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Critical Casimir Forces between Spherical Particles in Fluids

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Long-ranged correlations in a fluid close to its critical point T_c cause distinct forces between immersed colloidal particles and the container walls. We calculate such a force and its temperature dependence for the generic case of a spherical particle located at a distance D from a planar wall and find that the force attains a maximum at a temperature $T_{\max}(D)$ *above* T_c, which facilitates quantitative experimental tests. The corresponding effective pair interaction between the colloidal particles themselves, potentially leading to aggregation, is also discussed. [S0031-9007(98)06900-2]

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In 1948 Casimir [1] predicted that the confinement of quantum mechanical vacuum fluctuations of the electromagnetic field causes long-ranged forces between two conducting uncharged plates. Only recently, this so-called Casimir effect was tested experimentally [2] with high accuracy for the force on a conducting sphere near a conducting planar surface.

Thirty years later Fisher and de Gennes [3] pointed out that an analogous effect should occur in a thin film of a binary liquid mixture near the critical demixing point T_c of the bulk mixture. In this case the confinement of *critical fluctuations* of an order parameter field induces long-ranged forces between the surfaces of the film [4]. In recent years the so-called "critical Casimir effect" has attracted increasing theoretical interest [5,6]. In spite of these efforts—and in contrast to the quantum mechanical Casimir effect—the critical Casimir effect lacks so far an unambiguous experimental verification. This unsatisfactory state of affairs persists mainly due to a combination of two reasons. First, so far most theoretical studies have been restricted to the special case $T = T_c$. In this case the bulk correlation length $\xi_{\pm} = \xi_0^{\pm}|t|^{-\nu}$, where $t = (T - T_c)/T_c \gtrless 0$ and ν is a standard bulk critical exponent, is infinitely large which cannot be realized experimentally. In practice the divergence of ξ is limited, e.g., by a finite temperature resolution, spatial inhomogeneities of T, and external fields such as gravity. In addition, the knowledge of the temperature dependence of the critical Casimir force is indispensable for experimental tests in order to be able to subtract the regular background contributions due to the omnipresent dispersion forces. Second, most theoretical studies deal with the parallel plate geometry which happens to be unsuitable for actual measurements because, surprisingly, it turns out that it is too demanding to keep the plates sufficiently parallel. The preferential geometry consists of a sphere located near a planar wall [2] rather than of two parallel plates.

We consider the generic case of a spherical particle with mesoscopic radius R immersed in a binary liquid mixture at a distance D of closest approach surface-to-surface from a planar boundary wall. The particle may be regarded as a freely moving colloidal particle, but it can also model a sphere attached to the tip of an atomic force microscope. Close to the critical demixing point the force F exerted on such a sphere separates into a regular background contribution and a singular contribution F_{sing} of universal character, which is *attractive* if the same of the two coexisting bulk phases is enriched near the wall and sphere surfaces. We obtain quantitative results for F_{sing} by a multipronged approach consisting of a variety of theoretical techniques: full numerical analysis of the corresponding mean-field theory supported by renormalization group arguments, Derjaguin approximation, small sphere expansion, and suitable incorporation of exact results in two dimensions.

Figures 1 and 2 summarize our results for the case in which the critical demixing point is approached from the one phase region by varying the temperature T towards the critical temperature $T_c = T_c(p)$ at fixed pressure p and with the concentration x fixed at its critical value $x_c(p)$. The results for F_{sing} can be cast in the form

$$F_{\text{sing}}(T, D, R) = \frac{k_B T_c}{R} K_+\left(\Theta = \frac{D}{\xi_+}, \Delta = \frac{D}{R}\right) \quad (1)$$

with a *universal* function K_+ using $k_B T_c$ as the energy scale and expressing the dependence on $T - T_c$ in terms of the corresponding bulk correlation length ξ_+. We take ξ_+ as the *true* correlation length governing the exponential decay of the order parameter correlation function in the bulk. The most striking feature of $F_{\text{sing}}(T, D, R)$ is the appearance of a maximum as a function of T with D and R fixed. The maximum occurs at $T_{\max}(D, R) > T_c$ given by

$$\frac{T_{\max}(D, R) - T_c}{T_c} = \left[\frac{\Theta_{\max}(\Delta)}{D/\xi_0^+}\right]^{1/\nu}, \quad (2)$$

where $\Theta_{\max}$ is the position of the maximum in Fig. 1. The nonuniversal bulk amplitude $\xi_0^+ = \xi_0^+(p)$ is known experimentally for numerous fluids with values ranging

