Dynamical Relaxation of the Surface Tension of Miscible Phases

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(Received 26 July 1993)

The dynamical behavior of the surface tension of two initially immiscible phases on raising the temperature to a value greater than or equal to the critical temperature is studied using analytic techniques, mean field dynamical equations, Monte Carlo simulations, and molecular dynamics simulations. Distinct behavior is predicted in situations with a conserved order parameter and when no conservation law is operative. A novel scaling form is obtained for a system evolving to equilibrium at its critical temperature.

PACS numbers: 47.20.−k, 05.70.Ln

Recent experiments have focused on the physical integrity of the nonequilibrium interface between miscible fluids [1–5]. In analogy with the surface tension of an equilibrium interface between immiscible fluids, an effective surface tension may be defined as [6]

$$\sigma \propto \int \left(\frac{\partial c}{\partial z} \right)^2 dz , \tag{1}$$

where c is the local composition and z is the direction normal to the interface.

In this Letter, we study the dynamics of surface tension in a variety of situations using a multipronged approach. We consider an initially immiscible two phase system and study the effective surface tension as defined in (1), on raising the temperature to a value above or equal to the critical temperature. Most of our results have been obtained in the context of an Ising model in both the mean field limit and incorporating fluctuations. In the Ising model, the two phases correspond to up and down magnetizations. Cases involving a conserved order parameter and no such conservation law are shown to have qualitatively different behaviors. The dynamical surface tension is found to have distinct temporal behavior depending on whether the final temperature of a system with an initial sharp interface is above or equal to the critical temperature (T_c) of the system. A novel feature of our work is the derivation of Langevin equations for soft Ising spins on a discrete lattice that lead to the exact equilibrium state at any arbitrary temperature. On turning off the noise, these equations reduce to a mean field approach. Our numerical calculations are complemented by an analytic analysis of the equations of motion in a linearized approach and with an approximate incorporation of the nonlinearities in a self-consistent manner. Finally, molecular dynamics simulations of a two-fluid system and a liquid-vapor system are presented to demonstrate the distinct dynamical response of the two cases.

We begin with a summary of our results:

$$\text{model A}: \; T_f > T_c , \quad \sigma \sim e^{-t} ; \tag{2}$$

$$\text{model B}: \; T_f > T_c , \quad \sigma \sim 1/t^{1/2} ; \tag{3}$$

$$\text{model A}: \; T_f = T_c , \quad \sigma \sim m_0^2 t^{-x_i} f_A(t m_0^{z_m}) , \quad \text{with } z_m = \nu z/\beta ; \tag{4a}$$

$$\text{model B}: \; T_f = T_c , \quad \sigma \sim m_0^2 t^{-x_i} \tilde{f}_B(t, m_0) ; \tag{4b}$$

which in the limit of $m_0 \to 0$, $t \to \infty$, $u \equiv t m_0^{z_m} \to$ const simplifies to

$$\sigma \sim m_0^2 t^{-x_i} f_B(t m_0^{z_m}) , \tag{4c}$$

where the final temperature is denoted by T_f; model A refers to the situation where there is no conservation law for the order parameter; model B is the conserved-order-parameter case [7], m_0 refers to the initial step in the order-parameter profile; ν is the correlation length exponent; z is the dynamical exponent; and β is the order-parameter exponent. The equation for z_m follows from scaling arguments: $m_0 \sim \xi^{-\beta/\nu}$ and $t \sim \xi^z \sim m_0^{-z_m}$, where ξ is the correlation length.

The exponent x_i is different for models A and B and so is z_m, since the dynamical exponent z differs for models A and B. Note the unusual scaling form for σ involving the initial step m_0. Our molecular dynamics (MD) results for $T_f > T_c$ indicate that a two-fluid system has model B type behavior whereas a liquid-vapor system shows the fast model A type relaxation. This result is due to the fact that unlike the two-fluid case, the liquid phase can be converted into the vapor phase and vice versa and no conservation law is operative.

