

Supplementary Information: Experimental observations of dynamic critical phenomena in a lipid membrane

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A. Introduction

This supplemental section contains details regarding analysis, calculation, and theory not found in the main text. Two movies are also included as supplementary material, where Movie 1 is at 30.25°C , and Movie 2 is at 29.75°C , with $T_c \approx 29.5^\circ\text{C}$. Both movies are $35\mu\text{m}$ wide. Section B contains additional information on analysis procedures. Section C explains why Fisher renormalization does not affect the observed static critical exponents in 2D Ising systems, and why the critical region is larger in 2D liquid-liquid membrane systems than it would be in analogous 3D ones. Section D details the Ising model simulations that we used to verify our analysis. Section E reviews previous theoretical results for purely 2D critical hydrodynamics.

B. Details of Analysis

In the definition of $S(\vec{k}, \tau) = \left\langle m(\vec{k}, t) \overline{m(\vec{k}, t + \tau)} \right\rangle$, the value of $S(k, \tau = 0)$ is guaranteed to be real as an expectation value and also from run to run since each term appears with its complex conjugate. For $\tau \neq 0$, the expectation value of the imaginary part of S is guaranteed to be real by time-reversal invariance expected of systems in equilibrium. However, each term contributes an imaginary component. Adding the complex conjugate and dividing by two leads to an effective measurement of $1/2(S(k, \tau) + S(k, -\tau))$, which for an equilibrium system is equal to $S(k, \tau)$. The inclusion of zeros required to pad the raw data in $m(k, t)$ introduces a small error in the calculation of $S(k, \tau)$, which can be corrected for by dividing $S(k, \tau)$ by the correlation function of pure ones and zeros in the real space correlation function. For calculations in k -space, there is no simple correction (the real space correction has an ill-posed Fourier transform and so introduces unacceptable noise in k -space). Nevertheless, any correction is expected to be small (values of $S(k, \tau)$ were similar when calculated with vs without zero padding). More importantly, any correction would cancel out of the main results presented here, where $S(k, \tau)$ is divided by $S(k, \tau = 0)$. For movies at the slowest frame rate, 0.5 fps, noise in $S(k, 0)$ caused an offset from the rest of the structure factor. For calculations made with

those data sets, the measured value of $S(k, 0)$ was replaced by the value extrapolated from an exponential fit to the 2nd through 5th points in $S(k, \tau)$.

C. Experimental advantages of lipid bilayers

This section explains why Fisher renormalization does not affect the observed static critical exponents in 2D Ising systems, and why the critical region is larger in 2D liquid-liquid membrane systems than it would be in analogous 3D ones.

Widom-Fisher rescaling leads to only an immeasurably small correction to 2D critical exponents: Concentration fluctuations consistent with static 2D Ising critical exponents were previously observed in membranes over our entire range of $k\xi$ [1]. As we show below, this observation is not at odds with the fact that our ternary system is subject to rescalings first discovered by Widom [2] and generalized by Fisher [3]. Rescaling corrections apply to any system with a quantity whose chemical potential smoothly affects the critical temperature. When a component is instead held at fixed composition (as our three components are) then the observed critical behavior receives non-analytic corrections, essentially because the chemical potential of the third component has singular behavior near the critical point when held at fixed composition. As a result, the singular form of the coexistence curve near the critical point is changed from its usual exponent β to $\beta' = \beta/(1 - \alpha)$. Here α is the static critical exponent for specific heat. Other critical exponents that relate singular behavior of a quantity to the distance in temperature from the fixed point (for example α , β , ν and γ) receive similar corrections. For example, the specific heat exponent itself becomes $\alpha' = \alpha/(1 - \alpha)$ [3]. The rescaling correction is not confined to ternary systems: binary systems held at fixed density, rather than fixed pressure undergo similar rescalings, as does any system in which a density variable is held fixed in a phase diagram rather than its conjugate field.

Fortunately for the current study, Widom-Fisher rescaling in the 2D Ising model leads to an immeasurably small change in the singular behavior and no change in the critical exponents themselves. As noted above, α is the static critical exponent for specific heat, C , which diverges as $C \sim ((T - T_c)/T_c)^{-\alpha}$. In the 2D Ising model, specific heat diverges as $C \sim \log((T - T_c)/T_c)$, which is slower than any power law divergence, so that α is said to be zero. As explicitly discussed in both [2] and [3], there is potentially a logarithmic correction to the singular be-

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havior of quantities whose critical exponents are usually multiplied by $(1 - \alpha)^{-1}$. For example, the correlation length ξ , which is usually written as $\xi \propto (\frac{T-T_c}{T_c})^{-\nu}$, becomes $\xi \propto (\frac{-\log(T-T_c)(T-T_c)}{T_c})^{-\nu}$ after rescaling. In this case, $\nu' = \nu$, so rescaling does not change the critical exponent. For a system described by the 3D Ising model (rather than the 2D Ising model as in the current study), $\alpha \approx 0.11$ [3, 4], such that the effect of rescaling is small but observable in the critical exponents.

Although the effect of rescaling on the dynamic exponent z is not discussed explicitly in the literature, we expect that z would not be affected by rescaling even for systems in which $\alpha \neq 0$. The dynamic exponent z describes scaling of the time scale as the length scale is changed, with $\tau_s \propto \xi^z$. The product νz describes critical slowing with respect to temperature, where $\tau_s \propto (\frac{T-T_c}{T_c})^{\nu z}$. As such, νz does describe the singular behavior of a quantity (here the time scale) as temperature is changed and it receives a correction of $\frac{1}{1-\alpha}$ through the parameter ν .

