

Nonuniversal Routes to Universality: Critical Phenomena in Colloidal Dispersions

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(Received 31 October 2007; revised manuscript received 2 January 2008; published 8 February 2008)

We investigate critical phenomena in colloids by means of the renormalization-group based hierarchical reference theory of fluids. We focus on three experimentally relevant model systems: namely, the Asakura-Oosawa model of a colloidal dispersion under the influence of polymer-induced attractive depletion forces; fluids with competing short-range attractive and longer-range repulsive interactions; solutions of star polymers whose pair potential presents both an attractive well and an ultrasoft repulsion at shorter distance. Our results show that the ability to tune the effective interactions between colloidal particles allows one to generate a variety of crossovers to the asymptotic critical behavior, which are not observed in atomic fluids.

DOI: [10.1103/PhysRevLett.100.055703](https://doi.org/10.1103/PhysRevLett.100.055703)

PACS numbers: 64.60.F-, 61.20.Gy, 64.60.A-, 82.70.Dd

The description of colloidal dispersions in terms of effective interactions acting between macroparticles [1,2] has opened the realm of complex fluids to modern liquid-state physics, and is the main reason for the rekindled interest in this discipline. On the one hand, using colloidal particles as macroatoms allows visual inspection of the fluid, solid and glassy states of matter which occur also in atomic substances [3]. On the other hand, the diversity of effective interactions, as well as the possibility of tuning them by changing the parameters which characterize the dispersion, leads to a phase behavior which is much richer than that encountered in atomic fluids [2]. This ability of engineering the phase diagram [4] is fascinating both in its own right and for its potential application in technology. Compared to the study of their overall phase behavior, critical phenomena in colloids have received less attention. A likely reason for this situation is that, in contrast with the menagerie of possible phase equilibria, the most relevant feature of critical phenomena is their universality, as expressed by the critical indices being the same for all the systems belonging to the same universality class. For fluid-fluid (FF) transitions, this is expected to be the Ising one for both simple and colloidal fluids such as protein solutions and colloid-polymer mixtures, so it might be argued that there is little to learn in going from simple fluids to colloids. However, while universality comes along asymptotically close to the critical point, the approach to the asymptotic regime is by no means universal: how the asymptotic critical regime is reached, and how far from the critical point critical fluctuations are expected to become important, are relevant questions whose answers can be quite different from those found in atomic fluids, since the specific features of colloid-colloid effective potentials may induce peculiar crossovers, and affect the size of the critical region.

In this Letter, we show how the onset of critical fluctuations is affected by the specific form of the interaction by

focusing on three model systems, all of which have received much attention because of their phase behavior and structural properties: the Asakura-Oosawa (AO) pair potential for hard-core colloidal particles in the presence of nonadsorbing polymer in solution; a hard-core two-Yukawa (HCTY) fluid with competing short-range attractive and longer-range repulsive interactions; a model of a star-polymer (SP) solution, where the ultrasoft repulsion between the stars is followed by an attractive well. We have investigated their critical behavior by the hierarchical reference theory (HRT) [5]. In HRT, the attractive part of the interaction in Fourier space is gradually switched on by introducing an evolving infrared cutoff Q such that at any intermediate stage of the process, fluctuations with characteristic length $L \gtrsim Q$ are strongly suppressed. The fully interacting system and the onset of long-range correlations are then recovered in the limit $Q \rightarrow 0$. HRT is optimally suited to the present study because it implements the renormalization-group (RG) method, and therefore yields a realistic, non mean-field-like treatment of the long-wavelength fluctuations which drive criticality and phase separation. On the other hand, this approach keeps all the information about the nonuniversal properties which are expected to depend on the specific features of the interaction, and would be lost in a coarse-graining approach. The crossover to the asymptotic power-law behavior can be described by introducing an “effective” critical exponent, defined as the local slope of the quantity in hand as a function of the reduced temperature t in a log-log plot. In the following, we will adopt the standard definition $t = (T - T_c)/T_c$, T_c being the critical temperature.

We first consider the AO model. The AO effective pair potential of polymer-induced depletion forces [6] consists of an attractive tail which vanishes identically beyond the polymer diameter, measured from the hard-core surface. The strength of the interaction is controlled by the fugacity z_p of the polymer or, equivalently, by the packing fraction

