

Coexistence diameter in two-dimensional colloid-polymer mixtures

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(Received 12 May 2006; published 13 July 2006)

We demonstrate that the law of the rectilinear coexistence diameter in two-dimensional mixtures of non-spherical colloids and nonadsorbing polymers is violated. Upon approach to the critical point, the diameter shows logarithmic singular behavior governed by a term $t \ln t$, with t the relative distance from the critical point. No sign of a term $t^{2\beta}$ could be detected, with β the critical exponent of the order parameter, indicating a very weak or absent Yang-Yang anomaly. Our analysis thus reveals that nonspherical particle shape alone is not sufficient for the formation of a pronounced Yang-Yang anomaly in the critical behavior of fluids.

DOI: [10.1103/PhysRevE.74.010102](https://doi.org/10.1103/PhysRevE.74.010102)

PACS number(s): 05.70.Jk, 64.60.Fr, 64.70.Fx

Critical phenomena have been studied extensively for decades. Nevertheless, a few important issues remain controversial. One long-standing problem concerns the critical behavior of the so-called coexistence diameter of fluids undergoing a phase transition from liquid to gas (the coexistence diameter is defined as the average density of the two coexisting phases). In 1964, Yang and Yang showed that the divergence of the constant-volume specific heat at the critical point implies that either d^2p/dT^2 or $d^2\mu/dT^2$ or both diverge [1]. Here, T is the temperature, p the pressure, and μ the chemical potential. A remarkable consequence, realized only recently by Fisher and co-workers [2], is that the divergence of $d^2\mu/dT^2$ implies that the coexistence diameter δ gains an additional term $t^{2\beta}$ which, assuming Ising universality, dominates the previously recognized term $t^{1-\alpha}$ [3,4]. As usual, t is the relative distance from the critical point; α and β are the critical exponents of the specific heat and the order parameter, respectively. The coexistence diameter near the critical point thus reads as

$$\delta_{\alpha \neq 0} = \rho_{\text{cr}}(1 + A_{2\beta}t^{2\beta} + A_{1-\alpha}t^{1-\alpha} + A_1t), \quad (1)$$

with ρ_{cr} the critical concentration, and nonuniversal amplitudes A_i . The divergence of $d^2\mu/dT^2$ is called a Yang-Yang (YY) anomaly, and $A_{2\beta} \neq 0$ if one is present. For symmetric fluids, such as the Widom-Rowlinson mixture [3], $d^2\mu/dT^2$ remains finite, in which case $A_{2\beta} = 0$ [5]. However, realistic fluids are typically asymmetric, in which case a YY anomaly cannot be ruled out.

Indeed, evidence for a YY anomaly was found in simulations of asymmetric three-dimensional (3D) fluids [6,7]. Experiments on propane and carbon dioxide also show evidence for a weak YY anomaly [8], while for ^3He the situation is less clear [9,10]. However, for 3D fluids, the analysis is extremely difficult. Assuming 3D Ising universality with $\alpha \approx 0.109$ and $\beta \approx 0.326$ [11], there are two singular terms in Eq. (1) that need to be distinguished not only from each other, but also from the leading analytic background term A_1t . A direct observation of the term $t^{2\beta}$ is consequently very difficult. Only very recently, after it was recognized that the amplitudes $A_{1-\alpha}$ and A_1 are coupled, could both singular terms in Eq. (1) be resolved from experimental data [12].

Nevertheless, due to the competition between terms in Eq. (1), investigations of the coexistence diameter in 3D fluids remain challenging. An attractive alternative, where the com-

petition between singular terms is less severe, is to consider a fluid where the specific heat diverges logarithmically at the critical point, implying $\alpha = 0$. The critical behavior of the diameter is then given by

$$\delta_{\alpha=0} = \rho_{\text{cr}}(1 + A_{2\beta}t^{2\beta} + A_0t \ln t + A_1t). \quad (2)$$

