ELECTRIC FIELD INDUCED INTERFACIAL INSTABILITIES

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ABSTRACT

The study of the interface in a charge-free, nonpolar, critical and near-critical binary fluid in the presence of an externally applied electric field is presented. At sufficiently large fields, the interface between the two phases of the binary fluid should become unstable and exhibit an undulation with a predefined wavelength on the order of the capillary length. As the critical point is approached, this wavelength is reduced, potentially approaching length-scales such as the correlation length or critical nucleation radius. At this point the critical properties of the system may be affected. In zero gravity, the interface is unstable at all long wavelengths in the presence of a field applied across it. It is conjectured that this will cause the binary fluid to break up into domains small enough to be outside the instability condition. The resulting pattern formation, and the effects on the critical properties as the domains approach the correlation length are of acute interest. With direct observation, laser light scattering, and interferometry, the phenomena can be probed to gain further understanding of interfacial instabilities and the pattern formation which results, and dimensional crossover in critical systems as the critical fluctautions in a particular direction are suppressed by external forces.

INTRODUCTION

Several systems exhibit an interfacial instability in response to a stress resulting from the application of an external field. Two such systems closely related to the proposed system of study are a ferrofluid/air interface in the presence of a magnetic field [1, 2], and the interface between two fluids when charged with ions [3, 4, 5, 6]. Both systems lead to the formation of a hexagonal dimple pattern. One of our collaborators, Prof. A. Onuki, has recently proposed that such an effect could be observed at the neutral two-phase interface of a critical system, such as a binary fluid near its consolute point, or a simple fluid near the critical point of its liquid/vapor transition, in the presence of an externally applied electric field [7]. Although the physics for the instability, as presented below, is very similar to that for the ferrofluid, the large surface tension in ordinary liquid/vapor systems requires prohibitively large electric fields. However, in a two-phase critical system, the surface tension vanishes as the critical temperature is approached, so the instability may be observed within experimentally accessible electric fields near the critical point. An added benefit of the critical system is that as the surface tension is reduced, the length scale of the instability is also reduced, leading to interesting physics as this length scale approaches that of the critical fluctuations or nucleation droplets . In the absence of gravity, the entire nature of the instability changes, leading to an instability at all long wavelengths. These items will be discussed below.

EFFECT OF ELECTRIC FIELD ON THE MACROSCOPIC INTERFACE

Through rigorous derivation, Onuki [7] has found the free energy of a surface wave with wave number k to be

$$G_k = \sigma k^2 + g(\Delta\rho) - C_E k, \tag{1}$$

where σ is the surface tension, g is the gravitational acceleration, and $\Delta\rho$ is the mass density difference between the two phases, taken to be positive. The parameter C_E represents the effect of electric field, here

taken to be normal to the interface,

$$C_E = \frac{1}{4\pi}\frac{(\varepsilon_2 - \varepsilon_1)^2}{\varepsilon_1\varepsilon_2(\varepsilon_1 + \varepsilon_2)}D_0^2 \quad , \tag{2}$$

where D_0 is the electric induction in the unperturbed state.

The first two terms in Equation (1) are the standard expressions used to describe a capillary wave on a liquid surface. The third term is the effect of the electric field and the source of the instability. Due to this term, the free energy exhibits a minimum at wave number

$$k^* = C_E/2\sigma. \tag{3}$$

The relevance of this experiment to microgravity investigation arises due to the stabilizing effect of gravity on the interface. In the absence of gravity ($g = 0$), this minimum, due to the presence of an electric field oriented normally to the interface, will always correspond to a negative free energy. Hence, thermal excitations with wavevectors near and less than k^* will have diverging amplitudes, resulting in a distortion or breakup of the interface on a length scale of the reciprocal critical wavevector, Equation (3). In a gravitational field, the second term of Equation (1) will force the free energy minimum to be positive except for the case of large electric field, for which the surface fluctuation at $k = k^*$ becomes unstable for

$$C_E > 2\sqrt{\sigma g \Delta\rho} \qquad \text{and} \qquad k^* > [g(\Delta\rho)/\sigma]^{1/2} = 1/a_g, \tag{4}$$

a_g being the so-called capillary length. The difference between the two cases is clear: In a gravitational field, only wavevectors in the vicinity of k^*, Equation (3), are unstable and only at a sufficiently large field; in the absence of gravity, all wavelengths larger than $1/k^*$ are unstable, for an arbitrarily small field.