η_p^r of the pure polymer solution in osmotic equilibrium with the colloid-polymer mixture. This “reservoir” packing fraction plays the role of the inverse temperature in a thermal fluid. Consistently with the above definition of t , we have set $t = (\eta_{p,\text{crit}}^r - \eta_p^r)/\eta_p^r$, $\eta_{p,\text{crit}}^r$ being the critical value of η_p^r . A HRT study of the overall phase diagram and asymptotic critical behavior of several thermodynamic quantities has been presented elsewhere [7,8]. However, the approach to criticality has not been studied before. In Fig. 1 we have plotted, for several polymer-to-colloid size ratios q , the effective exponents γ_{eff} , ν_{eff} normalized by their asymptotic values γ , ν , which describe the divergence of the (reduced) compressibility χ_{red} and correlation length ξ on the critical isochore as T_c is reached. In HRT one has $\gamma = 1.378$, $\nu = \gamma/2 = 0.689$. Figure 1 also shows the effective exponents of a hard-core Yukawa (HCY) potential with attractive tail and inverse-range parameter $z = 1.8$, which is appropriate to model the pair potential of simple atomic fluids (inverse ranges are in units of σ^{-1} , σ being the hard-sphere diameter). As expected on the basis of the RG predictions [9], as q is decreased, the asymptotic critical regime is reached at larger reduced temperatures, and for $q = 0.4$, γ_{eff} is about 95% of its asymptotic value already at reduced effective temperatures $t \sim 0.1$. This is different from what is observed in the HCY fluid, whose γ_{eff} at these reduced temperatures is still mean-field-like. We did not consider size ratios $q < 0.4$, since our implementation of HRT is not suited to very narrow potentials. Moreover, in the AO potential, FF phase separation is preempted by freezing for $q \lesssim 0.4$ [7,10], even though at smaller q it can still be observed as a metastable transition.

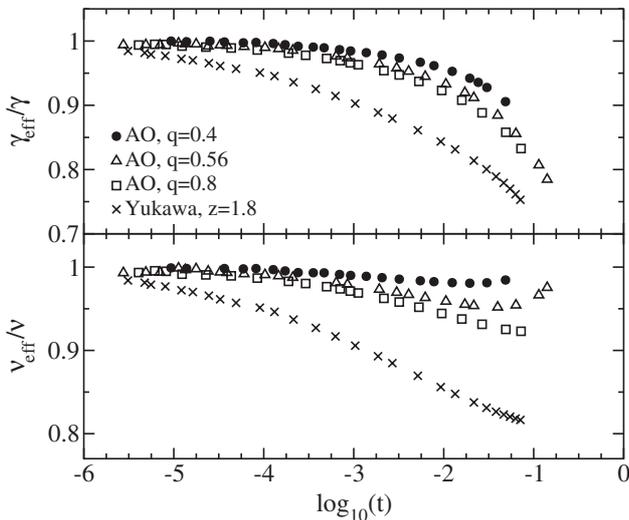


FIG. 1. AO effective exponents γ_{eff} (upper panel) and ν_{eff} (lower panel) for χ_{red} and ξ , normalized by their asymptotic values, compared with the effective exponents of an attractive HCY potential with inverse-range parameter $z = 1.8$. For the AO potential, the reduced effective temperature t is $(\eta_{p,\text{crit}}^r - \eta_p^r)/\eta_p^r$, where η_p^r is the reservoir packing fraction.

For the values of q considered here, the AO depletion interaction has many-body contributions, which are not accounted for by the effective pair potential which we have used. However, the critical behavior is captured satisfactorily already at the pair potential level [8]. On the basis of our results, we expect AO colloid-polymer mixtures to exhibit nearly asymptotic Ising scaling at reduced effective temperatures $t \approx 0.1$. We also note that there is no exponent renormalization due to the binary nature of the system, provided the *reservoir* packing fraction is used as the relevant field driving criticality.

In a recent paper [11], the critical behavior of the correlation length of colloid-polymer mixtures has been investigated experimentally, and the critical exponent ν was found to be close to the mean-field value $\nu = 0.5$. On the other hand, Monte Carlo studies supplemented by finite-size scaling unambiguously proved that the AO model belongs to the Ising universality class [8,12]. This raises [13] an interesting question about the possible presence of an unforeseen long-range interaction in the mixtures studied in Ref. [11].

Besides the tunable short-range attractions of which the AO potential represents the best-known example, fluids where the short-range attraction is followed by a repulsion which takes over at long distance have been receiving increasing attention. It has long been acknowledged [14] that the competition between attraction and repulsion leads, for strong enough repulsion, to the disappearance of bulk FF phase separation. As the temperature is lowered, this is replaced by the occurrence of nonhomogeneous phases that may have different morphologies [15], e.g., cluster- or stripe-shaped.

