basic explanation of what drives the liquid–gas phase separation in simple molecular fluids [1]. This work had its lasting value not because of its quantitative accuracy, which has since been surpassed by that of more accurate empirical equations of state, but because of the simple physical picture of criticality that it provided. The fundamental insight of vdW was to modify the ideal-gas equation of state by including two fundamental effects:

- (1) The hard-core for each molecule.
- (2) The short-ranged intermolecular interaction.

Thus, vdW suggested modifying the ideal-gas equation of state by replacing the total volume  $V$  in  $PV = nRT$  by an *effective* volume available to a given molecule,  $V_{\text{eff}} = V - bN$ , where  $b$  is a factor proportional to the molecular volume and  $N$  is the total number of particles. This means that because of the hard-core repulsion, each particle moves not inside the total volume  $V$  but in the reduced volume  $V_{\text{eff}}$ , which excludes the space occupied by other particles. Furthermore, he realized that in order to retain the cohesiveness of the fluid, molecules must attract one another. Not knowing the precise nature of intermolecular forces, but on the basis of physical insight and understanding of thermodynamics, vdW argued that the forces must be short ranged. Actually, the idea of hard impenetrable atoms interacting by means of short-ranged attractive forces can be traced all the way back to Isaac Newton. However, in his writings Newton was never fully committed to this position. Depending of the subject, he switched

between atoms which interacted with short-ranged attractive forces [2] and atoms which repel their nearest neighbours [3] with a force proportional to  $1/r$ . The first clear commitment to short-ranged attractive interatomic forces appeared in the work of Laplace [4] in 1822. He used the existence of these forces to account for the surface tension and capillarity of liquids. de Laplace believed that attractive forces acted when the atoms were close together—as in solid or liquid—while the repulsive forces dominated in gases. The notion that the nature of atoms and the forces by means of which they interact depends on the thermodynamic phase, i.e. solid, liquid, or gas, seems to have dominated much of the early 19th century atomic theory [5]. The idea that all three states of matter should be explained with the same atomic model did not take hold until the work of vdW in 1873 [5].

Of course, if the attraction between particles exists, it must reduce the pressure  $P$  below that of an ideal gas at the same density, so  $P = P_{\text{id}} - \Delta P$ . On the basis of the kinetic theory introduced earlier by Clausius [6] and Maxwell [7], van der Waals suggested that the ideal-gas equation of state still applies, but in the form  $P_{\text{id}} V_{\text{eff}} = nRT$ . The following question, however, remained: what is  $\Delta P$ ?

To answer this question vdW proposed what is now called the ‘mean-field approximation’. Since forces between particles are short ranged, each molecule interacts only with its neighbours, i.e. with the particles which are within some radial distance  $\delta$  from it. Now, how many molecules are within distance  $\delta$  of any given particle? Since on average particles are uniformly distributed with density  $\rho = N/V$ , the number of molecules within radius  $\delta$  of a given particle is  $\rho 4\pi\delta^3/3$ . It is reasonable to think of  $\Delta P$  as an effective energy density of interaction. Therefore, we conclude that

$$\Delta P = \frac{\epsilon N \rho}{2V} \frac{4\pi\delta^3}{3}. \quad (1)$$

In this formula,  $\epsilon$  is the energy of ‘pair interaction’ and the factor  $1/2$  is to account for the double counting. Substituting this into the modified ideal-gas equation, we are led to the celebrated vdW equation of state:

$$P + \frac{a}{v^2} = \frac{k_{\text{B}}T}{(v-b)} \quad (2)$$

where  $v$  is the volume per particle,  $a = 2\pi\epsilon\delta^3/3$ , and  $k_{\text{B}}$  is the Boltzmann constant.

The derivation above also makes it clear what are the main effects omitted on the way to equation (2). By concentrating just on the average distribution of particles, we have neglected the role of correlations. It is evident that if we fix one particle and look at the distribution of other molecules around it, due to attractive forces there will be an enhanced probability of finding another molecule in the vicinity of the fixed particle. Certainly this kind of effect is not accounted for in the vdW equation of state. For a class of ‘simple’ fluids, the correction due to positional correlations between particles, however, is not very important and does not change, other than quantitatively, the basic predictions of the theory.

