

THE CRITICAL CASIMIR EFFECT UNIVERSAL FLUCTUATION-INDUCED FORCES AT WORK

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▲ The demixing of water and the solvent 2,6-lutidine (seen here in false colours), is Hertlein and colleagues' laboratory for measuring the critical Casimir force.
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It is well known that nothing comes from nothing. In physics, however, this is not always the case. Surprisingly indeed, two electrically neutral conducting metallic plates placed in vacuum about half a micrometer apart attract each other, even at zero temperature, due to a force which was theoretically predicted in 1948 by the Dutch physicist Hendrik Casimir [1]. This force originates from the quantum mechanical fluctuations of the electromagnetic field in vacuum - so, apparently, from nothing.

In the absence of the plates, these fluctuations are the same everywhere. But if the plates are introduced, a distance L apart, the fluctuation modes need to have a node at the plate surfaces, so that only waves with wavelength $\lambda = nL/2$ and integer n are permitted in the gap between the plates. Outside, instead, there is no such restriction. As a consequence the total field outside the gap produces a pressure on the plates which is higher than the one produced from inside, so the surfaces are pushed together by a force F . The force per unit area A of the plates takes the form

$$\frac{F}{A} = -\frac{\pi^2 \hbar c}{240 L^4} \quad (1)$$

for distances L large compared to a characteristic microscopic length $L_c \approx c/\omega_p$. The value of L_c is roughly set by the material-dependent frequency ω_p above which the actual metal is no longer conducting ($L_c \approx 0.1 \mu\text{m}$ for copper).

The asymptotic expression of this long-ranged force has a universal character in that it depends only on the speed of light c and on Planck's constant \hbar but not on the material properties of the plates which determine only the actual value of L_c . The absence in Eq. (1) of

such material parameters, which might be sources of experimental uncertainties, makes its experimental verification a particularly stringent test.

The first attempts to verify Casimir's prediction date back to 1958, but a sufficiently accurate measurement of F at the micrometer scale has been accomplished first only in 1997 [2] due to the relative weakness of the force: Two plates of area $A = 1 \text{mm}^2$ at a distance $L = 1 \mu\text{m}$ attract each other with a force of 10^{-9}N . Nonetheless, this effect is responsible for the stiction (static friction) occurring in currently available microelectromechanical systems (MEMS), in which different device parts cling together, hampering their functioning [3].

Casimir, in collaboration with D. Polder, actually had already derived Eq. (1) by showing that the interaction potential $V(R)$ between two neutral atoms at a distance R , due to their fluctuating electric dipole moments, is affected by the finite speed of light c (retardation). As a result $V(R)$ changes from the London-van der Waals behaviour $1/R^6$ to $1/R^7$ as R increases. Equation (1) actually reflects this asymptotic behavior for large R . Surprised by the fact that the final result of their lengthy calculation for $V(R)$ was so simple in the limit $R \rightarrow \infty$, Casimir (following a suggestion by Niels Bohr) looked for a simpler derivation focussed on

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vacuum fluctuations. This kind of focus has far-reaching consequences when carried over to cases in which fluctuations of a different nature occur. Casimir's line of argument, indeed, does not rely on the fact that the fluctuating quantity is actually the electromagnetic field of the vacuum and that its fluctuations are of *quantum* nature. What really matters is the presence of any such a quantity and a mechanism by which physical boundaries modify the spectrum of its allowed fluctuations, so that the corresponding total free energy depends on the distance between the boundaries. Due to this dependence, as Casimir pointed out, the boundaries experience an effective, fluctuation-induced force. These basic requirements are so modest that indeed one encounters such kind of fluctuation-induced forces in a wide range of circumstances, well beyond the context of quantum electrodynamics, ranging from cosmology to statistical physics, making the subject really fascinating (see, e.g., Ref. [4]).