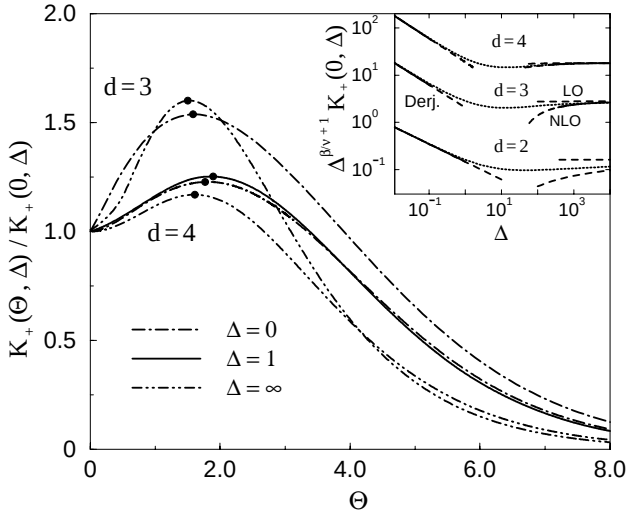

FIG. 1. Scaling function $K_+(\Theta, \Delta)$ in Eq. (1) normalized with the corresponding function at $T = T_c$ vs $\Theta = D/\xi_+ = t^\nu D/\xi_0^+$ for fixed length ratios $\Delta = D/R$. Shown are the limiting cases $\Delta = 0$ [Derjaguin approximation (4)] and $\Delta = \infty$ [small sphere expansion (6) and (7)]. The line for $\Delta = 1$ has been calculated numerically. The dots indicate the maxima. Results are given both for the physical dimension $d = 3$ and for $d = 4$. The inset shows $K_+(0, \Delta)$ as used for normalization [for $d = 4$ we actually show the finite limit for $d \nearrow 4$ of $(4 - d)K_+$]. There the dashed lines have the same meaning as in Fig. 2(b) below. The lines for $d = 2$ display exact results [see J. L. Cardy, Nucl. Phys. **B275**, 200 (1986)].

between 2 and 4 Å. The universal dependence of $\Theta_{\max}$ on $\Delta = D/R$ and the corresponding universal maximal values of K_+ in Eq. (1) are shown in Fig. 2.

The critical fluctuations of the fluid inducing the effective interaction are described by the standard Hamiltonian

$$\mathcal{H}\{\Phi\} = \int_V dV \left\{ \frac{1}{2} (\nabla\Phi)^2 + \frac{\tau}{2} \Phi^2 + \frac{u}{24} \Phi^4 - h\Phi \right\} \tag{3}$$

for a scalar order parameter $\Phi(\mathbf{r})$ in cylindrical coordinates $\mathbf{r} = (\rho, z) \in \mathbb{R}^d$ supplemented by boundary conditions $\Phi = +\infty$ at the wall and sphere surfaces corresponding to the critical adsorption fixed point [7]. The volume V consists of the half-space $z \geq 0$ except for the volume occupied by the sphere. The field h is conjugate to the deviation of the concentration from the critical composition. When the binary liquid mixture is *at* the critical composition, i.e., $h = 0$, the singular contribution $(\delta f)_{\text{sing}}$ to the free energy of interaction between the wall and the sphere in units of $k_B T_c$ depends on ξ, R, and D in terms of the universal scaling functions $(\delta f)_{\text{sing}} = f_\pm(D/\xi_\pm, D/R)$ for $T \gtrless T_c$. This implies $K_+ = R \frac{d}{dD} f_+$ [see Eq. (1)].