The vdW equation provides us with insight into the mechanism of liquid–gas phase separation. The phase transition appears as a violation of the thermodynamic inequality  $\partial P/\partial\rho \geq 0$  below some critical temperature  $T_c$ . Also the free energy must be a convex function of the density. If convexity is violated, it leads to the appearance of two phases—liquid and gas—which together have free energy lower than that of the ‘anomalous’ homogeneous state. It took further work by Maxwell, Boltzmann and Gibbs [8] to clarify the details of this seemingly simple observation. The basic picture of fluid criticality, however, remained unchallenged for seventy years. This situation changed when the work of Onsager showed that there was a significant flaw in the mean-field picture based on the vdW equation. Onsager [9] was able to solve exactly a related model for the appearance of magnetization in ferromagnetic

materials. What he found was that near the critical point, the magnetization behaved very differently from the prediction of a mean-field theory. The situation remained unclear until the pioneering work of Wilson, Fisher, and others [10, 11], in the early 1970s, almost exactly a hundred years after the original work of vdW. These authors showed the essential role played by thermal fluctuations in the vicinity of a critical point, and provided an explanation for the existence of various universality classes of critical behaviour. These universality classes are characterized by the numerical values of critical exponents associated with the second-order phase transitions. It was found that very different systems can belong to the same universality class. In particular, it was demonstrated that the liquid–gas criticality belongs to the same universality class as the paramagnetic–ferromagnetic transition in metals. This universality class is now called the Ising class. Furthermore, all systems in which interactions between the particles are short ranged, and whose Hamiltonian does not possess specific symmetries, belong to the same Ising universality class. Recently, however, something very surprising has happened. A new universality class of critical behaviour has been observed. It was first noticed in the critical behaviour of solutions containing organic salts [12]. Thus, it was found experimentally that the criticality of systems in which the Coulomb force plays the dominant role appeared to exhibit mean-field critical behaviour. At first this observation might not sound very surprising—after all, the Coulomb force is extremely long ranged, while the Ising universality class is specifically for systems in which the interactions are short ranged. On closer examination, the situation does not appear so clear. Although the *bare* Coulomb force is extremely long ranged, the *effective* interaction between any two particles of an electrolyte is dynamically screened by the other ions and is short ranged [13]. Furthermore, all the theoretical arguments appear to converge to the conclusion that criticality in a Coulomb fluid should not be any different to that in systems dominated by short-ranged forces [14–16]. Specifically, it is possible to characterize the width of a critical region, in which scaling is observed, by a so-called Ginsburg parameter. All theoretical arguments suggest that the critical region of a Coulomb fluid should be comparable to that of a simple vdW fluid [14, 16]. Experimentally, however, if one insists on fitting the data to the Ising universality class, one finds that the Ising critical region is at least two orders of magnitude narrower than the critical region for a simple fluid with short-ranged interactions [17]. Outside this region, the critical behaviour appears completely mean-field-like. The theoretical challenge is to account for the mean-field criticality observed in organic electrolytes or—if the critical behaviour is convincingly proven to be Ising—to explain the narrowness of the Ising critical region.

There is a striking difference between the mechanism of phase separation in a vdW fluid and that in a Coulomb fluid. Recall that the phase separation in a vdW fluid is driven by the competition between hard-core repulsion and interparticle attraction. In contrast to this, the hard-core repulsion plays only a small role in coulombic criticality [14]. The reason for this is that for electrolytes and molten salts, the critical point is located at very low reduced density and temperature—about a factor of ten lower than these values for a vdW fluid [18]. Clearly at such large separations, hard core repulsion is only a marginal perturbation. On the basis of the pioneering ideas of Debye, Hückel and Bjerrum [13, 19], it is possible to construct a theory which accounts quantitatively for the location of the critical point in a Coulomb fluid [14, 15]. Within this theory one can explicitly see that the hard-core, free-volume term, which is so essential to the understanding of criticality in simple fluids, is completely negligible for Coulomb systems. In fact, the phase separation in these systems is purely the result of an electrostatic instability [14]. If one studies coulombic criticality, one also notices another striking difference from systems with isotropic short-ranged attractions. Let us consider a simple model of an electrolyte idealized by the restricted primitive model (RPM). Within the RPM, ions are treated as an equal-sized hard spheres of positive and negative charge, and the

solvent as a uniform dielectric background. We shall restrict our consideration to charge-neutral systems. The condition of charge neutrality is essential in order to have the thermodynamic limit. Since on average the particles of an electrolyte are uniformly distributed throughout the volume, it is evident that the average electrostatic potential is zero. This means that the mean-field correction to the ideal-gas pressure is also zero! The fact that the RPM does have a liquid–gas phase transition must, therefore, be attributed to effects not present at the mean-field level. These effects are the correlations between positive and negative ions, neglected within the mean-field approximation. At very low reduced temperatures, at which the phase separation occurs, the RPM is a strongly correlated fluid. It is precisely these correlations which drive the liquid–gas phase separation [14, 15].