Instead of considering the nonhomogeneous phases, here we focus on a regime of relatively weak repulsion, such that the competition is not so strong as to cause the disappearance of FF phase separation, and investigate the effect on the critical behavior. Our model interaction is the HCTY potential with inverse-range parameters $z_1 = 1$, $z_2 = 0.5$ for the attractive and repulsive contribution, respectively [16]. The relative amplitudes A of the repulsion is close to the value above which the FF transition disappears, and microphase formation is expected. This regime is characterized by an extremely flat FF coexistence curve [16]. In Fig. 2, χ_{red} and ξ have been plotted together with the effective critical exponents. The most striking effect is the steep increase of χ_{red} and ξ at reduced temperatures $t \approx 0.1$, with a corresponding sharp crossover of the effective exponents. The enhancement of large density fluctuations can be traced back to the tendency towards cluster formation triggered by the competition. A sign of this “incipient clustering” is that, unlike in Lennard-Jones (LJ)-like fluids with purely attractive tail potentials, one finds damped oscillatory decay for the correlations even for states very close to critical [17]. On further approaching the critical point, the decay becomes monotonic, but takes a double

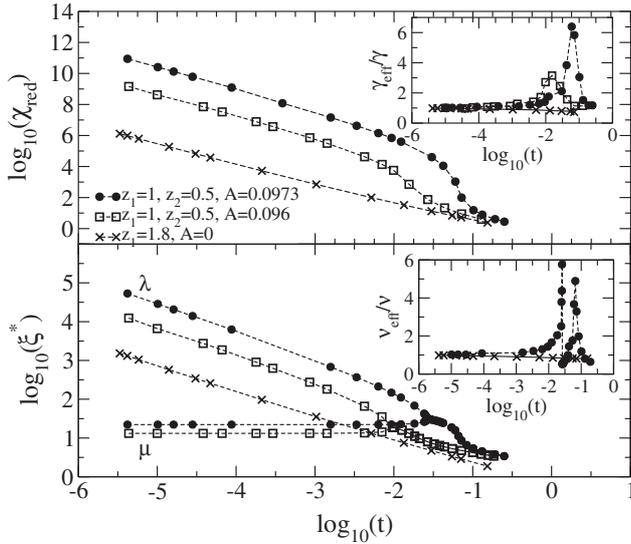


FIG. 2. Reduced compressibility (upper panel) and correlation length (lower panel) in units of the particle diameter of a HCTY fluid with competing short-range attraction and longer-range repulsion. The insets show γ_{eff} , ν_{eff} compared with the effective exponents of a HCY potential (ν_{eff} for $A = 0.096$ has been omitted for clarity). See text for the meaning of the lengths λ and μ . In the oscillatory regime, only the real part of λ and μ has been shown. Lines are a guide for the eye.

exponential form described by *two* characteristic lengths λ , μ [16,18]. A similar behavior has in fact been found in many frustrated systems [19]. In our treatment, λ and μ are obtained from expanding the reciprocal of the structure factor $S(k)$ at small wave vector k up to k^4 . Asymptotically close to the critical temperature, λ reduces to the usual Ornstein-Zernike (OZ) correlation length, while μ saturates at a finite value. The change from oscillatory to monotonic behavior is marked by the bifurcation in Fig. 2, where λ , μ turn from complex conjugate to real. This is an example of the well-known Kirkwood crossover [20]. We observe that ν_{eff} shows both a peak at a temperature slightly higher than that of the bifurcation, and a divergence at the low-temperature side of the bifurcation, where λ takes a vertical slope. The latter feature is due to the coalescence of λ and μ at the Kirkwood line.

It is tempting to interpret the above scenario as a cluster-driven criticality, whereby particles are first strongly correlated within regions of size $\sim \mu$, which in turn become correlated over length scales of size $\sim \lambda$ as the critical point is reached. In the asymptotic critical regime, χ_{red} diverges as λ^2 like in the OZ picture, but with an amplitude $\sim \mu^2$, much bigger than that of LJ-like fluids; see Fig. 2. The possibility of clusters behaving like superatoms has already been pointed out in the context of the glass transition [21]. In our case, however, clusters denote regions of enhanced particle-particle correlations, rather than stable particle aggregates.

The anomalous crossover of the HCTY model close to the stability limit of the liquid-vapor transition has not been observed experimentally yet. However, it seems likely that such a regime can be experimentally reached. As an example, let us consider the system studied by Cardinaux *et al.* [22] as a model of lysozyme solutions. They investigated cluster formation for volume fractions η of lysozyme in the range $0.085 \leq \eta \leq 0.201$ in a solution of sodium hydroxide at concentration $c = 8$ mM. An estimate of the electrolyte concentration below which the liquid-liquid transition is expected to disappear can be obtained within the random phase approximation by locating the concentration at which the convexity of the Fourier transform of the potential at zero wave vector k turns from positive to negative. According to this criterion, $c = 8$ mM is indeed well inside the cluster region, while at $\eta = 0.201$, the threshold concentration is at $c \approx 56$ mM.