We have carried out extensive numerical calculations in order to minimize $\mathcal{H}\{\Phi\}$ for fixed D, R, and $\tau > 0$ [8]. For $d \nearrow 4$ this mean-field solution with $\xi_+ = \tau^{-1/2}$ leads to the *exact* result for the order parameter profile $\Phi(\mathbf{r})$ and for the scaling function $K_+(\Theta, \Delta)$. The numerical analysis

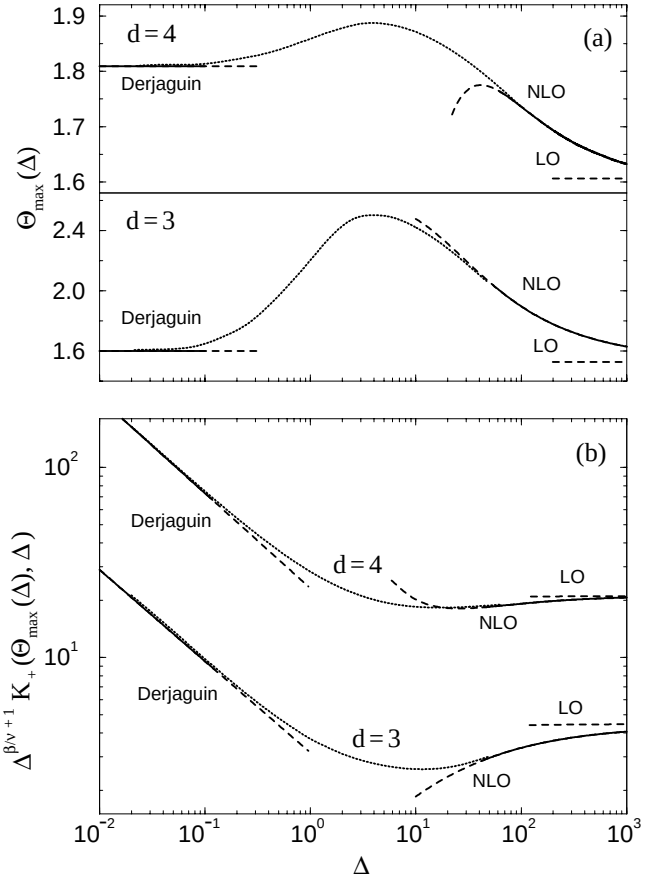

FIG. 2. (a) Values $\Theta_{\max}(\Delta)$ in Eq. (2) of $\Theta = D/\xi_+$ for which $K_+(\Theta, \Delta)$ in Eq. (1) attains its maximum for $\Delta = D/R$ fixed and (b) the behavior of $K_+(\Theta_{\max}(\Delta), \Delta)$ vs Δ [for $d = 4$ we show the limit $d \nearrow 4$ of $(4 - d)K_+$]. The solid lines show the Derjaguin approximation (4) and the small sphere expansion (6) and (7) in leading order (LO) and including the next-to-leading order (NLO). The dashed parts of these lines indicate where they start to fail. The dotted lines for $d = 4$ have been calculated numerically.

is complemented by the following analytic considerations for the asymptotic behavior of $K_+(\Theta, \Delta)$ for $\Delta \to 0$ and $\Delta \to \infty$.

