Casimir Interaction of Spheres in a Fluid at the Critical Point

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Critical fluctuations give rise to long-range Casimir forces between inert uncharged particles immersed in a fluid at the critical point. With simple, exact arguments utilizing conformal invariance, we analyze the Casimir force between two spheres in an unbounded critical fluid, and between a single sphere and the planar boundary of a semi-infinite fluid. The Casimir force has a much longer range than the van der Waals force and should lead to aggregation of colloidal particles.

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Vacuum fluctuations of the electromagnetic field between infinite uncharged conducting plates with separation L lead to an attractive Casimir [1] force per unit area $-(\pi^2/240)\hbar c L^{-4}$.

There are comparable long-range forces due to critical fluctuations that also go under the name of Casimir forces. Consider a nearly critical fluid between parallel plates, for example, a one-component fluid near the liquid-vapor critical point, a binary mixture near the consolute (critical demixing) point, or liquid ^{4}He near the λ transition. The boundaries influence the system to a depth given by the bulk correlation length $\xi \sim |T - T_c|^{-\nu}$. For $\xi \ll L$ the fluctuation-induced force between the plates is negligible. At the critical point ξ diverges, and the force becomes long ranged.

In general, the free energy

$$F = -k_B T \ln \mathrm{Tr} \exp(-\mathcal{H}/k_B T) \tag{1}$$

of a d-dimensional critical system in the form of a film with thickness L, area M^{d-1}, and boundary conditions a and b on the two surfaces has the asymptotic form

$$F \approx k_B T_c M^{d-1}(L f_B + f_S^{(a)} + f_S^{(b)} + L^{-(d-1)}\Delta_{ab} + \cdots) \tag{2}$$

in the limits $L, M \to \infty$ with $M \gg L$. Here f_B and f_S are reduced bulk and surface free energies, respectively, and Δ_{ab} is the amplitude of the Casimir interaction. The L dependence of the Casimir term, derived in 1978 by Fisher and de Gennes [2], follows from scale invariance of the free energy. The amplitude Δ_{ab} is universal [3], depending only on the bulk universality class and the universality class of the boundary conditions. In recent years results for Δ_{ab} in several systems have been obtained with conformal-invariance methods [4–7] in $d = 2$ and with renormalized field theory [8–12] in $d = 4 - \epsilon$.

Equation (2) holds for both magnetic and fluid systems at criticality. The one-component fluid at the liquid-vapor critical point and the binary fluid at the consolute point belong to the Ising universality class. Each plate generally attracts one of the two phases preferentially, i.e., breaks the up-down Ising symmetry. These fluid systems correspond to the Ising model with $ab = \uparrow\uparrow$ boundary conditions if both plates prefer the same phase, and $\uparrow\downarrow$ boundary conditions if they prefer different phases. Liquid ^{4}He at the lambda transition belongs to the XY universality class with "ordinary" ($a, b = OO$) boundary conditions [13] that suppress the order parameter at the boundary and do not break the XY rotational symmetry.

In this Letter we consider the Casimir force between inert uncharged spherical objects, for example, colloidal particles immersed in a fluid at criticality. Satisfying the criticality condition $\xi \gg L$ experimentally for macroscopic L in the parallel-plate geometry requires extremely fine temperature resolution. The critical regime $\xi \gg r$ for particles with separation r in suspension is more accessible, and some experimental results have been reported [14]. In earlier theoretical work de Gennes [15] calculated the Casimir force between two spheres in a critical fluid approximately from a local free-energy functional. Attard, Ursenbach, and Patey [16] applied Ornstein-Zernicke theory in the nearly critical case. Here we analyze the Casimir interaction between two spheres in an infinite critical fluid exactly on the basis of conformal invariance [17] in general dimension d. It is shown that the Casimir interaction only depends on a single conformally invariant cross ratio. Exact analytical results are given for spheres that nearly touch and spheres that are widely separated.

As shown below, the Casimir potential of two widely separated spheres with symmetry-breaking boundary conditions decays as $r^{-2\beta/\nu}$, like the spin-spin correlation function of the corresponding magnetic system. If neither or only one of the spheres has symmetry-breaking boundary conditions, the Casimir potential decays as $r^{-2(d-1/\nu)}$, like the energy-energy correlation function of the magnetic system. This is fairly obvious but has not been clearly stated in earlier work. We will see that the Casimir

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force is attractive for equal boundary condition on both spheres and has a much longer range than the van der Waals force. It should give rise to aggregation of colloidal particles as the critical point of the host fluid is approached.

