DYNAMICS OF THE CRITICAL LIQUID–VAPOR INTERFACE CLOSE TO A SOLID WALL

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We discuss the dynamics of an interface separating two phases of a fluid close to its critical point and in the presence of a third, inert phase regarded as a solid wall. The dispersion relation for the interface undulations is derived and compared with the predictions of the theories of capillary waves and interfacial motion for a conserved order parameter.

The static and dynamic properties of a two-phase interface close to an inert third phase surface has recently attracted much attention particularly in the context of the wetting transition [1,2]. Although the static properties of the wetting layers and the corresponding interface properties are well understood the dynamics of the wetting phenomena is in a less satisfactory shape. One of the reasons for that is that the powerful methods of critical dynamics cannot be easily applied to the equation of motion for the wetting interface since that equation is strongly non-local in space and time. This nonlocality reflects the fact that the order parameter for the wetting transition is usually a conserved one.

Recently [3] we have proposed a model for the wetting transition hydrodynamics with a conserved order parameter. Specifically, we have considered a system consisting of a solid wall and two phases of a binary mixture, α and β. We have assumed wetting conditions, that is a thin layer of one phase, say α, intruding between the wall and the β phase. We were able to analyze the motion of the interface between α and β phases assuming that the bulk dynamics was governed by the usual diffusion equation. One of the results of ref. [3] was the dispersion relation for long wavelength, $k f_0 \ll 1$, "capillary" waves on that interface. Here $k$ is the wave vector and $f_0$ is the equilibrium thickness of the wetting layer. We found that the interface undulations behave like $\delta f \sim \exp(i\omega t - ik \cdot x)$ with:

$$\omega = - D \left( \frac{k^2}{f_0} + \kappa^2 \right)$$

with $D$ the diffusion constant, $l_c$ the capillary length and $\kappa^2$ is proportional to the second derivative of the effective potential between the solid wall and the interface.

In this Letter we shall address the closely related problem of the wetting when the solid wall is in contact with the liquid–vapor system close to the liquid–vapor bulk critical point. The dynamics of the free interface (that means without the presence of the wall) was analyzed in ref. [4] and subsequently discussed in refs. [5,10]. One of the conclusions was that in order to derive the dispersion relation for the capillary waves one has to take into account: (i) finite fluid compressibility, (ii) the presence of the heat mode. As a result one can analyze the motion of the interface by means of the set of boundary conditions, called Kotchine conditions, which we shall adopt for our purposes in this note.

Our basic assumptions are then as follows. To fa-
cilitate the use of the continuous description we consider situations in which the equilibrium thickness of the wetting layer and the wavelengths of interface perturbations are much greater than the bulk correlation length $\xi_0$. We assume also that outside the interfacial region (the thickness of which is of the order of $\xi_0$) we may use the concept of point thermodynamics [6]. This means that we may define local thermodynamic quantities, for example pressure or temperature, which are related among themselves like in the bulk macroscopic phases.

Now, the changes of the density $n$, temperature $T$ and velocity field $u$ in each of the phases, $\alpha$ = liquid or vapor, are governed by conventional hydrodynamic equations:

$$\frac{\partial n_\alpha}{\partial t} = -\nabla \cdot (n_\alpha u_\alpha),$$  

$$m n_\alpha D u_\alpha = -\nabla p_\alpha,$$  

$$n_\alpha C_v \frac{\partial T_\alpha}{\partial t} = -T_\alpha \left( \frac{\partial p}{\partial T} \right)_{n_\alpha} \nabla \cdot u_\alpha + \lambda_\alpha \nabla^2 T_\alpha. \tag{4}$$

The first equation is the continuity equation, the second one is the Euler equation and the third one comes from the energy balance. $m$ is the mass of the particle and $C_v$ is the specific heat at constant volume. In order to simplify the calculations we have assumed that the viscosity is negligible.

The above equations have to be supplemented with the proper set of the boundary conditions. Since we consider only long wavelength perturbations of the interface it is legitimate to treat the interface as a sharp one. Thus we shall specify boundary conditions not only at the wall but also at the interface. We assume that the solid wall is isothermal, so $T = T_v = \text{const}$ at $z = -f_0$ (we choose the origin of the coordinate system at the distance $f_0$ from the wall, i.e. at the equilibrium position of the interface). The other condition $u_z(z = -f_0) = 0$ expresses inpenetrability of the wall by the particles.

