Fluctuating Fluid Interfaces

Eirik G. Flekkøy and Daniel H. Rothman

1 Department of Earth, Atmospheric, and Planetary Sciences
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

2 Current address: PMMH, Ecole Supérieure de Physique et Chimie Industrielle,
10 rue Vauquelin, 75005 Paris, France.

(February 13, 1995)

Abstract

The equilibrium and non-equilibrium motion of an interface between two immiscible fluids and its coupling to spontaneous thermal fluctuations in the bulk is studied theoretically and by computer simulation. Simulations are performed with a two-dimensional momentum-conserving lattice-gas model. Results show that an initially flat interface roughens in a manner that satisfies the dynamical scaling law $W(L, t) = L^{1/2} f(t/L^{3/2})$, where $W(L, t)$ is the root-mean-square width of an interface with an initial length $L$. The equilibrium state of the system is characterized by the autocorrelation of the interface height, which is derived theoretically from a fluctuation-dissipation theorem. Both the equilibrium behavior and the roughening of the simulated interface is found to be in good agreement with theory over a remarkably large range of length and time scales.

Pacs numbers: 05.40.+j, 47.11.+j, 68.10.-m

Typeset using REVTeX
Interfaces between immiscible fluids fluctuate due to the molecular motion in the fluids [1,2]. Moreover, if an interface is initially flat, it roughens until it reaches equilibrium. This roughening is a non-equilibrium process (although not far from equilibrium) that is analogous to the relaxation from the ballistic to the diffusive phase of a Brownian particle. However, whereas the root-mean-square displacement of a Brownian particle increases linearly with time $t$ in the ballistic phase, the root-mean-square width $W$ of the interface has, in general, a nonlinear time dependence. Here we study both the dynamical roughening and the equilibrium state of hydrodynamic interfaces.

Recently, numerous models for the non-equilibrium growth of interfaces have been proposed and studied [3–5]. These models range from discrete-particle models for deposition on a substrate to continuum models given in terms of partial-differential equations, such as the Edwards-Wilkinson [6] and Kardar-Parisi-Zhang (KPZ) [7] equations. Such studies have typically been concerned with purely local growth, with the only relevant field being the interface itself. In contrast, here we study explicitly the coupling between interface growth and a fluctuating hydrodynamic field. Thus the underlying dynamics that governs growth in our case is qualitatively different from the aggregation processes usually studied in the kinetic roughening of growing interfaces [3–5]. Surprisingly, however—and presumably by coincidence—the values of the scaling exponents that describe roughening of interfaces in two-dimensional fluids match those which may be derived from the KPZ equation. In both cases, the correlation length along the interface grows in the same way by a kind of "super-diffusive" roughening. In the KPZ case, such a result relies crucially on the nonlinearity of the differential equation. The theory for our hydrodynamic problem, however, is completely linear.

Our study is composed of empirical results from computer simulations, a simple phenomenological theory based on equipartition of surface energy and capillary waves, and a fluctuation-dissipation theorem from which the phenomenological theory may be derived as a special case. Whereas our theoretical methods are essentially classical, our numerical method is not. To simulate fluctuating fluid interfaces, we use the immiscible lattice gas
[8,9], a variant of the hydrodynamic (momentum-conserving) lattice gases introduced by Frisch, Hasslacher, and Pomeau [10,11]. Lattice gases model fluids as a collection of identical, discrete particles that hop from site to site on a hexagonal lattice and obey simple collision rules that conserve mass and momentum. Immiscible lattice gases simulate fluid mixtures by allowing for two species of particles that interact in a way that creates surface tension at interfaces. Importantly, the discrete nature of lattice gases provides a natural noise source for microscopic fluctuations, which in turn give rise to fluctuating hydrodynamics at a coarse-grained scale. The precise relation of the macroscopic behavior of lattice gases to real hydrodynamics has been an active area of research [11–16]; the overall conclusion is that the behavior of the simplest lattice gases is very close to the Navier-Stokes equations of incompressible hydrodynamics. However, lattice-gas models of interfaces are less well understood [9], due in part to complications arising from the lack of energy conservation and the lack of detailed balance (i.e., the microdynamics is irreversible). Because our study is the first detailed investigation of moving interfaces in immiscible lattice gases, it also serves to quantify the degree to which these simplified models of immiscible fluids mimic real interface dynamics. Given that our theory is classical while our numerical method is not, the good agreement that we find between simulations and classical fluctuating hydrodynamics is remarkable.