Thermal fluctuations at work: the critical Casimir effect

In the following we focus on *thermal* fluctuations which occur in statistical physics, in particular close to continuous phase transitions where their effects are particularly pronounced, such that their confinement leads – in analogy to the Casimir force – to the so-called critical Casimir effect. In statistical physics fluctuations are due to the thermal motion of atoms and molecules. Therefore they typically occur on a molecular scale ξ_0 .

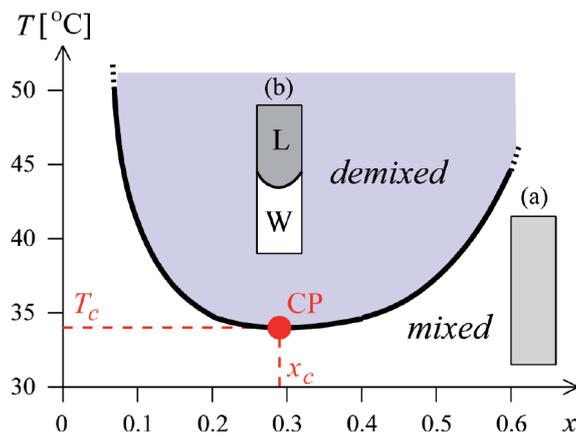
Consider the case of a liquid which is kept at room temperature T . If one sets out to measure its density from a sample of volume 1 mm^3 there is no chance to detect appreciable fluctuations around its average. In order to observe such fluctuations one has to decrease the volume to a few nm^3 , corresponding to the typical spatial linear scale ξ_0 at which fluctuation of the density of a fluid occur under normal conditions.

All fluctuation effects, including possible Casimir-like forces, are relevant at this scale and disappear at larger ones. In addition, one cannot expect these forces to be characterized by universal laws such as the one derived by Casimir, because the physical phenomena at the molecular scale are dominated by the specific microscopic details of the fluid.

There are instances, however, in which the fluctuations become relevant and detectable even at scales ξ much larger than the molecular ones, i.e., $\xi \gg \xi_0$.

This emerges upon approaching a second-order phase transition point (also called *critical point*, located at specific values T_c and P_c of temperature and pressure, respectively) which is characterized by the fact that due to the emerging collective behavior of the molecules,

fluctuations in the density are correlated across the so-called *correlation length* ξ which increases with a power law for $T \rightarrow T_c$. At scales large compared with ξ_0 the resulting physical behavior of the system turns out to be largely independent of its microscopic details (giving rise to the concept of “*universality*”). In a certain sense, a critical point acts as a magnifying glass for the fluctuations which occur in any case at the molecular scale. Critical points are present in the phase diagrams of a wide variety of microscopically different systems, ranging from classical and quantum fluids (for example ^4He close to the superfluid transition) to nuclear matter. In each case the relevant quantity – called “*order parameter*” –, the thermal fluctuations of which are magnified upon approaching the critical point, has a different physical nature but plays the same role in determining the free energy density of the system.



◀ FIG. 1: Schematic phase diagram of the liquid mixture of water with the oily liquid 2,6-lutidine (dimethylpyridine, C_7H_9N). At ambient pressure, the relevant thermodynamic variables are the temperature T and the mass fraction x of lutidine in the mixture. The schematic side view of a vertical test tube filled with the binary liquid mixture is shown by (a) and (b). In (b) W and L indicate the water- and the lutidine-rich phase, respectively.

The effective force resulting from the confinement of the fluctuations of the order parameter is called “*critical Casimir force*” [5] and was first discussed in 1978 by Michael Fisher and the late Pierre-Gilles de Gennes in their study of the behavior of a binary liquid mixture made up of two components and confined between two plates [6]. (An independent field-theoretical analysis was carried out by Symanzik [7].)

The phase diagram of a binary liquid mixture, for example water and lutidine (a clear oily substance), is depicted in Fig.1: For a fixed lutidine mass fraction x , the mixture forms a mixed solution at low temperatures (as indicated by the inset (a)), whereas it separates into a water-rich (W) and a lutidine-rich (L) phase if the solution is heated above the transition line (inset (b)).