Mean field dynamics for soft Ising spins.—Our equations of motion are obtained for the Ising Hamiltonian

$$H = -\tfrac{1}{2} \sum_{x,y} K_{xy} S_x S_y , \tag{5}$$

where $K_{xy} = K$ when x,y are nearest neighbors and $S_x = \pm 1$, by making a Hubbard-Stratonovich transformation and writing the partition function

0031-9007/93/71(21)/3465(4)$06.00

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$$Z=\prod_x \int_{-\infty}^{\infty} dm_x\, e^{-F\{m\}}$$

with the effective Boltzmann weight given by [8]

$$F\{m\}=\tfrac{1}{2}\sum_{xy} m_x K_{xy} m_y - \sum_x V\left(\sum_y K_{xy} m_y\right), \tag{6}$$

with $V(\phi)=\ln\cosh\phi$. Note that the discrete lattice is maintained while the discrete spin variable S_x has been replaced by m_x that takes on values between $-\infty$ and $+\infty$. Following Chandrasehkar [9], we derive a Langevin equation for the dynamics of m:

$$\dot{m}_x = f_x\{m\} + \sum_{y,\alpha} g^{\alpha}_{xy}\zeta^{\alpha}_y(t)\,. \tag{7}$$

For model B dynamics, the conservation law that $\sum_x \dot{m}_x = 0$ is imposed by requiring that

$$\sum_x f_x = \sum_{x,y,z} g^{\alpha}_{xy}\zeta^{\alpha}_y(t) = 0\,, \tag{8}$$

where $\zeta^{\alpha}_y(t)$ is a white noise (with a Gaussian probability distribution), satisfying $\langle \zeta^{\alpha}_x(t)\zeta^{\beta}_y(t')\rangle = 2\delta_{\alpha\beta}\delta_{xy}\delta(t-t')$. $\alpha = 1,2,\ldots,d$ where d is the dimensionality. In order to obtain the correct equilibrium distribution with the weight determined by (6), we choose

$$f_x\{m\} = \gamma\sum_y \sum_{z,\alpha} g^{\alpha}_{xz} g^{\alpha}_{yz} \frac{\partial F\{m\}}{\partial m_y}\,, \tag{9}$$

$$g^{\alpha}_{xy} = \delta_{y,x+\hat{\alpha}} - \delta_{y,x}, \quad \gamma = 1\,, \tag{10}$$

where $\hat{\alpha}$ is a unit vector in the αth direction. With this choice Eq. (8) is satisfied. Model A dynamics with no conservation law is obtained simply by choosing $g^{\alpha}_{xy} = \delta_{\alpha,1}\delta_{x,y}$ and $\gamma = -1$. In the naive continuum limit our equations reduce to the standard models [7] A and B in the bulk for T near T_c. Furthermore, turning off the noise leads to a mean field approach. The continuous variables m allow for more efficient averaging than the discrete Ising variables S.

We have used the model A equation with noise at T_c [of the infinite $d=2$ Ising model, which is known exactly for the Hamiltonian (6) due to its equivalence to Eq. (5)] for two-dimensional $L\times L$ systems with periodic boundary conditions with $L=4$, 8, and 16 to estimate the dynamical exponent z. Our result $z=2.1\pm 0.2$ is in accord with Monte Carlo estimates on discrete Ising spin models using Glauber dynamics. Our equations incorporate all the nonlinear terms (only the leading terms are present in the Cahn-Hilliard continuum equations valid for $T\sim T_c$).

The results of integrating the *mean field equations* are shown in Figs. 1 and 2. We choose an initial condition $m(x,0) = -m_0$ for $x<0$ and $+m_0$ for $x>0$. Equations (2)–(4) are found to hold with $x_i(A)=\frac{1}{2}$ and $x_i(B)=\frac{1}{4}$. Further, $f_A(u)=$const for $u\to 0$ and $f_A(u)\sim u^{x_i - x_f}$ as $u\to\infty$ with $x_f(A)=\frac{3}{2}$. (Note that $z_m=2$ for model A in the mean field limit.) Unlike the model A system at T_c, the crossover to the $u\to\infty$ limit is not observed for the model B case.