Another very interesting example of a highly correlated fluid is a system of dipolar hard spheres (DHS) [20–28]. This is probably the simplest model of a polar fluid. Indeed, it was expected that as the temperature was lowered, the DHS would phase separate into coexisting high-density liquid and low-density gas phases [20–22]. It came, therefore, as a big surprise when the simulations in the early 1990s were unable to locate the anticipated liquid–gas transition [29–31]. Instead, as the temperature was lowered, the dipolar spheres aligned, forming weakly interacting polymer-like chains. It was argued that the formation of these chains prevented condensation of the DHS [27].

In fact, it is once again easy to see that the dominant correction to the ideal-gas behaviour is due to correlations between particles. Evidently, in a fluid phase, all the particles are uniformly distributed throughout the system, with dipolar orientation not having any preferred direction. This implies that the average electric field inside a dipolar fluid is zero, and the mean-field contribution to the pressure is, once again, zero. The dominant contribution to the excess free energy is due to correlations between the particles and not due to the mean field, as was the case for simple vdW fluids. In fact, we find that the correlations, in this case, are so strong as to wash out the phase separation altogether [27]. That is, the dipoles align, forming weakly interacting chains, instead of phase separating into coexisting high- and low-density phases. What is even more interesting is that the usual liquid–gas phase transition can be restored by adding to the DHS some dispersion interaction of the vdW,  $1/r^6$ , form [28, 30]. It can be shown that, depending on the amplitude of the dispersion, as compared to the dipole–dipole interaction, a liquid–gas phase transition can either be absent or present. We shall denote the relative strength of the dispersion force as compared to the dipole–dipole interaction by a parameter  $\lambda$ . Thus, when  $\lambda$  is near unity, the two interactions are more or less comparable in strength. When  $\lambda = 0$ , the usual DHS model is recovered. When  $\lambda = 1$ , we find that there is a phase transition, the location of which can be predicted, with about 30% accuracy, using a ‘correlated mean-field theory’ [27, 28]. This theory combines into single free-energy contributions from both the isotropic vdW force and from the dipolar correlations. The critical point is obtained from study of the convexity of this free energy. It is important to stress that the correlated mean-field theory still does not take into account the thermal fluctuations which are important near the critical point.

As the relative strength of the dispersion force decreases, and the net interaction between particles becomes dominated by the long-ranged dipole–dipole force, we find that the accuracy of the theory improves dramatically. In fact, for  $0.3 < \lambda < 0.5$  the values for the critical temperature predicted by the theory are in perfect agreement with the Monte Carlo simulations [28]. At  $\lambda \approx 0.3$  the phase separation disappears both in the simulations and in the theory [28, 30].

The fact that a theory which does not take into account thermal fluctuations can predict the location of a critical point with a high degree of accuracy carries some very profound implications. We note that the accuracy of the theory increases as  $\lambda$  decreases. As mentioned

already, for  $\lambda = 1$  the disagreement between the theory and the simulations is about 30%. This value is very much comparable to the accuracy of a mean-field theory for fluids with short-ranged dispersion force, such as argon. It is well known that the thermal fluctuations tend to depress the critical temperature by about this amount. What is interesting is that as the weight of an isotropic short-ranged interaction is decreased—by diminishing the value of  $\lambda$ —and the effective interaction becomes longer ranged, the agreement between simulations and theory improves significantly [28]. In fact, it is known that for infinitely long-ranged interactions of a Kac form, the critical fluctuations are not important and the mean-field theory becomes exact. Apparently, something very similar happens in the case of Stockmayer fluids (DHS plus dispersion interaction). As the net interaction between the particles becomes more and more dominated by the long-ranged dipole–dipole force, the critical fluctuations become less and less important. For  $0.3 < \lambda < 0.5$ , this should also lead to a mean-field-like scaling in the neighbourhood of the critical point, with Ising-like behaviour appearing only very close to the critical point. In fact, the width of the Ising-like critical region should be a very strongly decreasing function of  $\lambda$ . It would be nice to see how these predictions compare with Monte Carlo simulations.

We have discussed two models of strongly correlated fluids: the RPM of electrolytes and the dipolar hard-sphere model of polar fluids. In both cases the bare interactions between particles are long ranged, and the excess free energy is dominated by the electrostatic correlations, with the mean-field contribution being identically zero. These are but two examples of an infinite number of strongly correlated fluids. In spite of the ubiquity of this important class of systems, their critical behaviour—even the very existence of phase transitions—remains uncertain [32–34].

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