In other words, the term $t^{1-\alpha}$ is replaced by a (much weaker) logarithmic singularity [13]. In order to detect the YY anomaly, one thus needs to distinguish power law behavior from logarithmic behavior, which is expected to yield a more pronounced numerical signature. To this end, one could consider a 2D fluid, where $\alpha = 0$ and $\beta = 1/8$ (assuming 2D Ising universality). Note that mean-field systems do not qualify, despite having $\alpha = 0$. For mean-field systems, $\alpha = 0$ corresponds to a finite discontinuity in the specific heat, yielding a purely rectilinear diameter [13]. Still, even though the numerical analysis of a 2D fluid with Ising critical behavior may become simpler, this is no guarantee that a YY anomaly will be found. The absence or presence of a YY anomaly is a nonuniversal feature: $A_{2\beta}$ may well be zero. It is not completely clear which features in a fluid determine the strength of the YY anomaly. Obviously, the fluid must be asymmetric. In addition, there are experimental indications that molecular shape and symmetry, in particular departures from spherical form, are important contributing factors [8]. From these considerations, it appears that the “minimal” fluid in which a YY anomaly may most easily be found should (1) be two dimensional and exhibit a 2D Ising critical point, (2) be asymmetric, and (3) contain nonspherical particles.

In this work, we will investigate a fluid with precisely these properties, and focus on the critical behavior of its diameter. We consider a 2D version of the colloid-polymer model of Asakura and Oosawa (AO) [14], but generalized to nonspherical colloids. In the original AO model, colloids and polymers are treated as spheres in 3D, assuming hard-core interactions between colloid-colloid and colloid-polymer pairs, while polymer-polymer pairs can interpenetrate freely (the AO model is thus clearly asymmetric). Since the polymers may overlap freely, their translational entropy is increased significantly when the colloids group together. Hence, there is an effective (depletion) attraction between the colloids. Provided polymer concentration and size are sufficiently large, the attraction is strong enough to drive phase separation in the AO model, whereby the system splits

up into a colloid-rich (polymer-poor) phase and a colloid-poor (polymer-rich) phase. As expected for systems with short-ranged interactions, the corresponding unmixing critical point belongs to the 3D Ising universality class [15]. Hence, it is anticipated, although one should plan to check, that the AO model in 2D will exhibit a 2D Ising critical point. The effect of nonspherical particle shape is incorporated by modeling the colloids not as spheres, but as line segments. Our minimal model is thus a 2D mixture of colloidal line segments of length l_c and effective polymer disks of diameter σ_p , interacting via AO potentials. In other words, overlaps between line segments as well as overlaps between line segments and polymer disks are forbidden, while the polymer disks may overlap freely.

The aim of this work is to check if a YY anomaly in this model can be found. We will do so using computer simulation and finite size scaling (FSS) in the grand canonical ensemble. In this ensemble, the total area of the system A , the temperature T , and the colloid (polymer) fugacity z_c (z_p), are fixed, while the number of colloids (N_c) and polymers (N_p) fluctuates. The thermal wavelength is set to unity, such that z_p reflects the average concentration N_p/A that a pure phase of polymers would have (recall that such a phase is simply an ideal gas). The remaining lengths are expressed in units of l_c . The colloid-to-polymer size ratio is set to $\sigma_p/l_c=0.95$. At the coexistence colloid fugacity, it is expected that the mixture phase separates into a colloid-poor phase (the gas) and a colloid-rich phase (the liquid), provided that the polymer fugacity exceeds a critical value $z_{p,cr}$. The phase separation is thus driven by z_p , which therefore plays a role analogous to inverse temperature in gas-liquid transitions of simple fluids. The relative distance from the critical point is written as $t \equiv z_p/z_{p,cr} - 1$, and $\rho_G(\rho_L)$ denotes the concentration $\rho_c \equiv N_c/A$ of colloids in the gas (liquid) phase. A natural order parameter is the density gap $\Delta \equiv (\rho_L - \rho_G)/2$, while the coexistence diameter reads as $\delta \equiv (\rho_L + \rho_G)/2$. In the limit $t \rightarrow 0$, we expect critical power law behavior $\Delta \propto t^\beta$ for the order parameter, and Eq. (2) for the coexistence diameter.

For our minimal model, the critical point must be located first, in particular the value of $z_{p,cr}$. Next, 2D Ising universality of the critical point must be established, after which the diameter can be investigated. To “guide” the simulations, the phase diagram is obtained approximately first, using a simple mean-field (MF) theory based on a free-volume approach for 2D rod-polymer mixtures. The free-volume fraction and the free energy for a pure system of 2D lines are derived from scaled particle theory [16]. The free energy is exactly the same as the one obtained within Onsager’s second virial theory [16]. The resulting binodal is shown in Fig. 1. The theory predicts the critical point at $\rho_{cr}^{MF} \approx 0.550$ and $z_{p,cr}^{MF} \approx 2.054$. No nematic ordering of the colloids is predicted in the direct vicinity of the critical point: the coexisting phases are isotropic. Since the theory ignores critical fluctuations, it is expected that $z_{p,cr}^{MF}$ underestimates the true value $z_{p,cr}$ significantly. Nevertheless, the theoretical result is important because it provides an indication in which regime the (time consuming) simulations need to be carried out. The simulations are performed in the grand canonical ensemble, on a 2D square of size $A=L \times L$ using periodic boundary

