Liquid-State Theory for Critical Phenomena

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We have developed a unified theory of classical fluids in the form of a hierarchy of integrodifferential equations for the free energy and direct correlation functions. This theory gives the correct $\epsilon = 4 - d$ expansion for critical phenomena. The presence of a hard core does not modify the Ising universality class to lowest order in ϵ. The simplest approximation gives $\gamma = 2\nu = 1.38$ in $d = 3$. Suitable truncation of the hierarchy gives the correct low-density (virial coefficients) and high-density (optimized random phase) limit.

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A realistic microscopic theory of the critical region of the liquid-vapor phase transition from the standpoint of liquid-state theory is still not known. A density-functional approach has been developed[1] but of this only a formal analysis has been performed. The present renormalization-group (RG) techniques can be applied to a fluid only after an initial operation of coarse graining has been performed or the space has been discretized, thus obtaining lattice-gas models. In both cases we lose the possibility of describing the correct short-range behavior of the system. Moreover we do not know if the short-range constraint, the so-called core condition, due to the presence of the strong short-range repulsive forces modifies the Ising universality class. It is also clear that there is no possibility of describing the crossover, which is not universal, from the critical to the noncritical region.

In this Letter we present a novel liquid-state theory able to cope also with the critical region. Our theory is a genuine theory of a fluid since at low density our equations give the correct virial expansion and at high density the theory can be related to an accurate approximation for dense fluids, the optimized random-phase approximation (ORPA).

We consider a system of classical particles interacting with a two-body short-range potential $v(r)$. As usual in the theory of liquids we divide $v(r)$ into two parts:

$$v(r) = v_R(r) + w(r), \tag{1}$$

where $v_R(r)$ contains the strong repulsive part of the interaction, whereas $w(r)$ corresponds to the attractive forces so that $w(r)$ is a regular function of r and has a well-defined Fourier transform $\tilde{w}(k)$. Moreover, we assume that the properties of the system interacting just with $v_R(r)$, the reference system, are known. Following the lesson of the RG approach we do not try to relate the properties of the fully interacting system directly to those of the reference system but we build up, step by step, the effects of fluctuations on different length scales. However, unlike the RG approach, we do not obtain this by eliminating degrees of freedom but, at any step, we maintain a full description of a suitable system over all its length scales. We accomplish this by considering a sequence of reference systems intermediate between $v_R(r)$ and $v(r)$. This approach was suggested some time ago by one of us[2] but now we construct this sequence in a different way. A member of the sequence is characterized by a wave vector Q $(0 \leqslant Q \leqslant \infty)$ such that $v^Q(r) = v_R(r) + w^Q(r)$ where $w^Q(r)$ has the Fourier transform $\tilde{w}^Q(k) = \tilde{w}(k)$ for $k \geqslant Q$ whereas $\tilde{w}^Q(k) = 0$ for $k < Q$. Using, for a generic value of Q, this Q system as a reference system we obtain, by standard expansion techniques,[3] the properties of the system with $v^{Q-dQ}(r)$ in powers of the perturbing interaction $\delta\phi^Q = -\beta(v^{Q-dQ} - v^Q)$. Specifically, we construct our equations in the following way. Using the grand canonical ensemble we expand the free energy A^{Q-dQ} in a power series in $\delta\phi^Q$ and chains of the interaction $\delta\phi^Q$ are summed over, thus introducing a renormalized interaction. As a result of the sharp cutoff of $\tilde{w}^Q(k)$ at $k = Q$ the pair correlation functions have a discontinuity at $k = Q$. We can avoid this by introducing a "modified" Q system for which the effect of $\tilde{w}(k)$ for $0 < k < Q$ on the free energy and on the pair correlation functions is also included but only in random-phase approximation (RPA). The higher-order correlation functions are left unmodified. This procedure gives a hierarchy of coupled equations for the correlation functions and the first two read

$$-d\tilde{a}^{Q}/dQ=\tfrac{1}{2}(2\pi)^{-d}\int d\Omega_p \ln\{[1+\tilde{F}^{Q}(p)\tilde{\phi}(p)][1-\check{F}_R(p)\tilde{\phi}(p)]\}, \tag{2}$$

$$-d\,\tilde{c}^{Q}(k)/dQ=M^{Q}(k), \tag{3}$$

$$M^{Q}(k)=\tfrac{1}{2}(2\pi)^{-d}\int d\Omega_p\{\check{c}^{Q}_{4}(\vec{k},-\vec{k},\vec{p},-\vec{p})+2\check{F}^{Q}(\vec{k}+\vec{p})[\check{c}^{Q}_{3}(k,p,-k-p)]^2\}\times[\tilde{F}^{Q}(p)]^2\tilde{\phi}(p)/[1+\tilde{F}^{Q}(p)\tilde{\phi}(p)]. \tag{4}$$