At the interface we have:

$$\mu_\alpha = \mu_v, \tag{5}$$

$$T_\alpha = T_v \tag{6}.$$  

$$\ln n_n(u_N^n - u_N^v)/\Delta = \left[ \lambda (\nabla T_k)^N - (\nabla T_v)^N \right], \tag{7}$$

$$n_k u_k^N - n_v u_v^N = (\Delta)^N \tag{8}.$$  

$$p_\alpha - p_v = -\sigma k^2 K(f(x, t)) + \sigma k^2 f(x, t) \tag{9}.$$  

Eqs. (5)-(8) are the classical boundary conditions known from the theory of continuous media with discontinuity surfaces [4]. The first two describe the fact that the chemical potential and temperature are continuous across the interface and the others are simply heat and mass balances during the interface motion. The subscripts $k$ and $v$ refer to liquid and vapor respectively and the superscript $N$ denotes component of a vector in the direction normal to the interface. $l$ is the latent heat per molecule, $V$ is the velocity of the interface and $\Delta n = n_n - n_v$. $f(x, t)$ describes the position of the interface, $K(f)$ its curvature and $\sigma$ is the interfacial tension between liquid and its vapor.

Eq. (9) requires clarification. The first term on the right-hand side of (9) is the usual Laplace difference in the pressures between two phases divided by a curved surface. The other term may be understood on the basis of the disjoining pressure concept introduced by Deryagin et al. [7]. According to ref. [1] the pressure inside the very thin liquid layer is different from that in the bulk of the same liquid with equal density and at the same temperature. The difference between these two pressures is called the disjoining pressure and its value is proportional to the first derivative of the effective wall–interface potential $V(f)$ [2]. Now in our case when the interface is flat and located at its equilibrium position $f(x, t) = 0$ the disjoining pressure vanishes since $\partial V(f)/\partial f|_{f=0} = 0$. Similarly the Laplace corrections do vanish. For a small departure of the interface from its stationary configuration, assuming a parabolic behavior of $V(f)$ in the vicinity of $f = 0$, we obtain eq. (8) with $k^2 \sim \partial^2 V(f)/\partial f^2|_{f=0}$.

In order to obtain the dispersion relation for capillary waves propagating on the interface we assume that $f(x, t) = \delta f \exp(\text{i} \omega t - \text{i} k \cdot x)$ and linearize the equations of motion and the boundary conditions around equilibrium. Following the procedure in ref. [3] we have obtained a rather complicated dispersion relation [8]; herewith we shall discuss its form in two limiting cases: for short and long wavelengths.

For $1/k \ll \zeta_0^{-1}$ we obtain the classical dispersion relation, i.e. $\omega^2 = \sigma k (k^2 + \zeta_0^2)/m(n_n + n_v)$. This means that for waves which have a length much smaller than the equilibrium thickness of the wetting layer, the influence of the wall is only through the disjoining pressure term which is an analog of the
gravitation field in the conventional capillary waves theory. This agrees with the result of Lipowsky [9] who derived the capillary wave dispersion relation for the wetting layer treating the fluids as incompressible and isothermal.

More interesting is the long wavelength limit. In this limit i.e. $k f_0 \ll 1$, we obtain:

$$\omega^2 - \frac{T \sigma (k^2 + \kappa^2)}{l^2 n_0^2 f_0} \omega - \left( \frac{k f_0}{m n_0} \right) \frac{-2 \kappa}{\kappa^2} = 0.$$ 

From eq. (10) we see, that for $k f_0 \to 0$ the third term on the left-hand side of eq. (10), which is the classical capillary wave dispersion relation for a finite depth liquid [9], becomes less important as compared to the second one. When $k f_0 \to 0$, the heat (diffusion-like) mode dominates the dynamics and in this limit the liquid–vapor system starts to behave as a binary mixture. In this limit, the frequency becomes imaginary and the waves decay according to $\omega = -\frac{2 n f_0}{m n_0} \left( k^2 + \kappa^2 \right)$, where the capillary length $l_c$ equals $\sigma C,T l^2 n_0$ and $D = \kappa n_0$. This relation has a form identical to the one obtained previously [3] for a binary mixture system, cf eq. (1).

The above result is in agreement with the universality hypothesis. The binary mixture and the liquid–vapor system are two microscopically different systems. Their dynamics is governed by quite different equations of motion, but their long wavelength behavior close to the critical point is completely equivalent.

In conclusion, we have analyzed the motion of the interface between liquid and vapor near their bulk critical point in the presence of the third phase, the solid wall. We think that the results we have obtained may be checked experimentally.

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References