Ising criticality in fluids: A counterexample

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It is commonly accepted that fluids interacting via short-ranged pair potentials yield liquid-vapor critical behavior that belongs to the universality class of the Ising model. That is, approaching the critical temperature \( T_c \) by varying the temperature \( T \), the correlation length \( \xi \), the order parameter \( \Delta \), and the order parameter fluctuations \( \chi \) reveal power law behavior

\[
\xi \propto |t|^{-\nu}, \quad \Delta \propto t^\beta, \quad \chi \propto |t|^{-\gamma}, \quad (1)
\]

\( t \equiv T_c - T \), with critical exponents \( \nu, \beta, \gamma \) characteristic of the universality class (\( \Delta \) is only defined for \( T < T_c \)). For liquid-vapor-type transitions, the usual situation is that the critical exponents assume Ising values, irrespective of the details of the pair potential. In \( d = 2 \) dimensions, these read as \( \nu = 1, \beta = 1/8, \) and \( \gamma = 7/4 \), where we note that hyperscaling \( \gamma/\nu + 2\beta/\nu = d \) is obeyed.

In this paper, we present a counterexample in \( d = 2 \) dimensions. An off-lattice fluid interacting via pair potentials that are strictly short-ranged, and featuring a liquid-vapor transition, is shown to exhibit critical behavior that is distinctly non-Ising. The pair potential is given by

\[
E = \sum_{i=1}^{N} \sum_{j=i+1}^{N} \epsilon (1 - |\vec{d}_i \cdot \vec{d}_j|^r) H(a - r_{ij}), \quad (2)
\]

with \( N \) the number of particles, \( r_{ij} \) the distance between (point) particles \( i \) and \( j \), interaction range \( a \), \( H(x) \) the Heaviside unit step function, and \( \epsilon \) a coupling constant to set the temperature scale (in what follows, \( \epsilon \) is the unit of length, \( \epsilon/k_B T = 2.5 \), with \( k_B \) the Boltzmann constant).

To each particle \( i \), we also assign a continuous internal degree of freedom \( \vec{d}_i \), the latter being a two-dimensional unit vector. In the case of anisotropic particles, such as liquid crystals, \( \vec{d}_i \) might indicate the particle orientation. Or, in the case of lipids, \( \vec{d}_i \) might encode the conformational state of the corresponding carbon chain. In Eq. (2), a pair of particles \( i \) and \( j \) within a distance \( a \) can lower the energy by aligning their internal vectors, either in parallel or anti-parallel directions. The parameter \( p \), which is a positive real number, sets the sharpness of the latter interaction. As \( p \) gets larger, the potential becomes increasingly selective about the degree of alignment. In the limit \( p \to \infty \), a pair of particles \( i \) and \( j \) would lower the energy only when the alignment of the vectors \( \vec{d}_i \) and \( \vec{d}_j \) is perfect.

We first summarize the main properties of a many-particle system interacting via Eq. (2). Since the summand in Eq. (2) is separable, i.e. the product of a radial and an internal part, it follows that long-range order in the vectors \( \vec{d}_i \) at any finite temperature is absent in the thermodynamic limit. A true nematic phase where all the vectors have macroscopically aligned is therefore forbidden, ruling out an isotropic-nematic transition (although phases where the vectors \( \vec{d}_i \) reveal power law decay of correlations are not excluded). In contrast, a liquid-vapor-type transition, where the principal difference between the phases (order parameter) is the density, is not forbidden. Indeed, provided the sharpness parameter \( p \) is large enough, Eq. (2) exhibits a strong first-order phase transition between a low-density vapor and a high-density liquid. A first-order phase transition in a two-dimensional system with continuous internal degrees of freedom may seem surprising, but has by now been firmly established. As \( p \) is lowered, the first-order transition becomes weaker, ultimately terminating in a critical point, at \( p = p_c \). For the model of Eq. (2), our analysis shows that the universality class of the latter critical point is distinctly non-Ising.