At the critical point $T_c \approx 34^\circ\text{C}$ and $x_c \approx 0.286$ (CP in Fig.1), the two phases do not form abruptly, like water solidifying into ice. Instead, at the critical concentration and below the critical temperature, fluctuating areas form in the mixture which contain more water or more lutidine. The closer the temperature gets to the critical point, the

larger these fluctuating areas grow and the longer they remain intact. Actually, the typical size of these correlated fluctuation diverges as $\xi \approx \xi_0 |1 - T/T_c|^{-\nu}$, where $\nu \approx 0.63$ characterizes the type of critical point. The order parameter for this mixture is the difference between the local concentration of water and lutidine compared with their average values and therefore it increasingly fluctuates upon approaching the critical point.

If two plates at close distance are introduced in the mixture, analogously to the quantum Casimir effect, each of them sets boundary conditions by preferring to be in contact with one of the two components of the binary mixture. The corresponding boundary conditions are referred to as $(++)$ (or $(--)$) if the two plates prefer the same component of the mixture and $(+-)$ (or $(-+)$) if they have opposite preferences.

The resulting critical Casimir force F on the plates of area A , a distance L apart, is theoretically expected to be largely independent of the microscopic details of the fluctuating medium and of the boundary conditions. Indeed, for $\xi, L \gg \xi_0$ it takes the form

$$\frac{F}{A} = \frac{k_B T}{L^3} \Theta(L/\xi) \quad (2)$$

where k_B is Boltzmann's constant and $k_B T$ the thermal energy. In contrast to the quantum Casimir effect, the range of the force F is now set by the correlation length ξ

of the critical fluctuations, which can be controlled by the temperature T . The function $\Theta(u)$ is *universal* in that it depends only on certain gross features of the critical behavior of the system and on the kind of boundary conditions imposed by the plates on the order parameter, *i.e.*, $(++)$ or $(+-)$ for a

binary liquid mixture of classical fluids. Most of the details about the molecular structure of the fluid and its microscopic interactions with the atoms constituting the plates are of no importance in determining F as long as the correlation length ξ and the distance L are much larger than the microscopic length scales of the system.

This universality allows one to determine the function $\Theta(u)$ by studying a slab of the Ising model with surface fields. For the type of fluid under consideration such a study has been recently carried out via Monte Carlo simulations [8]. It turns out that the force F can be made repulsive by changing the boundary conditions from $(++)$ to $(+-)$. Such a possibility is still debated for the quantum Casimir force. A rough estimate of F reveals that at room temperature, for two plates with $A = 1 \text{ mm}^2$ and at a distance $L = 1 \mu\text{m}$, the expected force is about 10^{-9} N .

Due to this weakness its experimental detection is particularly difficult. Indeed, only in 1999 the first indirect experimental evidence was provided by capacitance studies of wetting films of liquid ^4He close to the superfluid transition [9] and by X-ray studies of wetting films of a binary liquid mixture in 2005 [10]. Close to the corresponding critical points, the thicknesses of these liquid films change and this phenomenon can be successfully explained by the occurrence of critical Casimir forces.

In order to measure directly the force acting on an object, the simplest approach is to attach to it a suitable dynamometer and then read off the result from the scale. This approach would suggest the use of the cantilever of an atomic force microscopy, capable to measure forces with pico-Newton resolution ($1 \text{ pN} = 10^{-12} \text{ N}$), but this turns out to be still too difficult.