Star-polymer solutions differ from the two systems considered above inasmuch as the interaction which accounts for the excluded volume effect is not the hard-sphere potential, but an ultrasoft repulsion of entropic origin with a logarithmic core and a repulsive Yukawa tail [23]. The size of the star σ is of the order of the radius of gyration. It has been shown that, when an additional attractive interaction between the stars is present, the solution may display two FF transitions, each ending at a critical point [24]. Here we focus on the behavior in the neighborhood of the lower-density critical point, which we expect to be more easily accessible by experiments. We considered three values of the arm number or “functionality” f , namely $f = 12$, $f = 24$, $f = 32$. The attractive well was modeled by the same Fermi function used in Ref. [24]. Figure 3 shows the effective exponents γ_{eff} , ν_{eff} . The main qualitative difference with respect to the simple-fluid case represented by the HCY fluid with $z = 1.8$ consists in the nonmonotonic behavior of the effective exponents. As one moves away from the critical tempera-

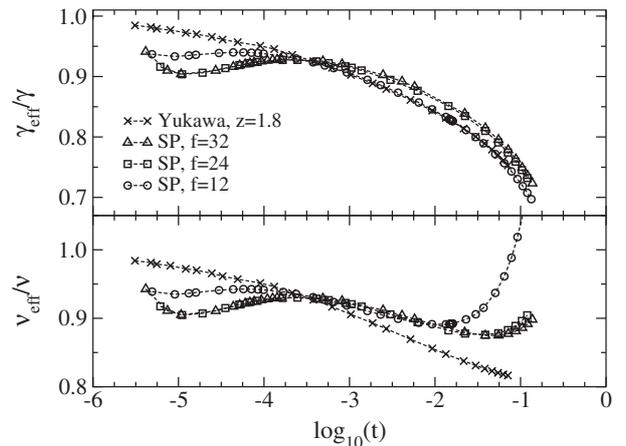


FIG. 3. Same as Fig. 1 for three SP solutions. Lines are a guide for the eye.

ture, ν_{eff} shows a minimum in the interval $10^{-2} < t < 10^{-1}$, and increases sharply as t is further increased. This is due to the effect of the soft repulsion which, at the small densities considered here, is more substantial than in a hard-core system of comparable size. Moreover, both γ_{eff} and ν_{eff} show another minimum at $t \approx 10^{-5}$ and bend towards their asymptotic values as t is further reduced. The accuracy limit entailed by our numerical calculation prevented us from reaching reduced temperatures smaller than $t \sim 10^{-6}$, so that the asymptotic exponents could not be observed. Notwithstanding this, the quantitative deviations from simple-fluid behavior for $t \lesssim 10^{-2}$ are rather small, and the effective exponents remain well apart from their mean-field values even in the region of the minimum, at least for the values of f investigated here. This behavior is different from what is found in the linear-polymer solutions considered in Ref. [25]. In that case, the correlation length ξ away from the critical point is considerably smaller than the polymer size σ . As the critical point is approached and ξ becomes comparable to σ , the solution shows a rather sharp crossover from mean-field to Ising critical behavior. Here, on the other hand, the size of the star σ is the natural length scale of both the repulsive and attractive interaction, so that ξ is of the order σ even away from the critical point. This requires that the quality of the solvent should be unchanged at the transition, so that the interstar attraction is not overwhelmed by the attraction between monomers within the same star. Experimentally this condition can be reproduced by considering effective depletion attractions between stars in multicomponent star-chain [26] or star-star mixtures [27]. These systems have been looked upon for a big component in solution with higher f than those we investigated here. Nevertheless, from the trends evidenced and the comparison between the effective interaction shapes, we expect the appearance of a stable low-density FF transition for highly or moderately asymmetric mixtures with small f ($f \ll 50$) for the big component.

In summary, we have presented an investigation of the critical behavior of three model fluids, whose pair interactions are relevant for a wide class of complex liquids, although they certainly do not aim at covering the whole subject of criticality in colloidal systems. In the AO model, nearly asymptotic Ising-like behavior is observed in a wide interval of reduced effective temperatures for the polymer-colloid size ratios at which the effective AO pair interaction is a reliable representation of the binary colloid-polymer mixture. In fluids with competing interactions, the enhancement of density fluctuations due to competition causes strong crossovers with anomalously high effective critical exponents γ_{eff} , ν_{eff} and critical amplitudes, as well as the emergence of two characteristic lengths. In star-polymer solutions with star-star attraction, we find a non-monotonic behavior of the effective exponents γ_{eff} , ν_{eff} close to the critical temperature. We expect that these

predictions can be tested by experiments in colloid-polymer and polymer-polymer mixtures and protein solutions.

This work is funded in part by the Marie Curie program of the European Union, Contract No. MRTN-CT2003-504712, and the Foundation BLANCEFLOR Boncompagni-Ludovisi, née Bildt. F.L.V. gratefully acknowledges discussion with Christos Likos and Christian Mayer.

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