Reentrant Wetting of Network Fluids

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We use a simple mesoscopic Landau-Safran theory of network fluids to show that a reentrant phase diagram, in the "empty liquid" regime, leads to nonmonotonic surface tension and reentrant wetting, as previously reported for binary mixtures. One of the wetting transitions is of the usual kind, but the low temperature transition may allow the display of the full range of fluctuation regimes predicted by renormalization group theory.

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A prominent feature of structured fluids [1] is the presence of self-assembled structures and complex behavior, with large macroscopic responses to weak external fields or changes in the particle interactions. The fluid structure, ranging from the molecular (angstroms) to the mesoscopic (microns) scale, can be tuned through the effects, for example, of external surfaces or through the intermolecular interactions [2,3]. Simple examples include the formation of spherical micelles, hexagonally packed cylinders, and lamellae in systems of liquid crystals, surfactants, and block copolymers [4].

An important subset of structured fluids are *network fluids*, where the self-assembly is anisotropic, leading to the formation of branched chain structures that can be tuned by changing the temperature and/or the ratio of the bonding interactions. Equilibrium polymers are the paradigmatic example of such a fluid [1]. One of the interesting features of network fluids is that under very general conditions, the liquid-vapor binodal is *reentrant* with the liquid (a network fluid with a large number of branches) and the vapor (a fluid of linear chains with little or no branching) densities vanishing at low temperatures [5,6].

In this Letter we consider the adsorption and wetting properties of network fluids. We show that the reentrant phase diagram leads to peculiar interfacial phenomena, such as nonmonotonic interfacial tension and reentrant wetting transitions, where a surface is wet by the liquid phase at high temperature (as in normal molecular liquids) and also at low temperatures. A particularly intriguing consequence of our results is the possibility of network fluids to display the full range of fluctuation-dominated behavior at the low-temperature wetting transition, long predicted by theory, but unobserved so far.

Our starting point is a simple Landau-like phenomenological theory proposed a decade ago by Tlusty and Safran [6], with the Landau-Safran free-energy density

$$f = -(2\phi)^{1/2}e^{-\varepsilon_1/T} - \frac{1}{3}(2\phi)^{3/2}e^{-\varepsilon_2/T} + \frac{1}{2}\phi^2, \tag{1}$$

where ϕ is the volume fraction and ε_1 and ε_2 are two energy scales related to the free-energy of chaining and branching, which are described by the first and second term, respectively. The last term accounts for repulsion between the constituents of the fluid. This free-energy density describes qualitatively the universal features (including the phase diagram reentrance, see Fig. 1) of a broad range of network fluids, from microemulsions to dipolar fluids and patchy colloids. The common feature of this class of fluids is that, in a region of the phase diagram, the thermodynamic behavior is dominated by equilibrium chaining and branching of the components. To see how these lead to the free-energy density [Eq. (1)] we follow the scaling argument of Tlusty and Safran [6]. Let $\Psi(\boldsymbol{r})$ be the probability that a chain starts or ends at the point $\boldsymbol{r}$. The probability that a chain goes through a point $\boldsymbol{r}$ is $\sim\Psi(\boldsymbol{r})^2$, as we might think of a point in a chain as the end and the beginning of two chains. Within mean field it follows that $\phi \sim \Psi^2$. The concentration of ends is thus $\rho_1 \sim \Psi e^{-\varepsilon_1/T} \sim \phi^{1/2}e^{-\varepsilon_1/T}$ and the concentration of chain branching points is $\rho_2 \sim \Psi^3 e^{-\varepsilon_2/T} \sim \phi^{3/2}e^{-\varepsilon_2/T}$ [6]. The