The measurement of the Casimir force is actually easier if, instead of considering the force acting between two parallel plates immersed in the fluctuating medium, one considers the force acting on an immersed spherical particle of radius R when it approaches the wall of the container of the mixture. As in the previous cases both the wall and the sphere impose boundary conditions on the order parameter and as a consequence a critical Casimir force F acts on the sphere. If the distance of closest approach z between the sphere and the wall is much smaller than the radius R , the potential $\Phi_c(z)$ of the critical Casimir force takes the form

$$\frac{\Phi_c(z)}{k_B T} = \frac{R}{z} \vartheta(z/\xi) \quad (3)$$

where the function ϑ can be expressed in terms of Θ [11] and it shares the same qualitative and universal properties. With this change in the geometrical setting the experimental challenge is to determine the force acting on the sphere. In order for the effects of F to be detectable on a sphere floating in the mixture, its magnitude has to be comparable with the typical forces at play. This suggests the use of micrometer-sized polystyrene particles, *i.e.*, *colloids*.

A femto-Newton dynamometer

The sensitivity necessary to directly measure the critical Casimir force can be achieved by total internal reflection microscopy (TIRM [12], see Fig.2) which actually is capable to measure forces with femto-Newton resolution [13] ($1 \text{ fN} = 10^{-15} \text{ N}$).

A laser beam is totally reflected at the silica wall of the container of the mixture, so that an evanescent wave penetrates into the mixture with an intensity $I_{ev}(z) \propto \exp(-\kappa z)$, which decreases exponentially upon increasing the distance z from the wall, with a decay length κ^{-1} . When the colloidal particle approaches the wall with surface to

The force we have measured can be easily turned from attractive to repulsive by suitable surface treatments

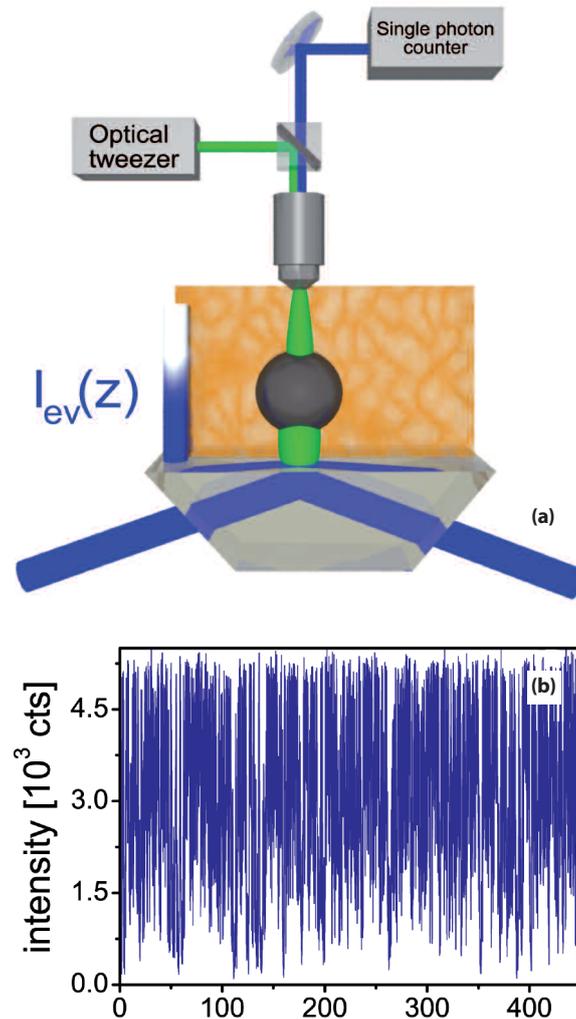
■ surface distance z , it scatters light off the evanescent wave and the scattered intensity is proportional to $I_{ev}(z)$. A single photon counter measures the scattered intensity $I_{sc}(z)$, from which one infers the distance $z = -\kappa^{-1} \ln[I_{sc}(z)/I_{sc}(0)]$. An optical tweezer provides the lateral force which avoids the drift of the particle out of the objectives of the microscope. The colloid is actually so small that it is sensitive to the collisions with the molecules of the fluid which cause it floating randomly in the mixture as in the celebrated Brownian motion. As a result, the distance z randomly changes in time and this is actually detected by the single photon counter which measures a randomly varying scattered intensity I_{sc} as a function of time (see Fig. 2(b)). From this signal one determines the probability distribution function $P(z)$ that characterizes the erratic motion of the particle. In thermal equilibrium $P(z)$ is given by the Boltzmann distribution associated with the total potential $\Phi(z)$ to which the particle is subjected: $P(z) \propto \exp\{-\Phi(z)/(k_B T)\}$. This theoretical relation allows one to determine the potential $\Phi(z)$ from the apparently meaningless random signal $I_{sc}(t)$ associated with the Brownian motion of the colloid.