We begin with two spheres with radii R_1 and R_2, boundary conditions a and b, and separation r (measured from center to center) in an infinite critical medium. The Casimir interaction $\Delta F_{ab}(r, R_1, R_2)$ is defined as the total free energy of the system minus its value for $r = \infty$. Scale invariance requires ΔF_{ab} to be a function of two independent scale-invariant variables [18], for example, $r^2(R_1R_2)^{-1}$ and $R_1R_2^{-1}$. Conformal invariance in general dimension d imposes the stronger constraint that ΔF_{ab} only depend on a single variable

$$\kappa = (2R_1R_2)^{-1}|r^2 - R_1^2 - R_2^2|. \tag{3}$$

In general d the conformal group consists [17] of homogeneous translations, rotations, and dilatations and the inversion $\mathbf{x}' = \mathbf{x}|\mathbf{x}|^{-2}$. The latter maps a sphere with radius R centered at $\mathbf{r}_0$ onto a sphere with radius $R' = R|r_0^2 - R^2|^{-1}$ centered at $\mathbf{r}_0' = \mathbf{r}_0(r_0^2 - R^2)^{-1}$. It is simple to verify that $\kappa' = (2R_1'R_2')^{-1}|r'^2 - R_1'^2 - R_2'^2| = \kappa$ under these transformations. The invariance of κ also follows from the conformal invariance of cross ratios [19]. The inversion maps two nonoverlapping spheres 1, 2 in an infinite critical medium onto two nonoverlapping spheres 1′, 2′ in an infinite critical medium if the origin or inversion point is chosen outside spheres 1 and 2. If the origin is chosen inside one of the spheres, say, sphere 2, sphere 1′ is completely enclosed by sphere 2′. This has also been pointed out by Gnutzmann and Ritschel [20]. Thus the free energies of two spheres in an unbounded critical fluid and of one sphere in a spherical tank of critical fluid are both given by the same universal function,

$$\Delta F_{ab}(r, R_1, R_2) = k_BT_c\mathcal{F}_{ab}(\kappa), \tag{4}$$

of a single variable κ, with $1 < \kappa < \infty$. Equation (4) also follows [19] from an analysis in terms of the stress tensor.

The asymptotic form of $\mathcal{F}_{ab}(\kappa)$ for $\kappa \to 1$ is determined by the Casimir interaction (2) for parallel plates. Considering the case $r = 0$ of concentric spheres and comparing Eqs. (2)–(4) in the limit $R_1, R_2 \to \infty$ with $L = R_2 - R_2$ fixed, we obtain

$$\mathcal{F}_{ab}(\kappa) \approx S_d\Delta_{ab}[2(\kappa - 1)]^{-(d-1)/2}, \qquad 0 < \kappa - 1 \ll 1. \tag{5}$$

Here $S_d = 2\pi^{d/2}\Gamma(d/2)^{-1}$ is the surface area of the d-dimensional unit sphere.

The asymptotic form (5) determines the Casimir interaction of two spheres in an unbounded critical fluid that nearly touch [18]. In the limit $D \ll R_1, R_2$, where $D = r - R_1 - R_2$ is the distance between the closest points of the spheres, $\kappa \approx 1 + (R_1^{-1} + R_2^{-1})D$, and

$$\Delta F_{ab}(r, R_1, R_2) \approx k_BT_cS_d\Delta_{ab}[2(R_1^{-1} + R_2^{-1})D]^{-(d-1)/2}, \quad D \ll R_1, R_2. \tag{6}$$

We now consider the opposite limit of spheres far apart in comparison with their radii. In the spirit of the operator-product expansion [17] we make a "small-sphere expansion" of the Boltzmann factor $\exp[-\Delta\mathcal{H}_a(\mathbf{r}, R)]$ of a sphere of radius R with boundary condition a centered at $\mathbf{r}$ in terms of a complete set of local operators in the form

$$\exp[-\Delta\mathcal{H}_a(\mathbf{r}, R)] = d_a[1 + c_a^{\phi}R^{x_\phi}\phi(\mathbf{r}) + c_a^{\varepsilon}R^{x_\varepsilon}\varepsilon(\mathbf{r}) + \cdots]. \tag{7}$$

Here only three terms in the expansion, the identity operator, the order parameter ϕ, and the energy density ε, are shown explicitly. The quantities d_a, c_a^{ϕ}, c_a^{ε} are constant coefficients, and x_ϕ and x_ε are the scaling dimensions of ϕ and ε, given in terms of conventional critical exponents by

$$x_\phi = \beta/\nu = \tfrac{1}{2}(d - 2 + \eta), \qquad x_\varepsilon = d - 1/\nu. \tag{8}$$

The factors $R^{x_\phi}, R^{x_\varepsilon}$ are required for scale invariance.