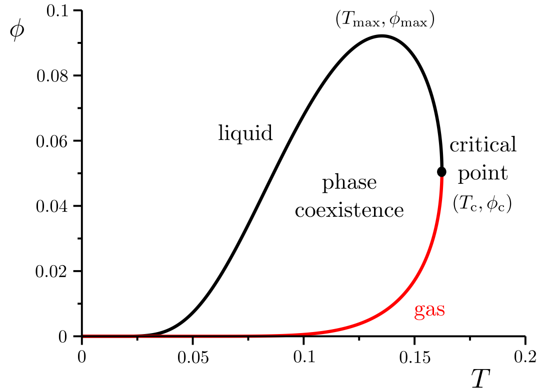

FIG. 1 (color online). Phase diagram of the Landau-Safran theory, with a reentrant phase diagram and a low density liquid at low temperatures. $\varepsilon_1 = 0.67$ and $\varepsilon_2 = 0.12$ [6]. The critical point is at ($T_c = 0.162$, $\phi_c = 0.0507$) and the maximum liquid density is at ($T_{\max} = 0.135$, $\phi_{\max} = 0.0921$).

temperature is measured in units of $2k_B/\varepsilon_1$, where k_B is the Boltzmann constant.

The Landau-Safran free-energy density is the network fluid equivalent of the standard "ϕ^4" Landau theory of critical fluids [7]. As in other Landau-type theories, this phenomenological approach gains in generality what it loses in specific details: the price to pay for such a general description is that the coefficients in Eq. (1) are best seen as parameters to be determined by a more detailed, specific, theory. In this Letter we use the values of $\varepsilon_1 = 0.67$ and $\varepsilon_2 = 0.12$ calculated for dipolar fluids [6]. In fact, the specific values are not important, as long as they correspond to a reentrant bulk phase diagram. Other values appropriate to other types of fluids can be calculated from microscopic theories. For example, it was shown recently that the Landau-Safran theory is obtained in the strong bonding regime of a general microscopic theory for network fluids with two types of bonding sites [8]. Another weakness of this type of coarse-grained descriptions is the inability to capture the finer details of the local structure and correlations of the liquid. However, none of this affects qualitatively our results, as the global wetting properties are known to be robust with respect to such details [9].

The knowledge of the bulk free energy density [Eq. (1)] is not sufficient to calculate the interfacial properties. The essential ingredient missing is a term that accounts for the free-energy cost of spatial changes in the density. In the spirit of van der Waals and Landau we simply augment the free-energy density by a square gradient term $\gamma(\nabla\phi)^2$. This can be considered the first term in an expansion on the gradient of the volume fraction. The constant γ can be calculated from more microscopic theories (such as density functional theory [10,11]) but it is best seen as a phenomenological parameter to be determined later, as in other Landau theories.

The next step to calculate the interfacial properties is to obtain the excess pressure (or excess free energy) $\Omega(\phi, T) = f(\phi, T) - \mu\phi + P$, where the chemical potential μ and the pressure P are evaluated at coexistence. We denote this quantity by $\Omega(\phi, T)$ as this is also the grand potential at coexistence for a given volume fraction. Ω plays the role of the usual "ϕ^4" potential in the Landau theory of critical phenomena [7].

Following Rowlinson and Widom [12], the liquid-vapor surface tension is given by

$$\sigma(T) = \int_{\phi_g}^{\phi_l} d\phi \sqrt{2\gamma\Omega(\phi, T)}, \tag{2}$$

where ϕ_g is the volume fraction of the gas and ϕ_l is the volume fraction of the liquid. We plot the surface tension for $\gamma = 1$ in Fig. 2. Clearly, the reentrance in the phase diagram leads to a nonmonotonic surface tension, with the surface tension vanishing both at the critical point and at zero temperature. Normally the surface tension is a decreasing function of the temperature. Note that the choice of $\gamma = 1$ is rather arbitrary. This constant can either be calculated from a microscopic theory or determined from the measured value of the surface tension of the network fluid, since it merely introduces a factor of $\sqrt{\gamma}$ in the calculated surface tension.