With this technique at hand one can study the onset of critical Casimir forces on the colloid as the temperature T of the binary mixture is increased towards its critical value T_c , at fixed critical concentration $x = x_c$.

First we consider the case of an hydrophilic colloid of radius $R = 1.2 \mu\text{m}$ and a hydrophilic wall, corresponding to $(--)$ boundary conditions. (With reference to the water-lutidine mixture we indicate by “+” and “-” the preferential adsorption of lutidine and water, respectively.) Far from the critical point the measured potential $\Phi(z)$ (apart from the contribution of buoyancy and of the optical tweezer, which are subtracted from the data presented in Fig. 3) is given only by the electrostatic repulsion between the colloid and the wall, as shown in Fig. 3(a) for $T_c - T = 0.30\text{K}$.

Upon heating the mixture, however, an increasingly deep potential well develops, which is due to the attractive Casimir force providing a negative contribution $\Phi_c(z)$. As expected theoretically, the spatial range ξ of this contribution increases upon increasing T . The set of measured $\Phi_c(z)$ can be compared with the corresponding theoretical prediction (Eq. (3), solid lines in Fig. 3(a)), resulting in a remarkable agreement. The maximum of the attractive force measured in this case is about 600 fN.

If one exchanges the hydrophilic colloid with an hydrophobic one (of radius $R \approx 1.8 \mu\text{m}$), the corresponding boundary conditions change from $(--)$ to $(+-)$ and on theoretical grounds one expects repulsion. Indeed, in this case, areas rich in water form at the wall, whereas those rich in lutidine stay close to the colloid. Since it takes free energy to make contact between these water- and lutidine-rich



◀ FIG. 2: The femto-Newton dynamometer. (a) Scheme of the TIRM set-up. A colloidal particle undergoes thermal motion in the evanescent field I_{ev} created by a totally reflected blue laser beam and scatters light, whose intensity $I_{sc}(z)$ is measured by a single photon counter. The lateral diffusion of the particle is prevented by a vertically incident green optical tweezer. (b) I_{sc} as a function of time, reflecting the random motion of the particle in the vertical direction. (Taken from Ref. [11].)

regions, the sphere is repelled. As in the previous experiment, far below the critical point, $\Phi(z)$ consists only of the electrostatic repulsion, as in Fig. 3(b) for $T_c - T = 0.90\text{K}$. Upon heating the mixture, the repulsive part of the potential curves shifts towards larger values of z due to the fact that, as expected, repulsive Casimir forces are acting on the particle and yield a positive contribution $\Phi_c(z)$ to the total potential $\Phi(z)$. As in the case of Fig. 3(a), one finds a remarkable agreement with the corresponding theoretical prediction (Eq. (3), solid lines in Fig. 3(b)).

By changing the adsorption preference of the silica wall from hydrophilic $(-)$ to hydrophobic $(+)$ via a suitable chemical surface treatment, attraction is recovered (data not shown). In contrast to the smooth onset of the critical Casimir force, in mixtures with $x \neq x_c$ and $(--)$ or $(++)$ boundary conditions one observes the abrupt formation of a potential well upon approaching the transition line. This occurs only on the side of the phase diagram where the mixture is poor in the component preferentially adsorbed by both surfaces and is due to the sudden formation of a liquid bridge which spans the space between the particle and the wall and is rich in the component preferred by the surfaces [11].