We consider an interface contained in a \(d\)-dimensional space of linear size \(L\). The width \(W\) is defined by \(W^2(t) = \langle \int dS \, h^2(x, t) \rangle / A = \sum_k |h_k(t)|^2\), where \(A\) is the initial area of the interface, \(h_k(t)\) is the Fourier transform of the height \(h(x, t)\) shown in Fig. 1, and Parseval’s relation has been used to write the spatial integral in terms of a sum over the wavevectors \(k\). From the simple physical prescription that a flat interface will roughen by the motion of pre-excited capillary waves, with amplitudes distributed according to the equipartition theorem, we write

\[
\langle |h_k(t)|^2 \rangle = \frac{2k_BT}{\sigma k^2 A} \sin^2(\omega_0 t)
\]  

(1)

where \(\sigma\) is the surface tension and \(k_BT\) is the product of Boltzmann’s constant and the
temperature. The factor \(2 \sin^2(\omega_0 t)\) describes standing capillary waves with frequencies \(\omega_0 = k^{3/2} \sqrt{\sigma/2\rho}\) given by the capillary-wave dispersion relation for inviscid fluids [17]; here each wave is initiated with the same (vanishing) phase and \(\rho\) is the mass density of the fluids. By taking the time-average of Eq. (1), we obtain

\[
\langle |k_k|^2 \rangle = \frac{k_B T}{\sigma k^2 A},
\]

which expresses the equipartition of surface energy [18]. Eq. (2) and the capillary-wave dispersion relation represent the statistical mechanical and hydrodynamic components of the theory, respectively. The former relies on the assumption that the time needed to reach local equilibrium is relatively small. The latter derives from Laplace's equation, which expresses the conservation of mass in a potential flow (i.e., a low viscosity flow). Below, after some further discussion, we introduce a fluctuation-dissipation theorem from which this phenomenological description can be derived.

From Eq. (2), we write

\[
W^2 = L^{(3-d)} \frac{k_B T}{\sigma} \sum_{n_i < L/a} (2\pi n)^{-2},
\]

where the sum is over the \((d - 1)\)-dimensional \(k\)-space and the substitution \(k_i = 2\pi n_i / L\), where \(n_i = \pm 1, \pm 2, \ldots\) and \(i\) is a Cartesian index, has been used. The length \(a\), which is the smallest wavelength available to the system, gives the cut-off \(n_{\text{max}} = L/a\) for the components of \(n\). The length \(a\) can be taken as the scale at which the hydrodynamic description breaks down. However, it cannot be given a meaningful, exact value, and it is therefore important to verify, where possible, that the end results are \(a\)-independent.

When \(d = 2\) the \(a \rightarrow 0\) limit of the sum exists, and for finite values of \(a\) the relative correction to the asymptotic result is \(O(a/L)\). When \(d = 3\) the sum will increase logarithmically with \(L/a\), and when \(d > 3\), the high wavenumbers dominate completely and the \(L\)-dependence goes away. Using the exact relation \(\sum_{n=1}^{\infty} 1/(2\pi n)^2 = 1/24\), the steady-state result for \(W\) takes the form

\[
W^2 = \frac{k_B T}{\sigma} \begin{cases} 
\frac{1}{12} L, & d = 2 \\
\log \left( \frac{L}{a} \right), & d = 3 \\
a^{(3-d)}, & d > 3
\end{cases}
\]
where the exact numerical prefactors are included only in the $d = 2$ results. The time dependence of $W(t)$ is obtained from Eq. (1), which gives

$$W^2(t) = \frac{2k_BT(2\rho)^{d/3-1}}{3\pi \sigma^{d/3}} t^{2(3-d)/3} \int_0^{\omega_a t} dx \frac{\sin^2 x}{x^{(3-2d)/3}},$$

(4)

where $\omega_a$ is the frequency of the capillary wave with wavelength $a$, the sum over $k$ has been replaced by an integral, and the substitution $x = \omega_k t$ has been used. When $d = 2$ and the dependence on the upper integration limit becomes negligible, the above time dependence is a power law and the simple scaling form $W(t) = L^{1/2} f(t/L^{3/2})$, also derived for KPZ interfaces for $d = 2$ [7], follows. On the other hand, when $d > 2$, $W(t)$ also depends on the time scale $1/\omega_a$, and is more complex. The relevant integral for $d = 2$, $I = \int_0^{\omega_a t} dx \frac{\sin^2 x}{x^{5/3}} = 1.58...$ was evaluated numerically. From Eq. (4) we get

$$W^2(t) = \begin{cases} \frac{2k_BT}{3\pi} \left(\frac{1}{2\rho^2}\right)^{1/3} I t^{2/3} & \text{when } d = 2 \\ \frac{k_BT}{\sigma} \log (\omega_a t) & \text{when } d = 3 \end{cases}$$

(5)

where $t > \omega_a^{-1}$ is assumed and we have used the average value of $\sin^2 x$ in the $d = 3$ case.