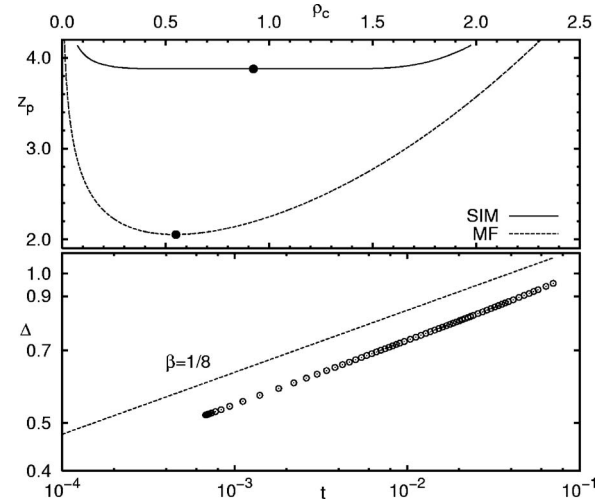


FIG. 1. Upper frame: Binodals of the 2D colloid-polymer mixture of this work, obtained using mean-field theory (MF) and simulation (SIM); circles mark critical points. Lower frame: Order parameter Δ as function of t , obtained using simulation and FSS; a value $z_{p,cr}=3.877$ in t was used.

conditions. We measure the distribution $P_L(\rho_c|z_p, z_c)$, defined as the probability of observing a system with colloid concentration ρ_c , at fugacities z_p and z_c , with L the system size. The insertion and removal of particles is performed using a cluster move [15], combined with a biased sampling scheme [17] to overcome the free-energy barrier separating the phases, and histogram reweighting [18]. To obtain a single distribution, around 100 CPU h for a small system ($L=22$), and 350 h for a large system ($L=30$), are required.

A standard route to obtain $z_{p,cr}$ in simulations, is to measure the L dependence of the cumulant $U_4 = \langle m^2 \rangle^2 / \langle m^4 \rangle$ along some path in the (ρ_c, z_p) plane. Here, $m = \rho_c - \langle \rho_c \rangle$, and $\langle \cdot \rangle$ denote grand canonical averages. The cumulant becomes system-size independent at the critical point [19]. Plots of U_4 as function of z_p for different system sizes L are expected to show a common intersection point, leading to an estimate of $z_{p,cr}$. Moreover, the value of the cumulant U_4^* at the intersection point is universal, and this gives an indication of the universality class. The result is shown in the upper frame of Fig. 2. The data were obtained using the colloid fugacity at which $\langle m^2 \rangle$ is maximized [6]. From the intersections, we obtain $z_{p,cr} = 3.881 \pm 0.005$, where the error reflects the scatter in the various intersection points. At the intersection point $U_4^* \approx 0.85$, which is very close to the accepted 2D Ising value $U_4^* \approx 0.856$ [20] (horizontal line in Fig. 2). While this already suggests 2D Ising universality, additional confirmation is obtained from the critical exponents. We consider β and ν , with ν the critical exponent of the correlation length. Here, ν is extracted from the cumulant slope $Y_1 \equiv dU_4/dz_p$ at the critical value of z_p . One expects that $Y_1 \propto L^{1/\nu}$, with L the system size. The lower frame of Fig. 2 shows Y_1 as a function of L , where the above estimate of $z_{p,cr}$ was used. The line is a linear fit through the origin, which describes the data very well, and thus confirms the 2D Ising value $\nu=1$. To obtain β , we apply the FSS algorithm of Ref. [7], using system sizes $L=20-30$. Starting with z_p significantly above