To arrive at this conclusion, we performed grand canonical Monte Carlo simulations of Eq. (2), i.e. at fixed chemical potential \( \mu \), and fluctuating particle number \( N \) (simulation cells are \( L \times L \) squares with periodic boundaries). We used standard single particle insertion and deletion moves, each attempted with equal \( a \) priori probability, and accepted conform the Metropolis criterion. The principal output of the simulations is the distribution \( P(N) \), which is the probability of observing a state containing \( N \) particles. To ensure \( P(N) \) is accurately measured, the simulations used a biased potential, \( V_{\text{sim}} = E + f(N), \) \( E \) given by Eq. (2), and \( f(N) \) a bias function constructed to achieve uniform sampling in \( N \).
An initial estimate of $f(N)$, which is a priori unknown, was obtained using Ref.\textsuperscript{11}, in which Wang-Landau sampling \textsuperscript{12} and transition matrix sampling \textsuperscript{13} are combined; this estimate was used as input for our production runs. The transition matrix elements were computed for zero chemical potential, as described in Ref.\textsuperscript{13}; from the latter, $P(N|\mu=0)$ can be constructed, which is readily extrapolated to a different chemical potential $\mu_1$ using histogram reweighting \textsuperscript{11}.

$$P(N|\mu = \mu_1) \propto P(N|\mu = 0) e^{\mu_1 N/k_BT} \; .$$

(3)

For Eq. (2), the relevant density range $\rho_{\min} = 1.35 \leq \rho = N/L^2 \leq \rho_{\max} = 3.5$ \textsuperscript{2}, to which our simulations were restricted. For large $L$, we “parallelized” by dividing the range into $\sim 10$ intervals, and assigning a single processor to each interval. Since the transition matrix elements are all collected for the same chemical potential ($\mu = 0$), the matrix elements obtained for each interval may simply be added afterward.

The distribution $P(N)$ depends on all the model parameters, in particular the sharpness parameter $p$, the chemical potential $\mu$, and the system size $L$. To accurately determine the universality class requires data for several $L$, such that a finite-size scaling analysis can be performed. In addition, we require data over a fine range in $p$. This poses a challenge because $p$ is not a field variable, i.e. it cannot be expressed as a prefactor of some term in the Hamiltonian (unlike $\epsilon$, which is a prefactor of $E$, or the chemical potential, which induces a term $\mu N$). Rather, by changing $p$, the shape of the potential is altered, and hence the underlying density of states. Consequently, there is no histogram reweighting analogue of Eq. (3) for $p$, and extrapolations in the latter will require a radically different approach.

To this end, we note that $P(N)$ is just the canonical partition sum, $P(N) = \text{Tr}_N(e^{-E})$, $E$ given by Eq. (2), with the trace over the positions and internal degrees of freedom of $N$ particles. Hence, $d\ln P(N)/dp = \langle X_1 \rangle_N$, the latter being the canonical expectation value of

$$X_a \equiv \sum_{|ij|} \epsilon \ y_{ij}^p \ (\ln y_{ij})^p \ , \quad y_{ij} = |\vec{d}_i \cdot \vec{d}_j| \; ,$$

(4)

where the sum is over all pairs for which $r_{ij} < a$. Similarly, $d^2 \ln P(N)/dp^2 = \langle X_2 + X_2^2 \rangle_N - \langle X_1 \rangle_N^2$. The canonical averages $\langle \cdot \rangle_N$ are trivially collected in a grand canonical simulation: At the end of each attempted move, one simply “updates” the average of $X_1$ and $X_2 + X_2^2$ for the current number of particles. This requires very little extra memory (only two additional arrays are needed) and the CPU cost is also negligible, since most quantities needed to compute $X_a$ are already needed for the energy calculation (by using a link-cell list, the computational effort per Monte Carlo move remains independent of $N$). The extrapolation of $P(N|p_1)$ measured at sharpness parameter $p_1$ to a different value $p_2$ then becomes a Taylor expansion

$$\ln P(N|p_2) \approx \ln P(N|p_1) + \langle X_1 \rangle_N \Delta p + \frac{1}{2} \left( \langle X_2 + X_2^2 \rangle_N - \langle X_1 \rangle_N^2 \right) \Delta p^2 \; ,$$

(5)

$\Delta p = p_2 - p_1$, with the canonical averages obtained at $p_1$ (higher order terms can optionally be included, but become increasingly cumbersome to calculate; our second-order scheme works well in practice).