The dimensionless part of the prefactor is correct only for $d = 2$. When $d > 3$ there is no systematic time dependence for $t > \omega_a^{-1}$.

An estimate of the crossover time $t_c$ to the equilibrium state can be obtained by assuming that $W(t)$ grows until the longest capillary wave has reached its maximum amplitude. This give $t_c = T/4$, where the period $T = 2\pi/\omega_0$ is estimated by the inviscid disperson relation, using $k = 2\pi/L$, resulting in the explicit estimate $t_c = \sqrt{L^3 \rho/(16\pi \sigma)}$.

Fig. 2 compares our theoretical predictions for $d = 2$ to results from simulations using the two-dimensional immiscible lattice gas (ILG) [8]; the density was $\rho = 4.9$ particles per site and the surface tension, obtained theoretically by a Boltzmann approximation, was $\sigma = 0.403$ [19]. The simulations were performed on an $N \times N$ lattice with the interface oriented in a direction perpendicular to a lattice direction. Six values of $N$, ranging from $N = 16$ to $N = 192$, were chosen and the heights of the interface were measured by the method described in Ref. [19]. Fig. 2 is a log-log plot of the rescaled width $W(t)/L^{1/2}$ as a function of rescaled time $t/L^{3/2}$ obtained from averages over ensembles containing at
least 500 independent simulations. There is excellent scaling behavior over the first two orders of magnitude in time, showing adherence to the prediction $W(t) \sim t^{1/3}$ given by Eq. (5); moreover the predicted crossover time $t_c$ to asymptotic roughening is remarkably consistent with simulations. The asymptotic roughness predicted by Eq. (4) also shows good accord with the simulations. Because the ILG satisfies neither detailed balance nor energy conservation, we were required to introduce an effective temperature $k_B T_{eff} = 0.126$ to construct the theoretical curves; this particular value was chosen to minimize the difference between theory and simulation for the asymptotic roughness for the cases $N \leq 64$. For $N \geq 92$, there is an unexplained departure from the prediction $W \sim L^{1/2}$; instead, these largest interfaces give $W \sim \sqrt{L/\log(L)}$. This correction to scaling might be due to the logarithmic divergence of transport coefficients in two-dimensional hydrodynamics [13].

The physical description of the interface dynamics in a viscous fluctuating fluid is non-Markovian on two levels. First, the equation of motion of an interface that is subjected to external forcing depends on the entire history of the forcing [20]. Second, in the absence of external forcing, the force due to the fluctuations in the fluid is itself correlated. The two levels are linked by a fluctuation-dissipation theorem. In other words, fluctuations, when averaged to a correlation function, decay as a macroscopic perturbation; i.e., they decay according to the (linearized) hydrodynamic response of the system [21]. Mathematically, the above statement can be written $(\hat{h}_k(t)\hat{h}_k(0))/(\hat{h}_k(0)^2) = \hat{h}_k(|t|)/\hat{h}_k(0)$, where the velocities $\hat{h}_k(t)$ on the left-hand side are due only to thermal fluctuations in the fluid, while, on the right-hand side, the $\hat{h}_k(t)$ are taken as non-fluctuating quantities. Hence, obtaining the corresponding time dependence of the correlation function is a pure hydrodynamic problem. The results are based on the following relations [20]. The linear response of the system is given by $\hat{h}_k(\omega) = \Gamma_k(\omega) \tilde{F}_k(\omega)$, where $\tilde{F}_k(\omega)$ is (the Fourier transform of) an arbitrary force per unit length on the interface and the response function $\Gamma_k(\omega) = (\gamma_k(\omega) + i\sigma k^2/\omega)^{-1}$ depends on the functions $\gamma_k(\omega) = 2\omega pq/(k(iq + k))$, where $q = k\sqrt{i \omega/(k^2 \nu)} - 1$ and the square root is defined by a branch cut along the negative imaginary axis.

