Dynamic critical phenomena near a liquid-gas critical point

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The normal-mode spectrum near a liquid-gas critical point is derived. The quantities which appear in the acoustic dispersion relations have a complex critical behavior, which cannot be described by simple scaling laws. Only the first terms of an expansion of the exact equations derived in this paper obey scaling laws. These exact equations are derived by summing infinite series of modified ladder diagrams.

1. Despite the huge number of studies of the critical points of liquids, there is still no systematic theory of dynamic critical phenomena. In this letter we propose a theoretical framework for describing dynamic fluctuation effects near a liquid-gas critical point.

The state of a liquid near its critical point is described by the momentum density $\vec{j}$ and by the deviations of the density of mass and entropy from their values at the critical point: $\rho-\rho_c$ and $s-s_c$. Only a single degree of freedom softens near the critical point. We denote this degree of freedom by Ψ, and we call it the "order parameter." The order parameter Ψ is then a strongly fluctuating variable near the critical point. The other variables ($\vec{j}$ and a linear combination of $\rho-\rho_c$ and $s-s_c$ which we denote by ϕ) are weakly fluctuating. There is some arbitrariness in the choice of the strongly fluctuating variable. We can exploit this arbitrariness to choose the following quantity as Ψ:

$$\Psi=\frac{s}{\rho}-\frac{s_c}{\rho_c}. \tag{1}$$

2. The general approach in a study of critical dynamics (Refs. 1–3, for example) is to construct an action I which is generated by the nonlinear hydrodynamic equations of the system under consideration. This action contains a dependence on Ψ, $\phi,\vec{j}$ and on their conjugate fields p_Ψ, p_ϕ, and p_i. Since the variables $\phi,\vec{j}$ (and p_ϕ, p_i) are strongly fluctuating, we need retain in action I only the terms which are linear and quadratic in these variables. We can integrate I over them. As a result, we find an effective action I_Ψ which depends on only Ψ and p_Ψ:

$$\exp(iI_\Psi)=\int Dp_i^\perp Dj_i^\perp \exp[\{p_i^\perp\delta_{im}^\perp \nabla_k(\nabla_k\Psi\nabla_m\Psi)-p_i^\perp\frac{\eta}{\rho}\nabla^2 j_i^\perp$$
$$+iT\eta(\nabla p_i^\perp)^2\}+\{p_\Psi(\frac{\partial\Psi}{\partial t}-\lambda\nabla^2\frac{\delta\mathcal{H}}{\delta\Psi})+p_\Psi\nabla_i\Psi\frac{p_i}{\rho}+iT\lambda(\nabla p_\Psi)^2\}]. \tag{2}$$

The superscript ⊥ here means the component in the direction perpendicular to the wave vector; η and λ are seed values of the shear viscosity and of the thermal conductivity; and $\mathscr{H}$ is the energy density.

The action I_Ψ is renormalizable. It describes the dynamics of the order parameter Ψ (the H model in the classification of Ref. 4). The correlation functions of the variables p_Ψ, Ψ, which characterize the critical mode, therefore obey a dynamic scaling theory. For example, the renormalized dispersion relation for the critical mode is (with $qr_c \ll 1$) $\omega \propto q^z$, where the dynamic exponent z has the value of 3.065 in the second ϵ approximation.[4] Here $r_c \propto |A_0|^{-\nu}$ is the critical radius; the quantity A_0 is given by $A_0 = (T - T_c)/T_c$; and ν is the critical exponent.

The comments above, however, are valid only in the frequency region in which the critical mode exists. As was first pointed out by Polyakov,[5] attempts to go outside this region result in a disruption of the scaling. If the fluctuation contributions to the noncritical degrees of freedom are to be taken into account correctly, it is necessary to sum the main sequences of diagrams for the dynamic correlation functions of the weakly fluctuating variables. Since I includes only terms which are linear and quadratic in the weakly fluctuating variables, only the modified ladder diagrams need be summed.[3] In this letter we present only the results; the details of the calculations will be reported in a separate paper.