Here we consider the case of a d-dimensional system and the integration is over the surface $|\vec{p}|=Q$. $\tilde{\phi}(k)=-\beta\tilde{w}(k)$ and $\check{c}^{Q}_{n}$ represents the n-body direct correlation function for the Q system. This differs from the commonly defined one[3] c^{Q}_{n} by the ideal-gas contribution:

$$\check{c}^{Q}_{n}(\vec{k}_1,\ldots,\vec{k}_n)=c^{Q}_{n}(\vec{k}_1,\ldots,\vec{k}_n)+(-1)^{n-1}(n-2)!/\rho^{n-1}. \tag{5}$$

We have defined $\tilde{a}^{Q}=-\beta\tilde{A}^{Q}/V$, and $\tilde{A}^{Q}$ and $\tilde{c}^{Q}(k)$ $[\tilde{c}^{Q}=\check{c}^{Q}_{2}-\beta(\tilde{w}-\tilde{w}^{Q})]$ are respectively the Helmholtz free energy and the two-point direct correlation function of the "modified" Q system. In addition we have $\tilde{F}^{Q}=-(\tilde{c}^{Q})^{-1}$ and $\check{F}^{Q}=-(\check{c}^{Q}_{2})^{-1}$. Symbols with label R denote quantities for the v_R system. Each higher-order function $\check{c}^{Q}_{n}$ satisfies an equation similar to (3) being coupled to $\check{c}^{Q}_{n+1}$ and to $\check{c}^{Q}_{n+2}$. When $Q=0$ all those functions represent the ones of the fully interacting system. The usual structure factor $S(k)$ is related to $\tilde{F}^{0}(k)$ by $S(k)=\tilde{F}^{0}(k)/\rho$. When $Q=\infty$, we have $\check{c}^{\infty}_{n}=c^{R}_{n}$, and $\tilde{a}^{\infty}$ and $\tilde{c}^{\infty}$ are the free energy and direct correlation function for the full interaction (1) but with $w(r)$ taken into account in RPA. This hierarchy [(2)–(4)] is formally exact and it must be integrated down to $Q=0$ starting from $Q=\infty$ where the correlation functions of the v_R system act as boundary conditions. Integration of these quantities allows us to follow how the correlations induced by the attractive interaction in RPA are modified by the effects of the nonlinear coupling between density fluctuations induced by the Fourier components of $w(r)$ with $k>Q$. Notice that for any value of Q one is considering a system over all its length scales and there is no reduction of degrees of freedom.

It is evident that any manageable approximation must introduce some sort of decoupling in the hierarchy. Since our equations are based on direct correlation functions, there is no guarantee that a certain approximation gives a radial distribution function $g(r)$ satisfying the core condition. We can use, however, a trick that is a generalization of the well-known optimization condition introduced by Andersen and Chandler[4] in the theory of liquids. Suppose that the repulsive interaction $v_R(r)$ is just the hard-sphere potential with diameter σ. In an exact theory the value of $w^{Q}(r)$ for $r<\sigma$ does not affect any observable quantity but this is not necessarily true for a truncated hierarchy. Thus we can ask if we can redefine the interaction inside the core,

$$W^{Q}(r)=w^{Q}(r)+B^{Q}(r),\quad r<\sigma,$$

in such a way that for the Q system $g^{Q}(r)=0$ for $r<\sigma$. This turns out to be possible and we find that dB^{Q}/dQ must satisfy a subsidiary integral equation. This equation turns out to represent also an extremum condition for the free energy as is the case with the usual optimization condition.[4] The evolution of B^{Q} induces additional terms in the hierarchy and in particular the equation for $\tilde{c}^{Q}$ now reads

$$\begin{aligned}&-d\,\tilde{c}^{Q}(k)/dQ=M^{Q}(k)-\beta\int d^dr\,\Lambda^{Q}_{\vec{k}}(\vec{r})[dB^{Q}(r)/dQ],\\&\Lambda^{Q}_{\vec{p}}(\vec{r})=e^{i\vec{p}\cdot\vec{r}}+\tfrac{1}{2}(2\pi)^{-d}\int d^dq\,e^{i\vec{q}\cdot\vec{r}}[\check{F}^{Q}(q)]^2\{\check{c}^{Q}_{4}(\vec{q},-\vec{q},\vec{p},-\vec{p})+2\check{F}^{Q}(\vec{q}+\vec{p})[\check{c}^{Q}_{3}(q,p-q-p)]^2\}.\end{aligned} \tag{6}$$

In the present case the boundary condition for $\tilde{c}^{Q}$ at $Q=\infty$ corresponds to the direct correlation function of the fully interacting system (1) in ORPA.