Concluding remarks

We have observed and measured the fluctuation-induced critical Casimir forces between a colloid and a wall [11]. Based on the general argument presented above, one expects them to act also between two or more colloidal particles immersed in a near-critical mixture, with interesting many-body phenomena due to the non-additivity of these fluctuation-induced forces. In contrast with other types of interactions which are typically acting among colloids (e.g., electrostatic) the critical Casimir force exhibits a striking temperature dependence which can be exploited in order to control the phase behaviour of such particles via minute temperature changes. This fact could be used, for example, in order to control the aggregation of colloids, which is a central problem in many areas of materials science where colloidal particles dispersed in a solvent form the basis of diverse substances such as milk or paints. The force we have measured can be easily turned from attractive to repulsive by suitable surface treatments. This property might be used in order to compensate the attractive quantum mechanical Casimir force which brings MEMS to a standstill. If these machines would work not in a vacuum, but in a liquid mixture close to the critical point, the stiction could be prevented by coating the machine parts so that the critical Casimir force has a repelling effect. Our combined experimental and theoretical approach demonstrates that the minute forces which result from random thermal fluctuations at the sub-micrometer scale can be harnessed to serve dedicated purposes. ■

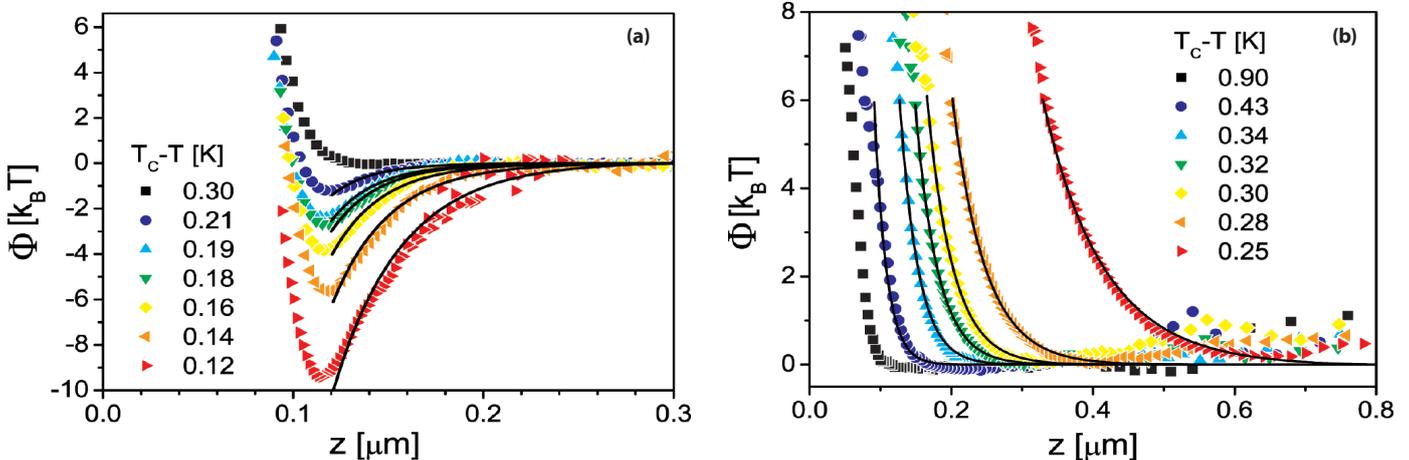
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▲ FIG. 3: Critical Casimir potentials for a colloidal particle in a water-lutidine mixture and close to a hydrophilic wall (from Ref. [11]). Upon approaching the critical point, an attractive Casimir force is observed with an hydrophilic particle (--- boundary conditions, (a)), whereas with an hydrophobic particle (+-) boundary conditions, (b) the force is repulsive. The solid lines in (a) and (b) correspond to the theoretical predictions for the Casimir potentials.