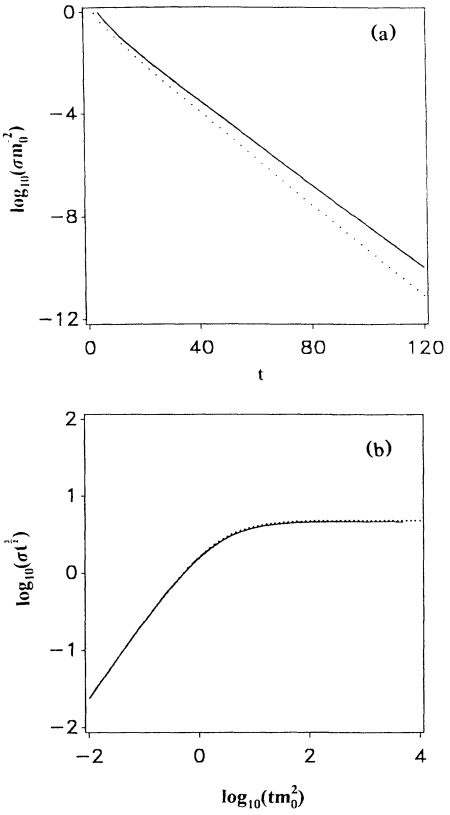

FIG. 1. (a) Exponential decay of σ for model A with $T_f > T_c$. The upper line is obtained on integrating the mean field equations ($K_c \equiv \frac{1}{9}$) for different initial steps $m_0 = 2^{-n}$, 4,5,6,7. The lower line is the analytic result in the linearized approximation [Eq. (12)]. (b) Mean field scaling plot for model A with $T_f = T_c$. The results are for initial steps $m_0 = 2^{-n}$, $n=0,1,2,\ldots,7$. The predictions of the self-consistent nonlinear model are shown as the dotted line.

Effect of fluctuations.—We have carried out Monte Carlo simulations at T_c for a $d=2$ discrete Ising model (5) with periodic boundary conditions in one direction and antiperiodic in the other using both Glauber and Kawasaki dynamics (Fig. 3). Our results again are consistent with the scaling form (4). In both cases, the initial power law x_i is the same as found in mean field theory. As in mean field theory, no significant crossover at late times is found for model B (Kawasaki dynamics). In the case of Glauber dynamics, one may readily estimate from the value of z_m in $d=2$ that the final power law exponent x_f should be $\frac{5}{8}$, which is sufficiently close to $x_i = \frac{1}{2}$, that we are unable to discern the difference in our simulations. We expect that in higher dimensions $x_i = \frac{1}{2}$, while x_f is determined from the corresponding z_m, which is a function of the dimensionality.

Analytic analysis.—The Cahn-Hilliard equation [7] obtained on expanding our equation of motion for $T \cong T_c$ is (in suitably chosen units)

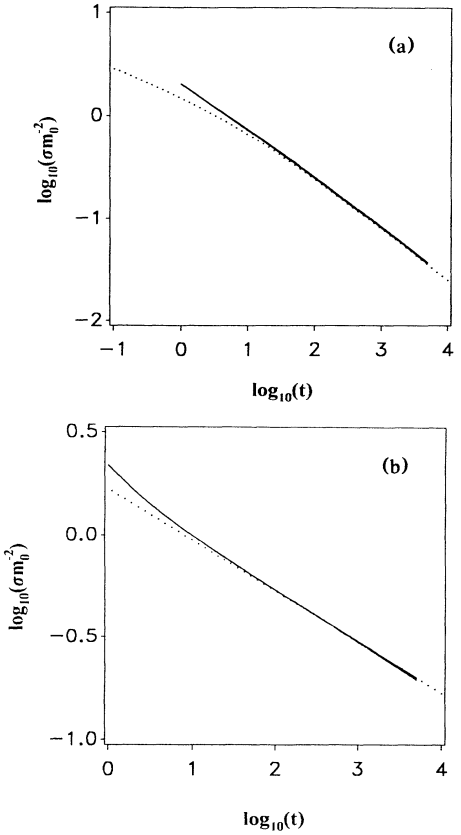

FIG. 2. (a) Mean field power law plot of σ vs t for model B, $T_f > T_c$, $m_0 = 2^{-n}$, $n = 2,3,\ldots,7$ (solid line). The dotted line is the analytic result in the linearized approximation. (b) $T_f = T_c$; $m_0 = 2^{-n}$, $n = 5,6,7$. The dotted line is the linearized analytic result.