We present now a summary of some results given by our equations. Full details will be presented elsewhere. We may expect that at low density the direct correlation functions of high order can be approximated by their low-density limit, the last term of Eq. (5). Indeed, if we substitute in (4) this low-density form for $\check{c}^{Q}_{3}$ and $\check{c}^{Q}_{4}$, Eq. (3) can be explicitly integrated and for $Q=0$ we find the correct form

$c(r)=\exp\{-\beta[v_R(r)+w(r)]\}$ for the Ornstein-Zernike direct correlation function. From the free energy Eq. (2) one then finds the correct first virial coefficient. If in the hierarchy we approximate $\check{c}\,^Q_n$ with its ideal-gas value starting from $n=m$ then the truncated system gives the correct low-density expansion for $c(r)$ up to order $m-2$.

In the opposite limit of high density the effect of the many-particle correlations becomes essentially irrelevant. In fact the strong effect of screening of $w(r)$ by the repulsive forces is manifest in (4) because $\tilde{F}(p)$ is very small in the region of small p where $\tilde{\phi}(p)$ is significant. Therefore to lowest order M^Q can be considered as a negligible quantity so that $\tilde{c}\,^0(k)\approx\tilde{c}\,^\infty(k)$ but $\tilde{c}\,^\infty(k)$ corresponds to the ORPA that is known as an excellent approximation for a fluid in the triple-point region.

We discuss now the region of the critical point where $S(0)=\rho^{-1}\tilde{F}\,^{Q=0}(0)>>1$. Then also $\rho^{-1}\times\tilde{F}\,^Q(k)$ will be large for small values of k and Q so that the terms unity in the integrands of the hierarchy can be dropped in comparison to $\tilde{\phi}(k)\tilde{F}\,^Q(k)$. Similarly, terms proportional to $\check{F}\,^Q(k)$ have to be kept only for $k\geqslant Q$, where $\check{F}\,^Q(k)=\tilde{F}\,^Q(k)$, because for $k<Q$, $\check{F}\,^Q(k)=\tilde{F}\,^Q(k)/[1+\tilde{\phi}(k)\times\tilde{F}\,^Q(k)]$ is a bounded quantity. Then in this low-momenta regime the hierarchy simplifies and, for instance, the evolution equation for $\tilde{c}\,^Q$ can be written in the form

$$\left(\frac{\partial}{\partial\ln Q}+x\frac{\partial}{\partial x}-2+\eta\right)u^Q_2(x)$$
$$=\tfrac{1}{2}(2\pi)^{-d}\int d\Omega_y\{u^Q_4(\vec{x},-\vec{x},\vec{y},-\vec{y})-2[u^Q_3(\vec{x},\vec{y}-\vec{x}-\vec{y})]^2/u^Q_2(\vec{y}+\vec{x})\}/u^Q_2(y), \tag{7}$$

where the momentum integration is over the surface $|\vec{y}|=1$ with the limitation $|y+x|>1$. Here we have introduced the scaled functions

$$u^Q_n(\vec{x}_1,\ldots,\vec{x}_n)=-Q^{n(d-2+\eta)/2-d}\check{c}\,^Q_n(\vec{x}_1Q,\ldots,\vec{x}_nQ)\quad\left(\sum_i^n\vec{x}_i=0\right) \tag{8}$$

for $n>2$ and $u^Q_2(x)$ is defined in the same way in term of $\tilde{c}\,^Q$. The exponent η is defined as the constant for which $\lim_{Q\to 0}Q^{-2+\eta}[\tilde{c}\,^Q(xQ)-\tilde{c}\,^Q(0)]$ is finite at the critical point. The evolution equation (7) for u^Q_2 and those for the u^Q_n are equivalent to the RG equations which can be deduced from the theory of Nicoll and Chang.[5] This can be shown by recasting our approximate hierarchy in the form of a differential generator for the free energy $\tilde{A}$ of an inhomogeneous system. In our case this generator involves the second functional derivative of $\beta\tilde{A}$ with respect to the local density, this being equal to $\tilde{c}$, in place of the local magnetization as in the case of Nicoll and Chang. The characteristic momentum Q corresponds to the momentum shell of integration in the RG. Thus the existence of a fixed point for our approximate hierarchy implies a scaling form for the correlation functions in the critical region.[6] The critical behavior given by our approximate hierarchy can be analyzed in the framework of the $\epsilon=4-d$ expansion and in fact, because of the equivalence already discussed, we recover the ϵ expansion for the critical exponents as obtained by RG technique for a one-component order parameter. It is known that to first order in ϵ the presence of vertices of odd order does not modify the Ising universality class.[7]