To facilitate finite-size scaling, $L = 10 - 40$ was considered. For each $L$, $S \sim 15$ values $p_k$ were simulated, distributed evenly over the range of interest, then combined: For each $p_k$, $P_k(N|\mu = 0)$ was constructed from the transition matrix elements, then extrapolated to $p = \bar{p}$ of interest using Eq. (5). The latter define the quantities

$$\Delta G_k(N) \equiv \ln \left( P_k(N)/P_k(N-1) \right) ,$$

(6)

where $H_k(N)$ counts how often the $k$-th simulation visited the state with $N$ particles (each simulation is thus weighted by its “distance” from $\bar{p}$, and the number of samples it contains). The distribution $P(N|\mu = 0)$ is obtained via recursion:

$$\ln P(N_{\min}) = 0 , \quad \ln P(N) = \ln P(N-1) + \Delta G(N) \; ,$$

(7)

$N_{\min} = \rho_{\min} L^2$, which can be extrapolated to different chemical potentials using Eq. (3).

To ensure that the system is at the liquid-vapor transition, the chemical potential $\mu(p)$, for some given $p$, is obtained by maximizing the variance $\langle N^2 \rangle - \langle N \rangle^2$ \textsuperscript{14}. Here, $\langle \cdot \rangle$ denotes a grand canonical average, $\langle N^a \rangle = \sum_N N^a P(N)/\sum_N P(N)$, with sum range $N_{\min} \leq N \leq N_{\max}$. For large $p$, where the transition is strongly first-order, $P(N)$ is distinctly bimodal, with the left (right) peak corresponding to the vapor (liquid) phase [Fig. 1(a)]. Upon approach of the critical point, by lowering $p$, the peaks smoothly approach each other; precisely at the critical point, $p = p_c$, they merge. To uncover the precise behavior we present a finite-size scaling analysis. To this end, we introduce the order parameter $\Delta = \langle |M| \rangle / L^2$, $M = N - \langle N \rangle$, which measures the distance between the peaks in $P(N)$, and the susceptibility $\chi = \langle M^2 \rangle - \langle |M| \rangle^2 / L^2$ \textsuperscript{10}. In the thermodynamic limit $L \to \infty$, $\Delta$ vanishes at $p_c$, while $\chi$ diverges. There is, however, one caveat: Since $p$ is not a field variable, one cannot identify $t \leftrightarrow p - p_c$ in Eq. (7). Possibly, $t = g(p - p_c)$, i.e. some function $g$ of $p - p_c$, but the precise form of $g$ is unknown. Consequently, Eq. (7) cannot be used directly to determine the universality class. Fortunately, in the context of finite-size scaling, critical exponent ratios remain well defined, which is how we proceed.

Fig. 1(b) shows $\chi$ versus $p$ for several $L$. In a finite system, the divergence is rounded, and so the curves reach...
The standard approach is to consider the Binder cumulant $U_4 = \langle M^4 \rangle / \langle M^2 \rangle$; owing to hyperscaling, the latter is $L$-independent at $p_c$. In Fig. 2(a), we plot $U_4$ versus $p$ for various $L$. We observe a scatter of intersections, between $18.9 < p < 20.4$, providing a rough estimate of $p_c$ (corrections to scaling appear to be quite strong, and so we restrict the analysis to the largest four system sizes in what follows). Note that $U_4 \sim 0.5$ at the intersections, which is significantly below $U_4 = 0.856$ of the $d = 2$ Ising model \cite{hong}, again emphasizing the non-Ising character. A more precise estimate of $p_c$ is obtained using the complete scaling algorithm of Kim and Fisher \cite{kim} which is also unbiased. For the practical implementation of the latter, our $p$-extrapolation scheme, i.e. Eq. (2), is absolutely crucial, since data over a wide range in $p$ are required (stretching from the critical to the first-order regime). The principal output of the complete scaling algorithm is the $L \to \infty$ value of the order parameter $\Delta$ as a function of $p$ [Fig. 2(b)]. From this, we conclude $p_c = 19.1 \pm 0.1$, i.e. the value where $\Delta$ vanishes. Note that this estimate is consistent with the cumulant intersections. Incidentally, we observe that the order parameter vanishes linearly $\Delta \propto p - p_c$. However, since $p$ is not a field variable, this does not imply that the critical exponent $\beta = 1$. A second output of the complete scaling algorithm is a scaling function $y(x)$, which is characteristic of the universality class [Fig. 2(c)]. In the limit $x \to 0$, $y(x) = 1 + x/2$, while at some $x_c > 0$, $y(x)$ diverges. We obtain $x_c \approx 0.42$, while for the $d = 2$ Ising model a significantly lower value $x_c \approx 0.115$ is observed \cite{hong}, again highlighting the non-Ising character. As a last unbiased method to obtain $p_c$, we consider the barrier $\Delta F$ of $\ln P(N)$, defined in Fig. 1(a) as the average height of the peaks (A and B) minus the height at the minimum (C). The barrier increases (decreases) with $L$ for $p > p_c$ ($p < p_c$), and remains $L$-independent at $p_c$ \cite{hong, stre}. The variation of $\Delta F$ with $p$ for several $L$.