3. The acoustic dispersion relation is determined by the equation

$$\rho\omega - \frac{\tilde{\beta}(\omega, q)}{\omega} q^2 + i\zeta q^2 = 0. \tag{3}$$

Here ζ is a seed value of the bulk viscosity, and all fluctuation effects are incorporated in the renormalized compressibility $\tilde{\beta}$:

$$\tilde{\beta} = \left(\frac{\partial P}{\partial \rho}\right)_\sigma - \frac{\Xi^2 F(\omega, q)}{1 + \Xi^2 \left(\frac{\partial P}{\partial \rho}\right)_\sigma^{-1} F(\omega, q)}. \tag{4}$$

Here P is the pressure, and Ξ is the coefficient of the $\phi\Psi^2$ term in the energy density. This coefficient has no singularities near the critical point. The function F has scaling properties:

$$F(t, \vec{r}) = \int D\Psi Dp_\Psi \exp(iI_\Psi)[\Psi^2(t, \vec{r})(p_\Psi \lambda \nabla^2 \Psi)(0,0)]. \tag{5}$$

The function F can be calculated in the Ornstein–Zernike approximation[6] or through an ϵ expansion[4–7] (for example). By virtue of the fluctuation dissipation theorem, the function F can be expressed in terms of the correlation function $\langle \Psi^2(t,\vec{r}), \Psi^2(0,0) \rangle$, whose critical behavior is determined by the specific heat exponent α.

In the low-frequency region we have

$$F = F_0 + iF_1 \omega |A_0|^{-z\nu}. \tag{6}$$

As the critical point is approached, F_0 and F_1 diverge as $|A_0|^{-\alpha}$. It thus follows from (3)–(6) that the sound velocity vanishes as $|A_0|^\alpha$, at the critical point, and the attenuation of sound exhibits a complex crossover behavior from an $|A_0|^{-z\nu-\alpha}$ law to an $|A_0|^{-z\nu+\alpha}$ law.

The dispersion relation for a shear mode is determined by

$$\rho\omega + \frac{i\eta q^2}{1-\Pi(\omega,q)\eta^{-1}} = 0. \tag{7}$$

The dynamic correlation function Π, which determines the fluctuation component of this mode, is

$$\Pi(t,\vec{r}) = i\int D\Psi Dp_\Psi \exp(iI_\Psi)[\nabla_i(\nabla_i\Psi\,\nabla_j\Psi)(t,\vec{r})$$
$$\times\frac{1}{\nabla^2}\left(\delta_{jm}-\frac{\nabla_j\nabla_m}{\nabla^2}\right)p_\Psi\,\nabla_m\Psi(0,0)]. \tag{8}$$

The function Π is calculated from the renormalized action. It obeys a dynamic scaling law. In the hydrodynamic region, for example, we have $\Pi\propto|A_0|^{-(z-3)\nu}$, and in the limit $|A_0|\to 0$ we have $\Pi\propto\omega^{(3-z)/z}$. In an actual experiment, the second of these formulas limits the increase in Π. The denominator in (7) thus does not become small. The purely hypothetical possibility of an instability of the shear mode or of the appearance of a gap in it will be discussed in a separate paper.

If fluctuation corrections are small ($\Pi\ll\eta$), we find a known expression[6,7] from (7):

$$\omega = -i\left[\frac{\eta}{\rho}+\Pi\right]q^2. \tag{9}$$

This is, however, only the first term of an expansion of the exact equation, (7). It follows from some recent experimental data[8] that the increase in the effective viscosity reaches 20% in the critical region at a frequency of 1 Hz. The discrepancy between Eqs. (7) and (9) is about 5% in this case and within the experimental error.[8]

Equations (3) and (4) solve the problem of the mode spectrum over a broad range of the temperature and the frequency near the liquid-gas critical point. It follows from these expressions that all the critical dynamics is determined by the behavior of two universal functions, F and Π, which have scaling properties. These functions can be calculated through an ϵ expansion in terms of the renormalized action I_Ψ in (2). They can also be determined directly, through a correct analysis of experimental data [based on Eqs. (3)–(7)].

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