Derjaguin approximation.—When R is much *larger* than D it is reasonable to apply the Derjaguin approximation [9], which replaces the sphere by a pile of immersed parallel plates with local distances $L(\rho) = D + \rho^2/(2R)$ from the wall. The force on the *sphere* is expressed in terms of the attractive force $k_+(L/\xi_+)(d - 1)L^{-d}$ per unit area in units of $k_B T_c$ between two *parallel plates* at distance L, where $k_+(y)$ is the corresponding universal scaling function. For $d = 3$ and 4 this leads to

$$K_+(\Theta, \Delta \to 0) = \omega(d)\Delta^{-(d+1)/2} \times \int_0^\infty d\alpha\, \alpha^{d-2}(1 + \alpha^2/2)^{-d} \times k_+\big(y = (1 + \alpha^2/2)\Theta\big) \tag{4}$$

with $\omega(3) = 4\pi$ and $\omega(4) = 12\pi$. Equation (4) has been shown to hold for $T = T_c$ [6] and is expected to hold also for $T > T_c$. Indeed our numerical results for $K_+(\Theta, \Delta)$ corroborate Eq. (4) (see Figs. 1 and 2). The Derjaguin approximation is, of course, also applicable for $d = 3$. Since at present $k_+(y > 0)$ is available for $d = 2$ [10] and $d = 4$ [5(c)] we interpolate these results suitably in order to obtain predictions for $d = 3$ [11] (see Fig. 3).

Small sphere expansion.—When on the other hand the radius R—albeit large on the microscopic scale—is much *smaller* than D and ξ, the statistical Boltzmann weight $e^{-\delta \mathcal{H}_S}$ characterizing the presence of the sphere centered at $\mathbf{r}_S$ can be systematically expanded in terms of increasing powers of R [6], i.e.,

$$e^{-\delta \mathcal{H}_S} \propto 1 + c_\uparrow^{\Phi} R^{x_\Phi} \Phi(\mathbf{r}_S) + c_\uparrow^{\Phi^2} R^{x_{\Phi^2}} \Phi^2(\mathbf{r}_S) + \ldots , \tag{5}$$

where $x_\Phi = \beta/\nu$ and $x_{\Phi^2} = d - \nu^{-1}$ (with the bulk critical exponents β and ν) are the scaling dimensions of $\Psi = \Phi, \Phi^2$. The ellipses stand for contributions which vanish more rapidly for $R \to 0$. The coefficients $c_\uparrow^{\Psi}$ are *fixed* by $c_\uparrow^{\Psi} = A_\uparrow^{\Psi}/B_\Psi$, where $A_\uparrow^{\Psi}$ and B_Ψ are, respectively, amplitudes of the half-space (hs) profile $\langle \Psi(z) \rangle_{\mathrm{hs}, T=T_c}^{\uparrow} = A_\uparrow^{\Psi} (2z)^{-x_\Psi}$ *at* the critical point of the fluid for the boundary condition $\uparrow$ corresponding to critical adsorption, and of the bulk two-point correlation function $\langle \Psi(\mathbf{r}) \Psi(0) \rangle_{b, T=T_c} = B_\Psi\, r^{-2x_\Psi}$ [6]. We apply Eq. (5) to $K_+(\Theta, \Delta)$ and obtain in lowest order in $\varepsilon = 4 - d$ [12]

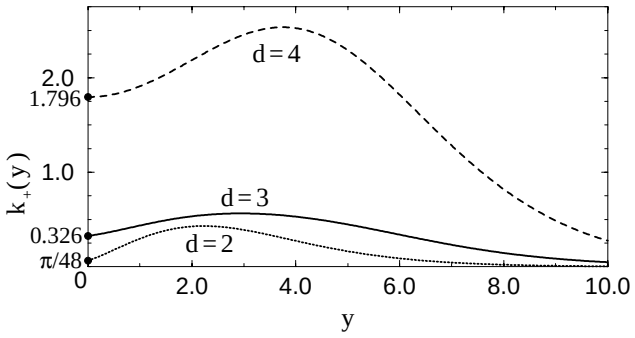

FIG. 3. Scaling function $k_+(y)$ [compare Eq. (4) and the preceding text; for $d = 4$ we show the limit $d \nearrow 4$ of $(4 - d)k_+$]. The results for $d = 2$ [10] and $d = 4$ [5(c)] are used for a pointwise interpolation to $d = 3$. The values $k_+(0) = -\Delta_{\uparrow,\uparrow}$ determine critical Casimir amplitudes.