The above equations give the time dependence, but not the prefactor, of the velocity
autocorrelation function. The prefactor can, however, be obtained by invoking the principle of equipartition of (surface) energy over the different Fourier modes [18]. The result is

$$|\hat{h}_k(\omega)|^2 = \frac{\Theta}{(2\pi)^2} \frac{k_BT}{\omega^2} 2 \text{Re} \{\Gamma_k(\omega)\},$$

where $\text{Re}$ denotes "the real part" and $\Theta$ is the length of the time integration domain.

The autocorrelation function of the height velocity, $(h_k(t)h_k(0))$, may be obtained from this power spectrum and can be shown to be exponentially damped in the long time limit. More precisely, in the low-viscosity limit (when $k^2 \nu \ll \omega_0$), we have $(h_k(t)h_k(0)) \sim \exp(-k^2 \nu t)/(k^2 \nu t)^{3/2}$ to leading order in $k^2 \nu$ [20]. Hence, correlations of fluctuating fluid interfaces decay exponentially, rather than algebraic, as in the case of Brownian motion [15,22,23].

In Fig. 3, the equilibrium power spectrum $|\hat{h}_k(\omega)|^2$, computed from simulated interfaces that evolved over $2^{20}$ time steps, is shown on a log-log plot along with the theoretical prediction (6) for different wavenumbers $k$. For the simulations, $\sigma$, $\rho$, and $k_BT_{\text{eff}}$ are each the same as in Fig. 2; here we also used the viscosity $\nu = 0.2357$ obtained from a Boltzmann approximation [9]. The three significant features predicted by theory, the peak at $\omega_0$ corresponding to a capillary wave of wavenumber $k$, the plateau to the left of this peak showing significant low-frequency behavior, and the $1/\omega^{7/2}$ decay at high frequencies, are all captured by the simulations. As in the case of the long time tails in the velocity autocorrelation function observed in molecular dynamics simulations [23], the hydrodynamic description is valid down to remarkably small scales. Here, the shortest wavelength is roughly 8 lattice units. It is likely that the departure from the theoretical predictions, which is observed above the frequency $c_*/N$, where $c_* = \sqrt{3}/7$ is the speed of sound in the lattice gas [11] and $N = 32$ is the size of the box, are due to sound waves and other compressibility effects. The high frequency tail $|h(\omega)|^2 \sim 1/\omega^\alpha$, where $1.0 < \alpha < 1.2$, could possibly be predicted from a Landau-Placzek type theory [24].

In conclusion, we have found dynamical scaling behavior for roughening hydrodynamic interfaces and found that the predictions of theory agree well with results from lattice-gas
simulations. The equilibrium state, as characterized by the frequency power spectrum, was found to be well captured by a theoretical description based on a fluctuation-dissipation theorem and incompressible hydrodynamics. These results have two important ramifications. First, they may be necessary for understanding the physics of droplet breakup [25]. Second, they show a surprising accord between the predictions of classical fluctuating hydrodynamics and the behavior of a non-classical hydrodynamic lattice gas. However, we have been required to define an effective temperature for the lattice gas, and have also observed unexplained logarithmic corrections to scaling large small systems. These last points may be resolvable by a Green-Kubo theory for the lattice gas [26].

We thank Dik Harris and K. J. Måløy for helpful comments. This work was supported in part by NSF Grant 9218819-EAR and by the sponsors of the MIT Porous Flow Project. E. G. Flekkøy acknowledges support by NFR the Norwegian Research Council for Science and the Humanities, Grant 100339/431.
REFERENCES


FIGURES

FIG. 1. The height of the interface as a function of $x$ and $t$. $L$ is the system length. In three dimensions the $y$ axis points into the paper plane and the surface $A = L^2$.

FIG. 2. The interface width $W$ as a function of time $t$. Here $Y = W/L^{1/2}$ and $X = t/L^{3/2}$. The straight, full lines show the theoretical predictions given in Eqs. (3) and (4), using the same effective temperature in both equations. The dashed line shows the estimated crossover time $t_c$. The system sizes are $L = 16(\circ), 32(\circ), 64(\circ), 96(\circ), 128(\triangle), 196(\circ)$.

FIG. 3. The power spectrum $|\hbar_k(\omega)|^2/\theta$ for the wavenumbers $k = 2\pi/L$, $k = 2(2\pi/L)$, and $k = 3(2\pi/L)$. The solid lines show the theory, Eq. (6), and the dots, triangles and squares show the results of simulations for large to small wavelengths respectively.
E.G. Flekkoy and D.H. Rothman
Fig. 2