Conformal invariance implies a relation between the coefficients c_a^{ψ}, with $\psi = \phi, \varepsilon$ in Eq. (7), and the more familiar amplitudes B_ψ and A_a^{ψ} defined by the bulk correlation function

$$\langle\psi(\mathbf{r}_1)\psi(\mathbf{r}_2)\rangle_{\text{bulk}} = B_\psi\, r^{-2x_\psi} \tag{9}$$

and the profile

$$\langle\psi(r_\perp)\rangle^a_{\text{half space}} = A_a^{\psi}\,(2r_\perp)^{-x_\psi} \tag{10}$$

in the half space $r_\perp > 0$ with boundary condition a. This may be seen as follows: Outside a single spherical boundary centered at the origin of an infinite critical system,

$$\langle\psi(\mathbf{r})\rangle^a_{\text{sphere}} = A_a^{\psi}(R^{-1}|r^2 - R^2|)^{-x_\psi}, \tag{11}$$

as derived in [21] from a conformal mapping of the half-space profile (10). In the limit $r \gg R$, $\langle\psi(\mathbf{r})\rangle^a_{\text{sphere}}$ may also be calculated in the form $\langle\psi(\mathbf{r})\exp[-\Delta\mathcal{H}_a(\mathbf{0}, R)]\rangle_{\text{bulk}}\langle\exp[-\Delta\mathcal{H}_a(\mathbf{0}, R)]\rangle_{\text{bulk}}^{-1}$ with the small-sphere expansion (7). Equating the two expressions yields

$$A_a^{\psi}(R^{-1}r^2)^{-x_\psi} = \langle\psi(\mathbf{r})[c_a^{\phi}R^{x_\phi}\phi(\mathbf{0}) + c_a^{\varepsilon}R^{x_\varepsilon}\varepsilon(\mathbf{r})]\rangle_{\text{bulk}}. \tag{12}$$

Inserting Eq. (9) into (12) and setting $\psi = \phi$ and $\psi = \varepsilon$, we obtain

$$c_a^{\phi} = A_a^{\phi}/B_{\phi}, \qquad c_a^{\varepsilon} = A_a^{\varepsilon}/B_{\varepsilon}. \tag{13}$$

Unlike fixed-spin boundary conditions, ordinary (O) and special (Sp) boundary conditions [13] do not break the Ising up-down or XY rotational symmetry. Thus $c_O^{\phi} = c_{\mathrm{Sp}}^{\phi} = 0$, $A_O^{\phi} = A_{\mathrm{Sp}}^{\phi} = 0$ in Eqs. (7) and (10).

Including a contribution (7) for each sphere in (1), we write the free energy of n widely separated spheres in an infinite critical medium as

$$\Delta F_{a_1 \cdots a_n}(\mathbf{r}_1, \ldots, \mathbf{r}_n, R_1, \ldots, R_n) = -k_B T_c \ln \left\langle \prod_{i=1}^{n} [1 + c_{a_i}^{\phi} R_i^{x_\phi} \phi(\mathbf{r}_i) + \cdots] \right\rangle_{\mathrm{bulk}}. \tag{14}$$

For $n = 2$ only pair correlation functions (9) appear in Eq. (14), and from (9) and (13)

$$\Delta F_{ab}(r, R_1, R_2) \approx -k_B T_c \frac{A_a^{\psi} A_b^{\psi}}{B_{\psi}} \left(\frac{R_1 R_2}{r^2} \right)^{x_\psi}, \qquad r \gg R_1, R_2, \tag{15}$$

$$\mathcal{F}_{ab}(\kappa) \approx -\frac{A_a^{\psi} A_b^{\psi}}{B_{\psi}} (2\kappa)^{-x_\psi}, \qquad \kappa \gg 1. \tag{16}$$

Here $\psi = \phi$ for symmetry-breaking boundary conditions on both spheres, and $\psi = \varepsilon$ if neither of the two spheres or only one has symmetry-breaking boundary conditions. Note that for equal boundary conditions on both spheres the Casimir interaction (15) is attractive.