The critical region is larger in 2D liquid-liquid membrane systems than in analogous 3D ones. The point here goes beyond considerations that as dimension decreases, the critical region becomes larger due to changes in the Ginzburg temperature, which is the temperature at which a system crosses over from mean-field to critical behavior [4]. Correlation lengths of $\xi \sim 10\mu\text{m}$ are regularly observed in vesicle membranes. These correlation lengths are larger than those typically observed in 3D binary mixtures, even though control over lipid composition in membranes is coarser. This is because: (1) lipids are molecules with length scales of $\xi_0 \sim 1\text{nm}$, whereas the atoms employed in many studies of 3D critical phenomena are an order of magnitude smaller, with $\xi_0 \sim 0.1\text{nm}$, and (2) differences between critical exponents in the Ising classes are favorable to 2D systems. In 2D, $\nu = 1$ and $\beta = 1/8$, whereas in 3D, $\nu \approx 0.630$ and $\beta \approx 0.325$ [5]). The scaling form for correlation length can be written as $\xi = \xi_0 t^{-\nu} \mathcal{U}(|\phi|/\phi_0)^{1/\beta} t^{-1}$, where $t = (T - T_c)/T_c$ is reduced temperature, ξ_0 is a molecular scale, and ‘magnetization’ ϕ is a function of composition normalized by ϕ_0 , which is roughly the difference in composition between the two low temperature phases far from the critical point. $\mathcal{U}(x)$ is a universal function of its dimensionless argument x . $\mathcal{U}(x)$ has a maximal value at $x = 0$ and decreases to 0 as its argument increases. Tuning a system’s correlation length to ξ , requires tuning temperature to within approximately $\Delta T \sim T_c(\xi/\xi_0)^{-1/\nu}$. Consider a membrane with values observed here: $\xi \sim 10\mu\text{m}$, $\xi_0 \sim 1\text{nm}$, and $T_c \sim 300\text{K}$. In 2D, $\Delta T \sim .03\text{K}$, which is experimentally achievable. For 3D systems in which ξ_0 is typically 1Å , a $10\mu\text{m}$ correlation length would require tuning temperature to a much higher precision of $\Delta T \sim 10^{-4}\text{K}$. Similarly, extreme accuracy in composition is not required in 2D to observe fluctuations of $\xi \sim 10\mu\text{m}$. For a membrane to lie in the critical region, composition must be tuned such

that the argument of \mathcal{U} is of order 1. Given the difference between critical exponents in 2D vs 3D, far less precise experimental control of composition can be tolerated in 2D than in 3D.

D. Simulation details

Simulation procedures were standard [6, 7] and briefly explained here. The standard Ising Hamiltonian given by $H = -\sum_{\{i,j\}} s_i s_j$ was used, with spin variables $s_i = \pm 1$ and summation over the four nearest neighbors (j) of every state (i). Temperatures were in terms of the exact critical temperature given by the Onsager solution [8], $T_c = 2/\log(1 + \sqrt{2})$ so that a reduced temperature $t = (T - T_c)/T_c$ corresponds to a simulation temperature of $T_{sim} = 2.269(1 + t)$. In this section, T and ΔH correspond to temperature and to the change in energy between initial and final states, respectively. Both are in dimensionless units. In a Monte-Carlo ‘sweep’, 160,000 (400^2) pairs of spins were proposed to be swapped, such that each spin was proposed twice. Metropolis spin exchanges were used; each pair was exchanged or not to satisfy detailed balance [6, 7]. If the resulting configuration was lower in energy, the exchange was accepted. If energy increased, the exchange was accepted stochastically with probability $\exp(-\Delta H/T)$.

Note that any dynamics that satisfy detailed balance will lead to the same equilibrium ensemble of configurations [7]. To rapidly equilibrate the system, ‘nonlocal’ moves were employed in which each of a pair of spins were chosen from all sites on the lattice. Equilibration is very rapid using these nonlocal dynamics since they approximate ‘Model A’ for large systems where z is near 2 [9]. The system was equilibrated for 100,000 sweeps using nonlocal moves starting from a distribution that contained the desired fraction of up spins but was otherwise random. 100,000 sweeps is much longer than the decay time of the slowest decaying system used here. The decay time is approximately 1000 sweeps at $1.05T_c$, which can be seen qualitatively by inspecting successive snapshots or quantitatively by inspecting the decay of time dependent correlation functions. Once the system was equilibrated, dynamics relevant for the locally conserved order parameter (Kawasaki Dynamics) were employed. In this case, a single spin and one of its four nearest neighbors were chosen to form a pair proposed to be swapped.

E. Predictions for binary liquids in 2D

Model H for binary fluids in 2D predicts $z \approx 2$ using $z = 4 - \eta - x_\lambda$, where $\eta = 2\beta$ is a static critical exponent and x_λ must be calculated from an epsilon expansion (where $\epsilon = 4 - D$, and D is the number of dimensions). This yields $x_\lambda = 18/19(1 - (\text{constant})\epsilon + \mathcal{O}(\epsilon^2))$ where the constant is either 0.033 [10] or 0.039 [11]. Since the constant is small, it is plausible that the expansion applies

even when $\epsilon = 2$, yielding $z = 2.00$ (which also arises from a much simpler mean field argument) or 1.98. Simulations in 2D binary liquids are reportedly challenging

and we know of none that either verify or contradict the prediction that $z = 2$. Measurements in bulk 3D liquids far from T_c find that $z_{\text{eff}} = 2$ (e.g. [12–14]).

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