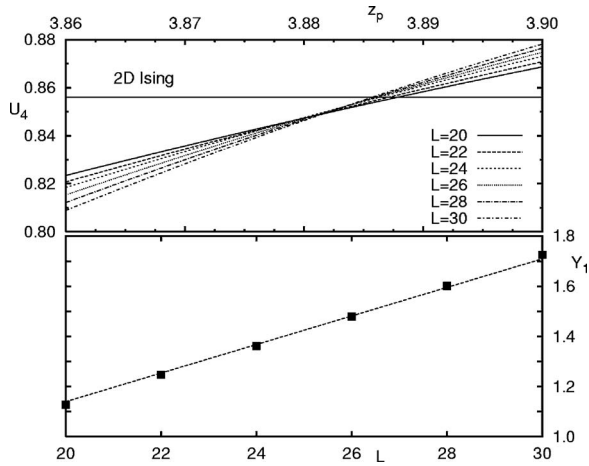


FIG. 2. Cumulant analysis near the critical point. The top frame shows U_4 as a function of z_p for various system sizes L as indicated. The lower frame shows the cumulant slope Y_1 at $z_{p,cr}$ as a function of L .

its critical value, the algorithm proceeds by plotting U_4 as a function of the average colloid concentration $\langle \rho_c \rangle$. The resulting plot reveals two minima, located at ρ^- and ρ^+ , with respective values Q^- and Q^+ at the minima. Defining the quantities $Q_{min} = (Q^+ + Q^-)/2$, $x = Q_{min} \ln(4/eQ_{min})$, and $y = (\rho^+ - \rho^-)/(2\Delta)$, the points (x, y) obtained for different system sizes L should, in the limit far away from the critical point, collapse onto the line $y = 1 + x/2$. Recall that Δ is the order parameter in the thermodynamic limit at the considered fugacity z_p , precisely the quantity of interest, which may thus be obtained by fitting until the best collapse onto $1 + x/2$ occurs. In the next step, z_p is chosen closer to the critical point, the points (x, y) are calculated as before, but this time Δ is chosen such that the new data set joins smoothly with the previous one, yielding an estimate of the order parameter at the new fugacity. This procedure is repeated as closely as possible to the critical point, where Δ vanishes. The output of the algorithm, Δ as a function of z_p , is then fitted to $\Delta \propto t^\beta$, in order to estimate $z_{p,cr}$ and β . We obtain $z_{p,cr} = 3.877 \pm 0.001$, which is consistent with the (less precise) analysis of Fig. 2. Shown in the lower frame of Fig. 1 is the order parameter as a function of t , on double logarithmic scales. The line has slope $\beta = 1/8$, and confirms the 2D Ising exponent in the simulation data. The FSS algorithm also yields the order parameter scaling curve $y = f(x)$ [7], with x and y defined as above, shown for completeness in the upper frame of Fig. 3. Away from the critical point ($x \rightarrow 0$), the scaling curve has the limiting form $y = 1 + x/2$; at the critical point, the scaling curve diverges. The significance of the scaling curve is its universal character: all systems with a 2D Ising critical point should yield a scaling curve for the order parameter similar to the one shown here [7].

At this point, sufficient evidence for 2D Ising universality has been provided. Since the order parameter is a scalar, and since the interactions are short ranged, there are in any case no theoretical grounds to contemplate a different universality class. Hence, we will now consider the coexistence diameter.

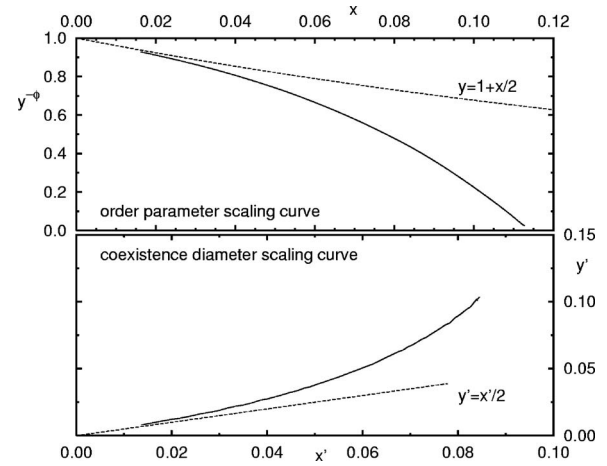


FIG. 3. Upper frame: Order parameter scaling curve $y = f(x)$ (solid line). Following convention [7], the scaling curve is raised to a negative exponent with $\phi = 1/\beta$, where the 2D Ising value $\beta = 1/8$ was used. Also shown is the small- x limiting form $y = 1 + x/2$ (dashed line). Lower frame: Coexistence diameter scaling curve $y' = g(x')$ (solid line). The dashed line shows the small- x' limiting form $y' = x'/2$.