$$K_+(\Theta, \Delta \to \infty) = \frac{18}{\varepsilon} \frac{\Theta^2 \cosh\Theta}{\sinh^2\Theta} \Delta^{-2} + \frac{9}{\varepsilon} \frac{\Theta^2}{\sinh^2\Theta} \times \left[-2\Theta \sinh\Theta - \frac{4\Theta}{\sinh\Theta} + 6 + [12\ln(\Delta^{-1}) - 12\ln 2 + 34]\Theta \coth\Theta + Q(\Theta) \right] \Delta^{-3} + \mathcal{O}(\Delta^{-4}), \tag{6}$$

where $Q(\Theta) = \Theta W(\Theta) \coth\Theta - \Theta W'(\Theta)/2$ and $W(\Theta) = -23 + 12C_E + 12\ln\Theta + 16\pi^2 C_+(\Theta)\sinh^2\Theta$ with Euler's constant C_E. For the lengthy expression of the function C_+ we refer the reader to Eq. (24) in Ref. [7(a)]. With the help of Eq. (6) we are able to extend the numerical results for $\varepsilon K_+(\Theta, \Delta)$ for $d = 4$ to the limiting case $\Delta \to \infty$ (see Figs. 1 and 2). Similar to the Derjaguin approximation, the expansion (5) can also be applied to $d = 3$. In this case we obtain

$$K_+(\Theta, \Delta \to \infty) = -\frac{a}{c_+} \frac{\Theta^{x_\Phi + 1}}{2^{x_\Phi}} P_+'(\Theta) \Delta^{-x_\Phi - 1} + \frac{a^2}{c_+^2} \frac{\Theta^{2x_\Phi + 1}}{2^{2x_\Phi}} P_+(\Theta) P_+'(\Theta) \Delta^{-2x_\Phi - 1} + \mathcal{O}(\Delta^{-x_{\Phi^2} - 1}). \tag{7}$$

Since $2x_\Phi \approx 1.036$ is smaller than $x_{\Phi^2} \approx 1.41$, Eq. (7) does indeed include the two leading contributions. The universal scaling function $P_+(z/\xi_+) = \langle \Phi(z) \rangle_{\mathrm{hs}, t>0}^{\uparrow} / \langle \Phi \rangle_{b, -t<0}$ and the universal amplitude c_+ governing the behavior $P_+(\zeta \to 0) \to c_+ \zeta^{-x_\Phi}$ [7(b)] characterize the order parameter profile at $T > T_c$ for critical adsorption on a planar substrate [7]. The ratio $a = (A_\uparrow^{\Phi})^2/B_\Phi$ is also universal [6]. For $d = 3$ we use the values $a \approx 7.73$ [13], $c_+ \approx 0.717$ [7(c)], and infer P_+ from the values in Table II in Ref. [7(c)].

The exact numerical calculation for $d = 4$ combined with the Derjaguin approximation and the small sphere expansion are sufficient to estimate the global behavior of $K_+(\Theta, \Delta)$ in $d = 3$ (see Figs. 1 and 2). The numerically calculated curves for $d = 4$ interpolate smoothly between the behavior for $\Delta \to 0$ and $\Delta \to \infty$ as implied by the Derjaguin approximation and the small sphere expansion, respectively. This provides a check of these approximations and, in addition, gives an impression of their range of validity. The small sphere expansion including the next-to-leading order as given by Eqs. (6) and (7) is reliable in a much larger Δ-range than in leading order. The interpolating curves for $d = 3$, which have been obtained by a suitable interpolation between the limiting behaviors as suggested by the corresponding lines for $d = 4$, are expected to constitute reasonable quantitative estimates. The results shown in Figs. 1 and 2 facilitate experimental tests of the critical Casimir force, which is characterized by its maximum at $(\Theta_{\max}, \Delta)$ and thus forms a *curved* "ridge" in the "landscape" $K_+(\Theta, \Delta)$. The corresponding maximum force can be measured and compared with Fig. 2(b) with no need of a high temperature resolution of