An estimate of this effect with $g = 980$ cm/s^2 in the perfluorohexane/hexane critical binary mixture follows: At 1 K below T_c the capillary wavelength is approximately 400 μm requiring a 16 kV/cm field to produce the instability. As the critical point is approached, both the capillary wavelength and the critical field decrease with a critical exponent of 0.46 and 0.07 respectively. The critical properties will become affected when $k^*\xi \approx 1$, which occurs at $T_c - T \approx 0.1$ mK at the onset of the instability. However by application of a field about ten fold greater than the critical field, this should occur at $T_c - T \approx 10$ mK.

It has also been demonstrated [7] that an electric field oriented parallel to a fluid interface will serve to stabilize that interface. Considering the presence of an electric field with arbitrary orientation with respect to the interface, the coefficient of the third term in Equation (1), C_E, is replaced by

$$C_E = \frac{1}{4\pi}\frac{(\varepsilon_1 - \varepsilon_2)^2}{\varepsilon_1 + \varepsilon_2}\left(\frac{1}{\varepsilon_1\varepsilon_2}D_0^2 - E_{0\perp}^2\right), \tag{5}$$

where $E_{0\perp}$ is the component of the electric field perpendicular to the surface normal, and D_0 is the component of the displacement field parallel to the surface normal. In the case $E_{0\perp} \geq D_0/(\varepsilon_1\varepsilon_2)^{1/2}$, the coefficient C_E becomes negative and the applied field serves to stabilize the interface. Besides the technological interest of stabilizing a two-phase boundary in zero gravity, this effect raises scientific interest in pattern formation and the suppression of critical fluctuations. This latter effect should manifest itself in the modification of the dimensionally dependent critical exponents for the system.

Hydrodynamic equations provide an alternative way of looking at this interfacial instability. Ignoring the effect of viscosity, Onuki [7] has found the dispersion relationship for capillary waves in the presence of an electric field,

$$\omega_k^2 = (\rho_1 + \rho_2)^{-1}k[\sigma k^2 - C_E k + g(\Delta\rho)] \quad , \tag{6}$$

where ρ_1 and ρ_2 are the mass densities in the two phases, and C_E is given by Equation (5). The instability occurs when $\omega_k^2 < 0$. Also of interest is the presence of negative wavepacket velocities ($d\omega/dk < 0$). It should be noted that near the critical point, these capillary waves may become overdamped due to viscosity.

EFFECT OF ELECTRIC FIELD ON NUCLEATION

The interaction between an electric field and the phase separation process through nucleation is complex. Physically it involves the competition of two opposing forces. While the electric field favors a homogeneous phase by rupturing droplets, thermodynamic forces favor the separation of the mixture into two phases. The analogous problem is the phase separation in the presence of a shear flow, where the mixing and shearing action of the flow induces the fragmentation of the minority phase [8, 9, 10].

In a traditional nucleation experiment, nucleation is usually viewed as a transient phenomenon [11]; one typically quenches or supersaturates a system and records the growth of droplets of the minority phase. But in this proposal, nucleation under the steady-state conditions will be studied.

We illustrate in the simplified way how a steady state can be achieved with an electric field and probed by light scattering. Initially, the system is driven into the two-phase state, where droplets are formed and grow. The electric field E is then abruptly turned on, rupturing those droplets which have grown to a sufficient size [7, 12]. Through the repeated mechanism of the growth and the destruction of droplets, the fluid mixture tends to a stationary state under the influence of the electric field. As the electric field is increased, droplets of an increasingly smaller size are fragmented. Eventually, a value of $E = E_c$ is reached, at which point, the droplets as small as the critical radius are ruptured. At this value of $E = E_c$, nucleation is therefore inhibited and the light scattered from the mixture abruptly decreases by orders of magnitude.

Simple Model

Nucleation can be induced by suddenly quenching an off-critical one-phase system through its coexistence temperature T_{cx} into the metastable state. The system then evolves toward a two-phase equilibrium by the formation and growth of droplets of the minority phase. For a small droplet, the surface free energy cost of creating the surface of the droplet outweighs the bulk free energy benefit of creating the state which represents the true minimum of the free energy. As a result, the homogeneous state is stable to such small fluctuations. On the other hand, if the droplet is sufficiently large, the bulk free energy overwhelms the surface energy, and the free energy of the system is reduced by the presence of big enough droplets. Hence the homogeneous state is unstable to such sufficiently large fluctuations. If the surface free energy is σ, and the bulk free energy per unit volume is e_f, then the difference in free energy between the system with one droplet of radius R and the system with no droplets is

$$\Delta\Phi(R) = -\frac{4}{3}\pi e_f R^3 + 4\pi\sigma R^2. \tag{7}$$

Note that $\Delta\Phi(R)$ has a maximum for the critical radius $R = R_c$, where $R_c = 2\sigma/e_f$. The droplets with $R < R_c$ shrink after they have been created, whereas droplets with $R > R_c$ grow. In summary, the mechanism of nucleation is the instability of the homogeneous fluid to the creation of droplets of critical size, $R = R_c$. Local thermal fluctuations initiate this instability and enable the system to surmount an activation energy barrier, $\Delta\Phi(R)$, which blocks the formation of droplets [13]