For arbitrary n the right side of (14) may be expanded in cumulants of many-point correlation functions. For widely separated spheres all but the two-point correlations may be neglected [22], and the Casimir interaction reduces to a sum of two-body terms (15).

The Casimir interaction of a single sphere with the planar boundary of a semi-infinite critical system follows from our results for two spheres in the limit $R_2 \to \infty$. Denoting the radius of the single sphere by R, and the distance from its center to the planar boundary by $R + D$, we obtain $\kappa = 1 + R^{-1}D$ from Eq. (3). From this result and Eqs. (4), (5), and (16),

$$\Delta F_{ab}(D, R) \approx k_B T_c \times \begin{cases} S_d \Delta_{ab} \left(\frac{R}{2D} \right)^{(d-1)/2}, & D \ll R, \\ -\frac{A_a^{\psi} A_b^{\psi}}{B_{\psi}} \left(\frac{R}{2D} \right)^{x_\psi}, & D \gg R, \end{cases} \tag{17}$$

where $\psi = \phi$ if both boundaries have symmetry-breaking boundary conditions and $\psi = \varepsilon$ otherwise.

For the Ising model in $d = 2$, $x_\phi = \frac{1}{8}$, $x_\varepsilon = 1$, and

$$(A_{\uparrow}^{\phi})^2 / B_{\phi} = \sqrt{2}, \qquad (A_O^{\varepsilon})^2 / B_{\varepsilon} = 1, \tag{18}$$

with $A_{\uparrow}^{\phi} = -A_{\downarrow}^{\phi}$, $A_O^{\varepsilon} = -A_{\uparrow}^{\varepsilon} = -A_{\downarrow}^{\varepsilon}$, as follows from Cardy's results [23] for $\langle \phi \phi \rangle$ and $\langle \varepsilon \varepsilon \rangle$ in the half plane. The exact scaling function $\mathcal{F}_{ab}(\kappa)$ for the $d = 2$ Ising model is shown in Fig. 1. The curves were calculated from the partition function of the finite critical Ising model on a cylinder [6], using a conformal mapping onto an annulus. The curves interpolate smoothly and monotonically between the asymptotic expressions (5) and (16), indicated by dashed lines. For equal boundary conditions $ab = \uparrow\uparrow$, OO, $\mathcal{F}_{ab}(\kappa)$ is negative, corresponding to an attractive Casimir force. For unequal boundary conditions $ab = \uparrow\downarrow$, $\uparrow O$, $\mathcal{F}_{ab}(\kappa)$ is positive, and the Casimir force is repulsive.

For the Ising model [24] in $d = 3$, $x_\phi = 0.518$ and $x_\varepsilon = 1.41$. In $d = 4 - \epsilon$

$$\frac{(A_{\uparrow}^{\phi})^2}{B_{\phi}} = 45\epsilon^{-1} \left(1 - \frac{62}{27}\epsilon + O(\epsilon^2) \right), \tag{19}$$

$$\frac{(A_O^{\varepsilon})^2}{B_{\varepsilon}} = \frac{1}{2}[1 + O(\epsilon^2)],$$
$$\frac{(A_{\mathrm{Sp}}^{\varepsilon})^2}{B_{\varepsilon}} = \frac{1}{2} \left(1 + \frac{2}{3}\epsilon + O(\epsilon^2) \right), \tag{20}$$

where A_O^{ε} and $A_{\mathrm{Sp}}^{\varepsilon}$ have opposite signs [19]. Assuming that $(A_a^{\psi})^2 B_{\psi}^{-1}$ varies monotonically with d for $2 \leq d \leq 4$ and comparing Eqs. (18) and (19), we expect $(A_{\uparrow}^{\phi})^2 B_{\phi}^{-1}$ in $d = 3$ to be somewhat larger than $\sqrt{2}$ and $(A_O^{\varepsilon})^2 B_{\varepsilon}^{-1}$ and $(A_{\mathrm{Sp}}^{\varepsilon})^2 B_{\varepsilon}^{-1}$ to lie between $\frac{1}{2}$ and 1. For the XY model [24] in $d = 3$, $x_\phi = 0.519$, and $x_\varepsilon = 1.51$.