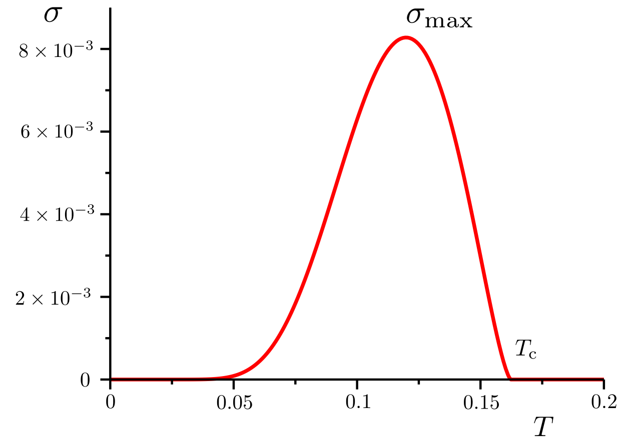

FIG. 2 (color online). Liquid-vapor surface tension σ as a function of the temperature T for $\varepsilon_1 = 0.67$, $\varepsilon_2 = 0.12$, and $\gamma = 1$. The reentrance of the phase diagram is responsible for a nonmonotonic surface tension, which vanishes at the critical point $T_c = 0.162$, as usual, and in the limit $T \rightarrow 0$, a feature of the network fluid. The maximum value of the surface tension $\sigma_{\max}$ occurs at $T'_{\max} = 0.112$ which differs from the temperature $T_{\max} = 0.135$ where the liquid reaches the maximum density.

To study the wetting behavior of a network fluid we put this fluid in contact with a surface. There are several ways of modeling a surface but the simplest is to impose a fixed volume fraction ϕ_s at the surface, which we place at $z = 0$. Under these conditions the contact angle is

$$\cos\theta = 1 - \frac{2\sigma_{\mathrm{sl}}(T, \phi_s)}{\sigma(T)}, \tag{3}$$

where the surface-liquid tension is given by

$$\sigma_{\mathrm{sl}}(T, \phi_s) = \int_{\phi_s}^{\phi_l} d\phi \sqrt{2\gamma\Omega(\phi, T)}. \tag{4}$$

It follows, from inspection, that if $\phi_s = \phi_l$ then $\theta = 0$; i.e., there is a wetting transition at the temperature T_w where the liquid volume fraction equals the volume fraction at the surface $\phi_s = \phi_l$. This condition can be fulfilled either by changing the volume fraction at the surface or by changing the temperature, and thus the volume fraction of the liquid. For a surface that imposes a fixed volume fraction the wetting transition is always continuous (critical); a first-order wetting transition can be obtained with a more general type of surface [13–16].

If we fix ϕ_s then the contact angle as a function of the temperature displays two types of generic behavior. At $T = 0$ the surface is always wet due to the extremely low volume fractions of the coexisting liquid. At higher temperatures the behavior depends on the volume fraction

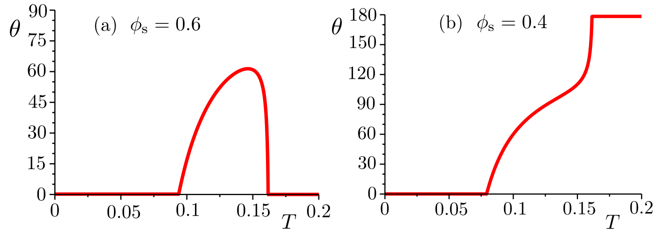

FIG. 3 (color online). Contact angle θ with temperature T for $\varepsilon_1 = 0.67$, $\varepsilon_2 = 0.12$, $\gamma = 1$. There are two types of generic behavior, depending on the ratio ϕ_c/ϕ_s. (a) $\phi_c < \phi_s = 0.6$. The contact angle goes to zero at the upper $T_{w^+} = 0.1616$ and lower $T_{w^-} = 0.0938$ wetting transitions (vanishing when the surface is wet) and has a finite value for intermediate values of the temperature. (b) $\phi_c > \phi_s = 0.4$. The contact angle spans the entire range of values, going to zero at the wetting transition for low temperatures $T_{w^-} = 0.0792$ and to 180° at the drying transition (or wetting by the gas) $T_{w^+} = 0.1614$ close to the critical point.

at the critical point ϕ_c. If $\phi_s > \phi_c$ then the surface is again wet as we approach the critical temperature ($T \longrightarrow T_c$). This wet–nonwet–wet sequence is known as *reentrant wetting* [17,18]. If, on the other hand, $\phi_s < \phi_c$ the surface is completely dry (wet by the gas phase) as $T \longrightarrow T_c$. In Fig. 3 we plot the contact angle for these two cases, which have analogues in binary mixtures [17,18].