$$\text{model A}: \dot{m}_A = \nabla^2 m_A - a m_A - m_A^3 + \cdots ,$$
$$\text{model B}: \dot{m}_B = \nabla^2 (a m_B + m_B^3 - \nabla^2 m_B) + \cdots , \tag{11}$$

with $a \propto T - T_c$.

For $T_f > T_c$, at large t, $m(x,t) \sim 0$ allowing the neglect of the nonlinear terms in (11). Fourier transforming (11) and solving for the surface tension, one obtains

$$\sigma(t) \sim \frac{2m_0^2}{\pi} \times \begin{cases} e^{-2at}\sqrt{\pi/2t}\,, & \text{A}\,, \\ \left(\dfrac{\pi}{2at}\right)^{1/2}\left[1 - \dfrac{3}{2a^2 t} + O\left(\dfrac{1}{t^2}\right)\right], & \text{B}\,. \end{cases} \tag{12}$$

Exactly at T_c, by setting $a = 0$, one finds the initial behavior of $\sigma(t)$ as

$$\sigma(t) \sim \frac{2m_0^2}{\pi} \times \begin{cases} \sqrt{\pi/2t}\,, & \text{A}\,, \\ 2^{7/4}\Gamma(\frac{1}{4})\, t^{-1/4}, & \text{B}\,. \end{cases} \tag{13}$$

The validity of (13) at long times is questionable because of the neglect of nonlinear terms. We attempt to take into account the nonlinearities in a self-consistent manner with the equation

$$\dot{m} = -\Gamma[-\nabla^2 + a + \overline{m^2(t)}]m(x,t) \tag{14}$$

with $\Gamma = 1$ for A and $-\nabla^2$ for B.

The self-consistency is imposed by requiring that

$$\overline{m^2(t)} = \frac{1}{L}\int_{-L/2}^{L/2} dx\, m^2(x,t)\,,$$

where L is the size of the system. Note that our approach is equivalent to a Berlin-Kac model [10] at $T = 0$. Fourier transforming as before and carrying out some tedious, but straightforward algebra, we find complete agreement with the scaling form (4) with

$$x_i(A) = \tfrac{1}{2}\,, \quad f_A(u) = (\sqrt{2/\pi})2/(2+u) \tag{15}$$

and

$$x_i(B) = \tfrac{1}{4}\,, \quad f_B(u) = u^{1/4}\int_0^{1/m_0} e^{-x^2(1+x^2)u}\,dx\,.$$

The apparent lack of crossover in model B is due to the fact that unlike $f_A(u)$ which is a function of u alone, $f_B(u)$ is also seen to depend on m_0. Indeed, numerically carring out the integral in $f_B(u)$, one finds a power law behavior characterized by exponent $\frac{1}{4}$ in excellent agreement with the numerical integration of the mean field equations.

Molecular dynamics simulations.—We have carried out MD simulations [11] (in three dimensions) of a Lennard-Jones fluid with a liquid-vapor interface. There are 1372 molecules in a 3D box of 11.3σ (σ is the molecular length scale) in the two lateral directions and 22.6σ in the longitudinal direction. We calculate the dynamic surface tension by monitoring the profiles. Starting with an equilibrium initial configuration at a reduced temperature $T^* = 0.75$, the systems are allowed to relax at a tem-

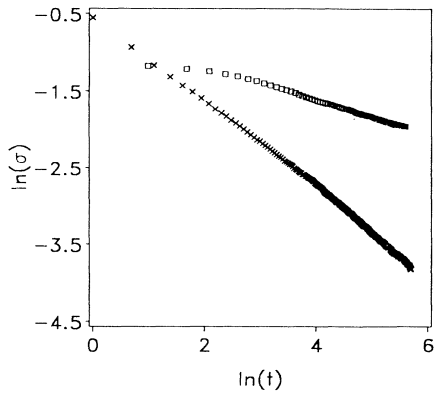

FIG. 3. Monte Carlo results for $T_f = T_c$. The crosses denote model A (the results were averaged over 1000 systems of 64×64 size) and the squares model B (averaged over 500 systems of 48×48 size). The data for model B have been shifted by 5 units to the left.