FIG. 1: (a) Example distribution $W \equiv \ln P(p)$ for $p = 75$ and $L = 15$. The extrema $X(p_X, W_X), X \in \{A, B, C\}$, define the order parameter $\chi = p_1 - p_A$, the coexistence diameter $\delta = (p_C + p_A)/2$, and the barrier $\Delta F = (W_A + W_C)/2 - W_B$. (b) Susceptibility $\chi$ versus $p$ for $L = 25, 30, 35, 40$ (top to bottom). The curves reach finite maximum values $\chi_{\text{max}}$ at $p = p_X$. (c) Susceptibility maximum $\chi_{\text{max}}$ versus $L$. (d) Order parameter $\Delta$ at $p = p_X$ versus $L$. The dashed curves in (c,d) are power law fits.

FIG. 2: (a) Binder cumulant $U_4$ versus $p$ for several $L$. The intersections mark $p_c$. (b) Order parameter $\Delta$ versus $p$ obtained following Kim and Fisher \cite{kim}. At $p_c$, the order parameter vanishes. (c) The (inverse) scaling function $y(x)$ of the Kim-Fisher algorithm (solid). Also shown is the $x \to 0$ limiting form (dashed), which our data indeed approach. (d) The barrier $\Delta F$ versus $p$ for several $L$. Consistent with a critical point, the curves for different $L$ intersect.
is shown in Fig. 2(d). Consistent with a critical point, the curves for different $L$ intersect, at values of $p$ consistent with those of the cumulant analysis. Note that the barrier at criticality is extremely small, $\Delta F \sim 0.25$. In contrast, for $d = 2$ Ising universality, $\Delta F \approx 3.1$.

For completeness, we still compute the $L \to \infty$ phase diagram. Kim also provides an (unbiased) scaling algorithm to obtain the $L \to \infty$ coexistence diameter $\delta$ from finite-size simulation data [24]. The latter is defined as the average density of the vapor and liquid phase [Fig. 1(a)]. In Fig. 3(a), we plot $\delta$ versus $p$. Near the critical point, some downward curvature in the data is apparent, but we emphasize again that no conclusions about the critical exponents can be drawn from this. The order parameter and coexistence diameter yield the binodal, i.e. the density of the vapor ($\rho_{\text{vap}} = \delta - \Delta/2$) and liquid ($\rho_{\text{liq}} = \delta + \Delta/2$) as a function of $p$ [Fig. 3(b)]. Note that the vapor and liquid branches form a “kink” at the critical point, since $\Delta$ vanishes linearly with $p - p_c$.

In summary, we have observed non-Ising liquid-vapor critical behavior in a fluid with short-ranged pair potentials, a finding which is not a priori expected [8]. A prerequisite is that the particles pose continuous internal degrees of freedom, in addition to translational ones, with a pair potential that is minimized when the internal degrees of freedom of closely particles are sufficiently well aligned. We expect non-Ising criticality to arise when the internal degrees of freedom develop quasi-long-ranged order, i.e. with correlations that decay as a power law with distance. Such order is to be expected for the particles studied here, since the corresponding internal degrees of freedom are two-dimensional unit vectors (reminiscent of the XY-model). If, instead, three-dimensional unit vectors are used (Heisenberg case), quasi-long-ranged order is not expected, in which case Ising universality would result. A potential experimental realization of Eq. 2 may be a lipid bilayer near its main transition. In agreement with Eq. 2, the lipid translational degrees of freedom are $d = 2$ dimensional, while the lipid chain conformations represent the continuous internal degrees of freedom.

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