To obtain the diameter, the FSS algorithm of Ref. [7] is used. Similarly, also for the coexistence diameter, a scaling curve $y' = g(x')$ is generated, based on different quantities x' and y' defined in Ref. [7]. In contrast to the order parameter, the scaling curve of the diameter is *not* universal. For our model, the corresponding curve is shown in the lower frame of Fig. 3. For small x' , it correctly approaches the exact limiting form $y' = x'/2$ [7]. The curvature at $x' \gg 0$ already suggests singular behavior. According to Eq. (2), this may reflect the YY anomaly, or logarithmic behavior, or both. To quantify this, the diameter itself is shown in the upper frame of Fig. 4. The quality of the data is such that δ can be resolved down to $t \approx 0.0015$. A fit to Eq. (2) yields $\rho_{cr} = 0.9270 \pm 0.0006$, $A_{2\beta} \approx 0$, $A_0 = -0.29 \pm 0.01$, and $A_1 = 0.76 \pm 0.03$, where the er-

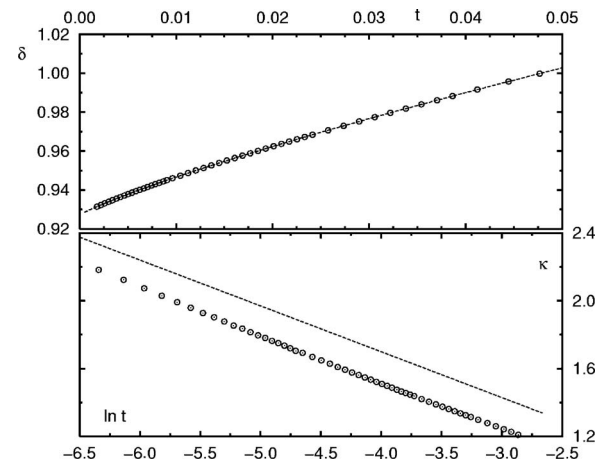


FIG. 4. Upper frame: Coexistence diameter δ as a function of t (circles). The dashed line is a fit to Eq. (2). Lower frame: κ as a function of $\ln t$ (circles). The straight line (dashed) confirms the logarithmic nature of the divergence. In both plots, $z_{p,cr} = 3.877$ in t was used.

ror reflects the scatter resulting from the range over which the fit is performed. The fit describes the data perfectly well, without the need for a term $t^{2\beta}$, indicating logarithmic singular behavior. In other words, despite the nonspherical particle shape in our model, the present analysis does *not* reveal a YY anomaly. For completeness, in the lower frame of Fig. 4, the derivative $\kappa \equiv d\delta/dt$ is plotted as a function of $\ln t$. In the case of singular behavior, κ is expected to diverge as $t \rightarrow 0$. The (logarithmic) divergence is clearly visible. Finally, by combining the coexistence diameter and order parameter data, the binodal in the thermodynamic limit was constructed, see the top frame of Fig. 1.

In conclusion, we have shown that 2D colloid-polymer mixtures, with nonspherical colloids, do not display a pronounced YY anomaly, at least not for the colloid-to-polymer size ratio $q=0.95$ considered by us. Although the diameter becomes singular upon approach to the critical point, the singularity is logarithmic, and well described by the theoretically expected term $t \ln t$. While it has been suggested [8] that nonspherical particle shape may be an important contributing factor to the formation of the YY anomaly, this seems not to be the case for our 2D model. If a YY anomaly is present in our 2D model nevertheless, it is very weak, and

negligible down to $t \approx 0.0015$ accessible in our simulations. In contrast, our results may be compatible with the very recent Ref. [12], where it is argued that a YY anomaly is expected when $\rho^* = \rho_{cr} a_i$ is small, where a_i represents the typical interaction volume. For our model, $a_i \approx q^2$, and so $\rho^* \approx 0.8$. This value even exceeds $\rho^* \approx 0.75$ of the Widom-Rowlinson mixture [3], for which no YY anomaly was detected either [5]. In order to detect a YY anomaly in our 2D model, it seems that smaller size ratios q are required; this could be a topic for further simulations. It is tempting to speculate if the 2D model considered in this work can also be realized experimentally. Colloidal particles, due to their mesoscopic size, pose many advantages over atomic fluids. This has already enabled the investigation of critical phenomena in 3D, whereby the particles are visualized directly using confocal microscopy [21]. Other applications may be found in order-disorder phase transitions in adsorbed monolayers of atoms or small molecules at surfaces.

This work was supported by the Deutsche Forschungsgemeinschaft under the SFB-TR6/D3. H.H.W. also acknowledges the Alexander von Humboldt foundation. We thank M. A. Anisimov and K. Binder for valuable comments.

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