the experimental setup and without knowledge of the correlation length ξ in the binary liquid mixture. Upon inserting values $R \approx 10^{-6}$ m and $D \approx 10^{-8}$ m typical for atomic force microscopes and $T_c \approx 300$ K one infers from Fig. 2(b) $F_{\rm sing} \approx 10^{-10}$ N for the critical Casimir force, which is experimentally accessible. The corresponding van der Waals force $F_{vdW} = 2A/[3R\Delta^2(\Delta + 2)^2]$ with the typical value $A \approx 10^{-20}$ J for the Hamaker constant yields $F_{vdW} \approx 10^{-11}$ N. We conclude that near T_c the critical Casimir force even *dominates* over the background dispersion forces.

Regarding the flocculation of colloidal particles in a binary liquid mixture close to its critical point [14] we also consider the Casimir force between a pair of spheres with equal radii R and a distance vector $\mathbf{r}$ between their centers. This system is again described by Eq. (3) and boundary conditions at the sphere surfaces corresponding to critical adsorption [4,15]. We include the case in which the binary liquid mixture is *off* the critical composition, i.e., $h \neq 0$ in Eq. (3). When Eq. (5) is applied to the free energy of interaction one obtains $K_{\pm}^{\rm pair} = R\frac{d}{dr}f_{\pm}^{\rm pair}$ with the universal function $f_{\pm}^{\rm pair}(r/\xi_{\pm}; R/\xi_{\pm}, M_b\,\xi_{\pm}^{x_\Phi}) = -aR^{2x_\Phi}C_b \times [1 - 2\sqrt{a}\,R^{x_\Phi}M_b + \mathcal{O}(R^{x_{\Phi^2}-x_\Phi})]$. Here $M_b(t,h) = \langle\Phi\rangle_{t,h}/\sqrt{B_\Phi}$ is a convenient measure for the deviation of the bulk composition from its critical value and $C_b(r;t,h) = \langle\Phi(0)\Phi(\mathbf{r})\rangle_{t,h}^{\rm cum}/B_\Phi$ is a bulk cumulant. The first term in square brackets gives rise to an attractive effective force which is *increased* by the second term if M_b is negative, i.e., if the binary mixture is poor in the component preferred by the colloids, and vice versa [16]. This is consistent with—but may not yet explain—the asymmetry in the shape of experimentally observed flocculation phase diagrams [14]. If the flocculation of the colloids was driven by the critical Casimir forces close to the critical point of the binary liquid mixture the corresponding aggregation lines would exhibit a *universal* form in terms of $R/\xi_{\pm}$ and $M_b\xi_{\pm}^{x_\Phi}$. Thus it would be interesting to investigate experimental systems in which other aggregation mechanisms, such as screening effects [17], are absent or can be neglected.

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[11] We estimate $k_+(y)$ for $d = 3$ by extending the method according to which the estimate $\Delta_{\uparrow,\uparrow} \approx -0.326$ in Table I in Ref. [5(c)] has been obtained to values $y > 0$, leaving the prefactor -0.6853 in front of ε in Eq. (4.14) of Ref. [5(c)] unchanged and considering the prefactor in front of ε^2 as a function of y.

[12] The expansion (5) gives rise to poles $\sim\varepsilon^{-2}$ which cancel in the final expression (6) as it must be. The occurrence of the term $\sim\ln(\Delta^{-1})$ can be traced back to the fact that $2x_\Phi = 2 - \varepsilon + \mathcal{O}(\varepsilon^2)$ coincides with $x_{\Phi^2} = 2 - \varepsilon + \varepsilon/3 + \mathcal{O}(\varepsilon^2)$ for $\varepsilon = 0$.

[13] Using the expansion of a in $\varepsilon = 4 - d$ as given in the first Ref. [6] in conjunction with the value $a = \sqrt{2}$ for $d = 2$ the estimate $a \approx 7.73$ for $d = 3$ has been obtained by a suitable interpolation scheme following Ref. [7(b)].

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