The parameters σ and e_f depend on the state of the system. The surface tension σ is a function of temperature T near the critical temperature T_c and roughly equal to $\sigma = 0.1k_BT/\xi^2$, where k_B is the Boltzmann constant and ξ is the correlation length [14]. In the so-called "ϕ^4" model [15], e_f is roughly equal to $\sigma x/\xi$. The volume fraction of the minority phase x is related to the quench depth $\delta T = T_{cx} - T$ and $\Delta T = T_c - T_{cx}$ through the equation

$$x = \frac{1}{2} - \frac{1}{2}\left[\frac{1}{1+\delta T/\Delta T}\right]^{\beta} \approx \frac{\beta\delta T}{2\Delta T}, \tag{8}$$

with the latter approximation holding when $\delta T/\Delta T$ is small. The coexistence-curve exponent β has the value 0.31 [16].

The situation is very different when a binary liquid mixture, quenched to a temperature T, is exposed to an electric field E. The electric field creates a dynamic equilibrium by constantly rupturing droplets of the minority phase, which have grown to a sufficient size. The maximum droplet size $R = R_{max}$ that can exist in the presence of the electric field is given by the relation

$$C_E = \sigma/R_{max}, \tag{9}$$

where C_E is given by Equation 2 [7]. The result is a steady-state droplet distribution in which the size and the number density are determined by E and the degree of the supercooling, δT. That is, the steady state is completely characterized by two variables, δT and E, when droplets are present. These parameters are equivalent in the sense that both can change supersaturation.

The strength of the electric field necessary to suppress nucleation for a given value of the supercooling δT, is determined by whether the droplets are fragmented down to a radius $R < R_c$, where R_c is a function of δT. If this condition is satisfied, the droplets will disappear altogether, and the system will consists of one homogeneous phase. In mathematical terms, the value of the critical electric field $E = E_c$ solves the following equation

$$C_E(E_c) = \sigma/R_c. \tag{10}$$

It is this equation with which the measurements are compared.

An estimate for this effect in the perflourohexane/hexane mixture follows: We assume the Becker-Döring limit, which states that nucleation rate falls in a conveniently measurable range (i.e., 1 droplet/cm^3) when $\delta T/\Delta T \approx 0.15$. If use is made of the scaling law $\Delta\phi \equiv \phi_1 - \phi_2 = B(1 - T/T_c)^\beta$, then

$$C_E \cong (8\pi\varepsilon_{av})^{-1} B^2 \varepsilon'^2 E_0^2 (1 - T/T_c)^{2\beta}, \tag{11}$$

where ε_{av} is the average dielectric constant, $\varepsilon' \equiv d\varepsilon/d\phi \approx 0.32$, and the miscibility gap constant B is of the order three [17]. Since $\sigma/R_c \approx 0.44$ for an off-critical sample at $\Delta T = 15$ (mK), an electric field stronger than 25 kV/cm is required to rupture all the droplets of the critical radius.

CONCLUSION

A static instability in the interface between two dielectrically mismatched fluids can be generated by the application of an electric field oriented perpendicularly to the interface. In a gravitational field, the onset of this instability will occur at the capillary wavelength when a sufficiently large field is applied. In the absence of gravity, the length scale of the instability, and hence the minimum required field are determined by the size of the system. In a phase separating, off-critical system, this instability should effect the nucleation process by rupturing minority phase droplets larger that the instability wavelength. By application of a sufficiently large field, it is conjectured that the instability wavelength can be made small enough to prevent all nucleation.

These phenomena can all be probed through laser light scattering and interferometry. Diffraction of light off and interference of light through a two phase interface can lead to a measure of the length scale and topography of the instability. Dynamic light scattering from the interface can be used to measure the effect of the applied field on the capillary wave dispersion relationship. Finally, dynamic light scattering and turbidity measurements can be used to probe a phase separating binary fluid in the presence of an electric field to determine the nucleation droplet distribution.

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