So far we have not considered the effect of the core condition. When we use (6) in place of (3) we find that the extra term introduced by the core condition vanishes in the $Q\to 0$ limit faster than the other terms provided that

$$\begin{aligned}\check{c}\,^Q_4(\vec{q},-\vec{q},0,0)&=\partial^2\tilde{c}\,^Q(q)/\partial\rho^2;\\ \check{c}\,^Q_3(\vec{q},0,-\vec{q})&=\partial\tilde{c}\,^Q(q)/\partial\rho.\end{aligned} \tag{9}$$

These relations are satisfied by the exact correlation functions and we can construct simple decoupling schemes for the full $\check{c}\,^Q_3$ and $\check{c}\,^Q_4$ compatible with (9), for instance

$$\check{c}\,^Q_4(\vec{q},-\vec{q},\vec{k},-\vec{k})$$
$$=\tfrac{1}{2}[\partial^2\tilde{c}\,^Q(\vec{q}+\vec{k})/\partial\rho^2+\partial^2\tilde{c}\,^Q(\vec{q}-\vec{k})/\partial\rho^2]$$

and

$$\check{c}\,^Q_3(\vec{q},\vec{k},-\vec{q}-\vec{k})=\partial\tilde{c}\,^Q(\vec{q}+\vec{k})/\partial\rho.$$

When we use this closure in (4) we obtain a closed equation for $\tilde{c}\,^Q$ from which we can deduce the critical exponents in the framework of the ϵ expansion. These turn out to be

$$\begin{aligned}\gamma&=1+\tfrac{1}{6}\epsilon+O(\epsilon^2);\\ \nu&=\tfrac{1}{2}+\tfrac{1}{12}\epsilon+O(\epsilon^2);\\ \eta&=\tfrac{1}{54}\epsilon^2+O(\epsilon^3),\end{aligned} \tag{10}$$

and these are equal to the Ising values to leading order. An open question is if the basin of attraction of this fixed point also encompasses initial conditions for realistic fluid Hamiltonians.

As a first step in studying the hierarchy for a fluid in $d=3$ we consider the simplest decoupling scheme. We assume that $\eta=0$ so that $\tilde{c}^{\,Q}(k) = \tilde{c}^{\,Q}(0)-bk^2+o(k^2)$; moreover the coefficient b is assumed constant. Taking into account that $\tilde{c}^{\,Q}(0)=\partial^2 a^Q/\partial\rho^2$ we find that the hierarchy (2)-(4) truncates at the level of the first equation and it turns out to be equivalent to a RG equation derived by Nicoll, Chang, and Stanley[8] for the Ising model. It is known that it gives the first-order term of the ϵ expansion but not the second. We have studied numerically the fixed point and the largest eigenvalues λ_i for $d=3$. We find $\lambda_1=1.451$ and $\lambda_2=-0.581$ so that, from standard analysis,[6] the critical exponents turn out to be

$$\gamma=1.378, \quad \nu=\gamma/2=\lambda_1^{-1},$$

$$\beta=0.344, \quad \eta=0, \quad \delta=5,$$

and the first correction to the leading term for the correlation length vanishes as $(T-T_c)^{0.400}$.

In conclusion, we have presented a generalization of the theory of liquids based on the idea of relating the reference to the fully interacting system through the intermediary of a sequence of other systems for which the nonlinearity of density fluctuations is operating only up to a maximum length scale Q^{-1}, beyond which the fluctuations are taken into account in the random-phase approximation. By letting $Q^{-1}\rightarrow\infty$ one recovers the fully interacting system. This approach generates a formally exact hierarchy of equations for the free energy and the direct correlation functions of successively higher order. Systematic truncation of the hierarchy generates the correct low- and high-density limits. In the critical region, and at small momenta, the hierarchy becomes equivalent to the RG equations in differential form implied by the generator of Nicoll and Chang.[5] However, at variance with respect to RG equations, our full equations (2)-(4) describe the system over all of its length scales because we do not eliminate degrees of freedom. This allows us to describe also nonuniversal properties like the correlations at short range and the crossover to the noncritical region. All functions entering our equations have a manifest physical meaning and the trick[4] of optimization of the attractive interaction inside the core in order to impose the core condition can be be extended to our equations. As first applications we find that the core condition does not modify the leading terms of the ϵ expansion and a very simple approximation already gives acceptable critical exponents in three dimensions.

Our equations need no rewriting in the case of lattice-gas models also with an extended core. Our basic approach is general enough that it can be applied to study the global properties of other systems with a critical point like a binary mixture with a consolution point. Moreover, it could be useful also in noncritical problems when different characteristic length scales are present, like in some liquid metals.

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