Within our mean field framework we can also calculate the density profiles (or rather, the volume fraction profiles) by minimization of the grand potential. The profile is the solution of the differential equation

$$\frac{\partial \phi}{\partial z} = -\sqrt{2\gamma\Omega} \tag{5}$$

with boundary condition $\phi(0) = \phi_s$ at the surface. We obtain the profiles from the numerical solution of this equation and from these we can calculate the excess adsorption

$$\Gamma = \int_0^\infty dz(\phi(z) - \phi_g). \tag{6}$$

In Fig. 4 we plot the excess adsorption, and some representative profiles. We observe the expected (continuous) divergence of the adsorption at the two critical wetting transitions, separated by a region of finite adsorption, where the surface is not wet and the contact angle has a finite value [13–16]. One may ask what happens when the volume fraction at the surface increases, and approaches the maximum volume fraction of the liquid $\phi_{\max}$, on the edge of the reentrant region. It is easy to see that the two wetting transitions approach each other and "coalesce" when $\phi_s = \phi_{\max}$ and it is natural to inquire whether the description of the wetting transition changes at this point. Within mean field this "coalescence" does not seem to have any special features, as the excess adsorption always has a logarithmic divergence, independent of the thermodynamic path from the nonwet to the wet region. Recalling that the relevant scaling field for the wetting transition is the difference between the volume fractions of the liquid and the volume fraction at the wall $\phi_l - \phi_w$, changing the value of this quantity by controlling the temperature or the wall volume fraction is a matter of convenience, which

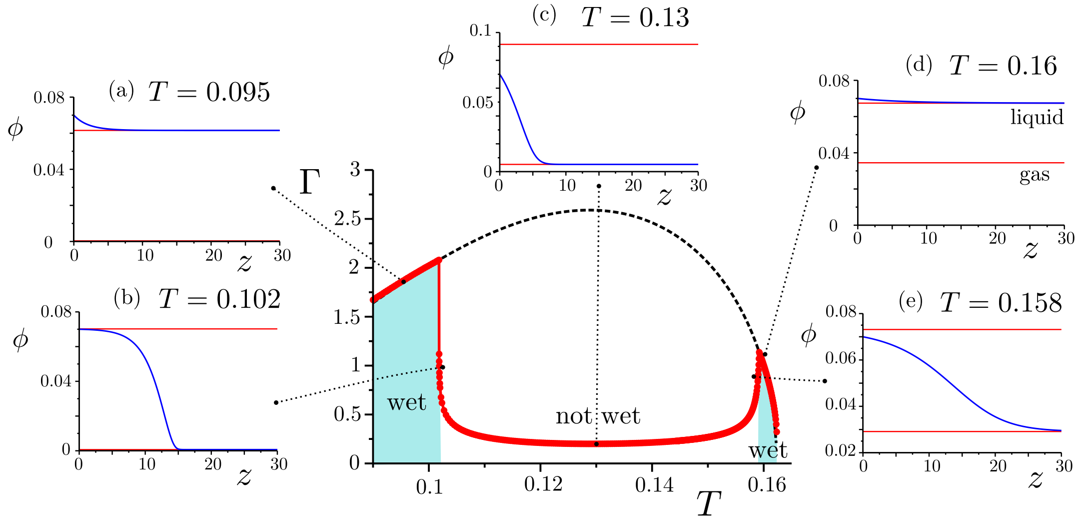

FIG. 4 (color online). Excess adsorption Γ with temperature T for $\varepsilon_1 = 0.67$, $\varepsilon_2 = 0.12$, $\gamma = 1$, and $\phi_s = 0.7$ and representative volume fraction profiles $\phi(z)$ for two wet surfaces (a) $T = 0.095$ and (d) $T = 0.16$, one nonwet surface (c) $T = 0.13$, and two profiles close to the wetting transitions (b) $T = 0.102$ and (e) $T = 0.158$. The wetting transitions are at $T_{w^-} = 0.1018$ and $T_{w^+} = 0.1592$. The adsorption is finite as we consider a finite system ($z = 30$). The dashed black line $[30 \times (\phi_l - \phi_g)]$ is an approximation of the adsorption of a wet surface. Upon changing the volume fraction at the surface ϕ_s towards the maximum value of the volume fraction of the liquid ($\phi_{\max} \approx 0.921$, at the onset of the reentrance) the two wetting transitions "collide."

does not affect the interfacial singular behavior, at least at mean field level.

