Criticality in strongly correlated fluids

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In this brief review I will discuss criticality in strongly correlated fluids. Unlike simple fluids, molecules of which interact through short ranged isotropic potential, particles of strongly correlated fluids usually interact through long ranged forces of Coulomb or dipolar form. While for simple fluids 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 existence of liquid-gas phase separation remains uncertain.

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

1. The hardcore for each molecule.
2. The short ranged intermolecular interaction.

Thus, van der Waals suggested to modify the ideal gas equation of state by replacing the total volume $V$ in the $PV = nRT$ by an effective volume available to a given molecule, $V_{\text{eff}} = V - bN$, where $b$ is a factor proportional to molecular volume and $N$ is the total number of particles. This means that because of a hardcore 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 keep cohesiveness of the fluid, molecules must attract one another. Not, knowing the precise nature of intermolecular forces, but based on a physical insight and understanding of thermodynamics, van der Waals argued that the forces must be short ranged. Actually the idea of hard impenetrable atoms interacting by short ranged attractive forces can be traced all the way to Newton. However, in his writings Newton was never fully committed to this position. Depending of the subject he switched between the atoms which interacted with short ranged attractive forces to atoms which repel their nearest neighbors with a force proportional to $1/r$. The first clear commitment to short ranged attractive interatomic forces appeared in the work of Laplace in 1822. He used the existence of these forces to account for the surface tension and capillarity of liquids. Laplace believed that attractive forces acted when the atoms were close together — as in solid or liquid — while the repulsive forces dominated in gases. Notion that the nature of atoms and the forces with 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. The idea that all three states of matter should be explained with the same atomic model did not take hold until the work of van der Waals in 1873.

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 that $P = P_{\text{id}} - \Delta P$. Based on kinetic theory introduced earlier by Clausius and Maxwell, 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 question, however remained: what is $\Delta P$?

To answer this question van der Waals proposed what is now called the “mean-field field approximation”. Since forces between particles are short ranged, each molecule interacts only with its neighbors, i.e. with the particles which are within some radius $\delta$ 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

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

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 van der Waals equation of state ($\text{vdW}$),

$$P + \frac{a}{v^2} = \frac{k_B T}{(v-b)}, \quad (2)$$

where $v$ is the volume per particle, $a = 2\pi\epsilon\delta^3/3$, and $k_B$ is the Boltzmann constant.

The derivation above also makes it clear what are the main effects omitted on the way to Eq. (2). By concentrating only 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, beyond quantitative, the basic predictions of the theory.

The \( vdW \) equation provides us with an insight into the mechanism of liquid-gas phase separation. The phase transition, appears as a violation of thermodynamic inequality \( \partial P/\partial \rho \geq 0 \) below some critical temperature \( T_c \). Also the free energy must be a convex function of density. If convexity is violated it leads to appearance of two phases — liquid and gas — which together have the free energy lower than the "anomalous" homogeneous state. It took further work of Maxwell, Boltzmann, and Gibbs 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 was able to solve exactly a related model of appearance of magnetization in ferromagnetic material. What he found was that near the critical point, magnetization behaved very differently from the prediction of a mean-field theory. The situation remained unclear until the pioneering work of Wilson, Fisher and the others, in the early 1970's, almost exactly hundred years after the original work of van der Waals. 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 behavior. These universality classes are characterized by the numerical value 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 Ising. Furthermore, all systems in which interactions between the particles are short ranged, and the 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 behavior has been observed. It was first noticed in the critical behavior of solutions containing organic salts. 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 behavior. At first this observation might not sound very surprising, after all the 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. Furthermore, all the theoretical arguments appear to converge to conclusion that criticality in a Coulomb fluid should not be any different than in systems dominated by short ranged forces. 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 van der Waals fluid. Experimentally, however, if one insists on fitting the data to 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. Outside this region the critical behavior appears completely mean-field-like. The theoretical challenge is to account for the mean-field criticality observed in organic electrolytes, or if the critical behavior is convincingly proven to be Ising, to justify the narrowness of the Ising critical region.

There is a striking difference between the mechanism of phase separation in a van der Waals fluid and that in a Coulomb fluid. Recall that the phase separation in a \( vdW \) fluid is driven by the competition between hardcore repulsion and interparticle attraction. Contrary to this, the hardcore-gas phase separation only a small role in coulombic criticality. 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. Clearly at such large separations, hardcore is only a marginal perturbation. Based on the pioneering ideas of Debye, Huckel, and Bjerrum, it is possible to construct a theory which accounts quantitatively for the location of critical point in a Coulomb fluid. Within this theory one can explicitly see that the hardcore, 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. 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 solvent as a uniform dielectric background. We shall restrict our attention to charge neutral systems. The condition of charge neutrality is essential in order to have 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 ideal gas pressure is also zero! The fact that the \( RPM \) does have liquid-gas phase transition must, therefore, be attributed to the 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 phase separation occurs, RPM is a strongly correlated fluid. It is precisely these correlations which drive the liquid-gas phase separation.

Another very interesting example of a highly correlated fluid is a system of dipolar hard spheres (DHS). This is probably the simplest model of a polar fluid. Indeed, it was expected that as the temperature is lowered, the DHS should phase separate into coexisting high density liquid and low density gas phases. It came, therefore, as a big surprise when the simulations in the early 90’s could not locate the anticipated liquid-gas transition. Instead, as the temperature was lowered, the dipolar spheres aligned forming weakly interacting polymer-like chains. It was argued that formation of these chains prevented condensation of DHS.

In fact, it is once again easy to see that the dominant correction to the ideal gas behavior 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 pressure is, once again, zero. The dominant contribution to the excess free energy is due to correlations between the particles and not due to mean-field, as was the case for a simple van der Waals fluids. In fact, we find that the correlations, in this case, are so strong as to wash out the phase separation altogether. 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 van der Waals, $1/r^6$, form. It can be shown that depending on the amplitude of dispersion, as compared to dipole-dipole interaction, a liquid-gas phase transition can either be absent or present. We shall denote the relative strength of dispersion force as it compares 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, location of which can be predicted, with about 30% accuracy, using a “correlated mean-field theory”. This theory combines into a single free energy contributions from both the isotropic van der Waals force and from the dipolar correlations. The critical point is obtained from the study of 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 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. At $\lambda \approx 0.3$ the phase separation disappears both in the simulations and in theory.

The fact that a theory which does not take into account thermal fluctuations can predict 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 $\lambda = 1$ 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. 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 neighborhood of the critical point, with Ising-like behavior 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 the Monte Carlo simulations.

We have discussed two models of strongly correlated fluids: the restricted primitive model of electrolyte and the dipolar hard sphere model of polar fluid. 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 their ubiquity, the critical behavior or even the existence of phase transition in this important class of systems remains uncertain.

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