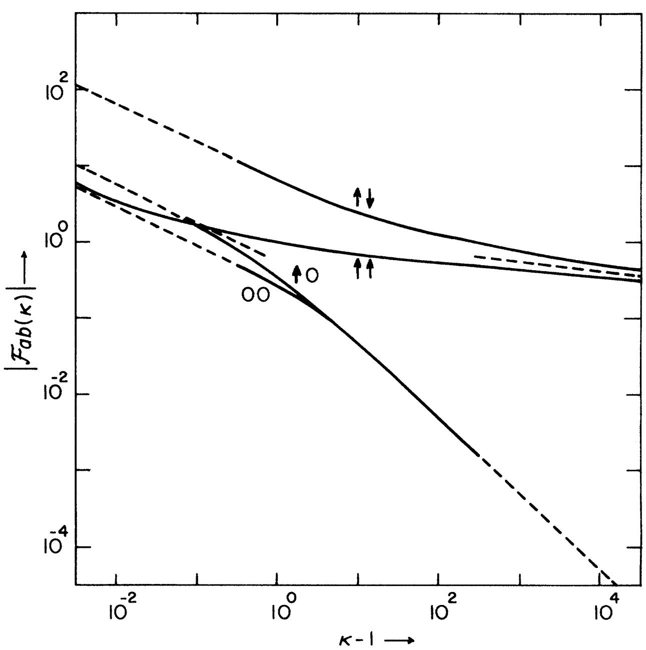

FIG. 1. Absolute value of the scaling function $\mathcal{F}_{ab}(\kappa)$ for the $d = 2$ Ising model. The absolute values of the asymptotic forms (5) and (16) are indicated by dashed lines. $\mathcal{F}_{ab}(\kappa)$ is negative for like boundary conditions $ab = \uparrow\uparrow$, OO and positive for mixed boundary conditions $ab = \uparrow\downarrow$, $\uparrow O$.

The values of x_ϕ and x_ε in $d = 3$ imply an $r^{-1.04}$ decay of the Casimir potential energy of two widely separated colloidal particles in a one-component fluid at the liquid-vapor critical point or a binary mixture at the consolute point (Ising model with $\uparrow\uparrow$ boundary conditions). This is in excellent agreement with the r^{-1} decay in de Gennes' approximate theory [15]. For colloidal particles in helium at the lambda temperature (XY model with OO boundary conditions) the Casimir potential decays as $r^{-3.02}$. The amplitude is given in Eq. (15), with $(A_a^\psi)^2 B_\psi^{-1}$ of order 1. The Casimir force decays much more slowly than the van der Waals force and is stronger than the van der Waals force for all $r \gtrsim R_1 + R_2$. For the $r^{-1.04}$ decay the volume integral $\int d^3r\, \Delta F_{ab}(r, R_1, R_2)$ diverges; i.e., the total potential energy of a homogeneous configuration of colloidal particles is more than extensive. In the case of the $r^{-3.02}$ decay the volume integral almost diverges. Note that the $r^{-1.04}$ interaction differs only slightly from the r^{-1} potential of Newtonian gravitation. The thermodynamics of systems controlled by gravitational forces is an extensively studied, still controversial topic [25].

Liquid-vapor-like transitions of colloidal particles in nearly critical fluids due to the van der Waals attraction of the particles have been analyzed theoretically and experimentally [26]. Even if the van der Waals force alone is not strong enough to produce a phase transition of the colloidal particles, they should form a condensed phase at the critical point of the fluid due to the strong, long-range Casimir force. Since the correlation length grows as the critical point is approached from above or below, we expect aggregation or flocculation due to the Casimir force for $T_1 < T < T_2$, where the temperatures T_1 and T_2 marking the onset of flocculation are on opposite sides of T_c.

Flocculation of colloidal particles in nearly critical fluids has been observed [14] experimentally. In addition to the Casimir force other possible mechanisms, such as a modification of the interparticle potential due to critical adsorption, have been suggested. We hope that our quantitative predictions will be useful in clarifying the role of the Casimir force in experiments of this type. It would be interesting to have experimental results on the behavior of colloidal particles in liquid ^{4}He near the lambda transition, since the ordinary boundary condition does not favor critical adsorption.

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