An intriguing issue raised by the reentrant wetting phenomena we just described is the possibility of observing the full range of fluctuation-dominated critical wetting phenomena. The renormalization group theory for critical wetting transitions predicts that the critical exponents are not universal, but depend on a ''wetting parameter'' $\omega = \frac{k_B T_w \xi^{-2}}{4\pi\sigma}$ [13–16], T_w is the wetting temperature, and ξ is the bulk correlation length of the liquid. For example, for the parallel correlation length of the interfacial fluctuations, $\xi_\| \sim |T - T_w|^{-\nu_\|}$, there are three regimes: $\nu_\| = \frac{1}{1-\omega}$ if $0 \le \omega < 1/2$, $\nu_\| = \frac{1}{(\sqrt{2}-\sqrt{\omega})^2}$ if $1/2 < \omega < 2$, and $\xi_\| \sim e^{1/(T_w - T)}$ if $\omega > 2$.

Since in normal fluids the wetting transition occurs close to a critical point the value of ω is dominated by the universal properties of the critical point and does not deviate much from the ''Ising value'' $\omega \approx 0.8$. The same will happen for reentrant wetting close to a lower critical point. For network fluids the upper wetting transition is Ising-like [19] but the low temperature wetting transition is not driven by a critical point, and thus there is no reason to constrain ω to the Ising-value $\omega \approx 0.8$. In fact, by tuning the surface and bulk properties independently, we can set the value of the surface tension as low as we like, scanning the entire range of values of the wetting parameter, opening the exciting prospect of checking the renormalization group theory predictions experimentally. As an example, for microemulsions, the surface tension [20], measured in units of $k_B T \xi^{-2}$, ranges from ≈ 100 to ≈ 0.3 and thus ω varies from 0–0.25. This means that the wetting transition for microemulsions will display behavior close to mean-field ($\omega = 0$) but $\mu_\|$ varies from the mean-field value $\mu_\| = 1$ to $\mu_\| \approx 1.33$. One final caveat: as intriguing as the above prospect might seem we must keep in mind that the critical wetting transition is the exception rather than the rule. In particular the Ising-like behavior predicted by theory has never been observed [13], and the theoretical description of the critical wetting transition is rather subtle, involving nonlocal effects [21,22].

To conclude, we used a simple Landau-like theory to study the wetting behavior of network fluids, and found a range of unusual properties: nonmonotonic surface tension, two wetting transitions, or a wetting transition followed by a drying transition. Particularly intriguing is the possibility of exploring the range of fluctuation-dominated critical behavior, predicted by theory but never observed. All of these are driven by the reentrant bulk phase diagram. In particular, the ''extra'' wetting transition at low temperatures is a direct consequence of the very low densities of the liquid phase as $T \rightarrow 0$, the ''empty liquid'' regime, driven by the branching of the chains.

A coarse-grained model is very valuable to guide the exploration of the interfacial phenomena of network fluids. In particular, patchy colloids have been a hot topic recently for their potential technological applications and interesting properties [23]. An appropriate microscopic theory will always be much more complicated than the Landau-Safran theory used here. Thus our results can provide useful guidance when dealing with surface and interfacial phenomena of patchy colloids. It is well known that the global interfacial properties derived from such simplified theories are useful and robust [9].

Wetting and interfacial phenomena can be used to control material properties. As an example, wetting has a profound effect on free-energy barriers between phases and thus allows control of the kinematics of transitions, such as condensation, gelation, or solidification. For example, the reentrant melting of DNA-coated colloids was shown to be effective in decreasing the kinetic barriers for crystallization over a wide range of temperatures [24].

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