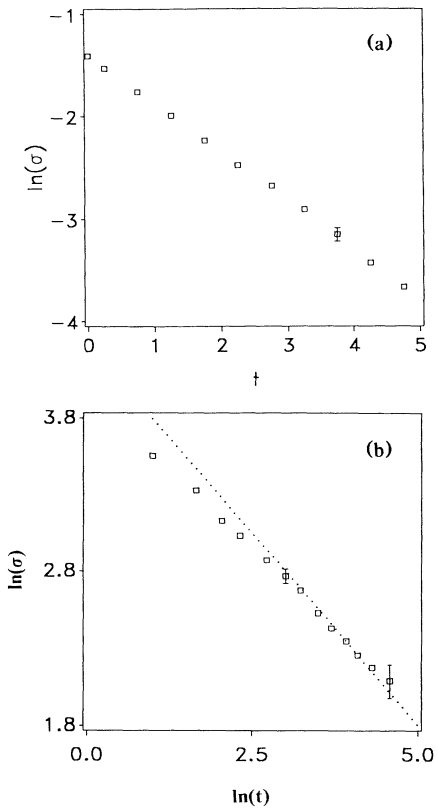

FIG. 4. (a) Molecular dynamics results for a liquid-vapor system. The system was equilibrated at reduced temperature $T^*=0.75$ and then evolved isothermally at $T^*=1.45$ ($T_c^* \approx 1.35$). The results are an average over 10 runs. (b) Molecular dynamics of binary liquids averaged over 10 runs. The dotted line is a guide to the eye and has a slope $-\frac{1}{2}$.

perature above T_c leading to an exponential decay [Fig. 4(a)]. We have also studied the relaxation of systems containing two initially immiscible liquids each having 2744 molecules in a box of $11.3\times11.3\times48.8$ (in units of σ). The attractive part of the interaction between the two species of molecules was a quarter of that between molecules of the same species when the systems were prepared initially at $T^*=1.4$. The ratio of the interactions was abruptly changed to 0.95 corresponding to $T_f \gg T_c$ and the relaxation of the profile was measured. Similar simulations on systems of two-thirds the longest edge length have been carried out to ensure the absence of finite size effects. The result is consistent with the $t^{-1/2}$ prediction and is strikingly different from the liquid-vapor system [Fig. 4(b)]. Our results also demonstrate that hydrodynamic modes in our MD simulation do not make a qualitative difference for $T > T_c$.

The May-Maher experiments [5].—We now turn to the anomalously tiny effective diffusion coefficient (the concentration gradients are smoothed by diffusion) estimated in Ref. [5] on employing a final temperature T_f very close to T_c [$(T_f-T_c)/T_c \sim 10^{-3}$] and fitting the surface tension with a $A/[B+(D_{\text{eff}}t)^{1/2}]$ form. Since our analysis shows that at T_c a $t^{-1/4}$ behavior should be obtained, for $T_f \gtrsim T_c$, one would expect an initial $t^{-1/4}$ behavior crossing over to the May-Maher fitted form. Indeed, our mean field equations show that for $(T_f-T_c)/T_c \sim 10^{-3}$, there is a long stretch of initial behavior of the $t^{-1/4}$ type, possibly accounting for the ultralow diffusion coefficient.

In summary, using a variety of complementary techniques, both numerical and analytical, we have studied the temporal behavior of the effective surface tension in a variety of situations. The predictions made here should be amenable to experimental verification.

We are indebted to Jim Maher for stimulating discussions. This work was supported by the NSF, NASA, INFN, NATO, the Pittsburgh Supercomputer Center, and the Center for Academic Computing at Penn State.

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