CONTROLLING AND HARNESSING CRITICAL CASIMIR FORCES

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This contribution provides a brief overview of recent advances in the theoretical and experimental study of the critical Casimir effect originating from the confinement of the enhanced thermal fluctuations which occur close to a critical point. The resulting effect turns out to be highly tunable, it influences the behavior of soft matter, from wetting films of fluids to colloidal dispersions, and therefore might find applications for the manipulation of matter at the micrometer and sub-micrometer scale.

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1. The critical Casimir effect

Quite generally, whenever a medium in which fluctuations of some physical nature take place is confined, effective forces arise on the confining boundaries. Perhaps the best-known example is the Casimir effect in quantum electrodynamics. An analogous effect arises in statistical physics when the relevant fluctuations are the thermal ones of the order parameter \( \phi \) of a near-critical medium such as pure \(^4\)He close to the normal/superfluid transition or a classical binary liquid mixture close to the demixing critical point. These fluctuations are characterized by a temperature-dependent spatial correlation length \( \xi \sim \xi_0 |T/T_c - 1|^{-\nu} \) which also sets the range of the resulting force. Here \( T_c \) is the temperature of the bulk critical point, \( \xi_0 \) a (microscopic) material-dependent length, and \( \nu > 0 \) a universal critical exponent. Assuming that the medium is confined within a film of thickness \( L \), if \( L \) and \( \xi \) are much larger than the microscopic molecular scale \( \xi_0 \), the temperature dependence of this critical Casimir force \( F \) becomes largely independent of the specific material properties of the medium and of the film surfaces but depends only on some of their gross features. In particular,
upon approaching the critical point, the specific interaction between the medium and the confining surfaces (provided by, e.g., a solid substrate or the interface between the fluid medium and its vapor), which locally affects the order parameter $\phi$, eventually results into effective boundary conditions (BCs) for $\phi$. The character of such BCs is again largely independent of the material properties of each surface and of its interaction with the fluid but depends only on the absence ($O$) or the presence of preferential adsorption with enhancement ($+$) or depletion ($-$) of $\phi$ at the surfaces. All these informations are encoded in the scaling function $\vartheta$, which is universal in the specific sense of critical phenomena and determines the force $F$ per area $S$ acting on the boundaries, as a function of the correlation length $\xi$ and the thermal energy $k_B T$:

$$ F = \frac{k_B T}{L^3} \vartheta(L/\xi). $$

(1)

Due to the universality which characterizes $\vartheta$, a theoretical analysis of critical Casimir forces in a certain system can be done by studying suitable representative models which belong to the same universality class as the medium and the boundaries and which lend themselves for an easier analytical or numerical study (primarily Monte Carlo simulations).

Below we briefly discuss how it is possible to detect and use critical Casimir forces in soft matter systems (a more comprehensive account and list of references can be found in Ref. 3).

2. Indirect evidence: Wetting films

In order to realize and control a film of microscopically large and constant thickness $L$ one can expose to a solid substrate a bulk vapor phase which is thermodynamically close to the condensation transition. Indeed, if the substrate is suitably chosen, a liquid wetting film of a certain equilibrium thickness $L$ condenses on it as a result of an effective repulsive Casimir-Lifshitz interaction. Substrates which strongly attract the fluid undergo complete wetting, so that $L$ becomes microscopically large and diverges as the undersaturation of the vapor phase vanishes. In the resulting wetting film the fluid is naturally confined between the solid/liquid and the liquid/vapor interfaces. If such a confined fluid is driven thermodynamically towards a critical point, the associated critical fluctuations of $\phi$ – which are confined within the wetting film – give rise to a force $F$ as described by Eq. (1). This force displaces the liquid/vapor interface from the equilibrium position it would have under the effect of dispersion forces alone, i.e.,
in the absence of critical fluctuations. Accordingly, by monitoring experimentally the temperature dependence of $L$ along a certain thermodynamic path one has indirect evidence of critical Casimir forces.\textsuperscript{5} This kind of approach was adopted for studying wetting films of pure $^4\text{He}$\textsuperscript{6} and $^4\text{He}/^3\text{He}$ mixtures\textsuperscript{7} close to the normal-superfluid transition and of classical binary mixtures close to the demixing critical point.\textsuperscript{8} These experimental studies turned out to be in a remarkable quantitative agreement with the theoretical predictions based on the Monte Carlo simulations of suitable models.\textsuperscript{9,10} Depending on the properties of the confining surfaces, $F$ can be either attractive [(±, ±) and (O, O) BCs] or repulsive [(±, +) and (±, O)], leading to the observed thinning\textsuperscript{6,8} or thickening\textsuperscript{7} of the wetting films.

3. Direct evidence and applications: Colloids

Similarly to the case of wetting films, a sphere which is immersed in a near-critical fluid is subject to a critical Casimir force when it approaches a flat substrate as the fluctuations of the order parameter are effectively confined within the gap between the surfaces of the sphere and of the substrate. This effect becomes particularly relevant for micrometer-sized particles, known as colloids. Indeed, colloids are typically characterized by an energy scale $k_B T$, i.e., the same as the critical Casimir force [see Eq. (1)]. Accordingly, colloids can be used for a direct measurement of such a force and conversely the latter can be used for manipulating colloids.

If the distance $z$ between the surface of the colloid and the substrate is much smaller than the radius $R$ of the colloid, the critical Casimir force $F$ acting on the sphere is

$$F(z \ll R) = k_B T \frac{R}{z^2} \vartheta_{\parallel}(z/\xi). \tag{2}$$

The scaling function $\vartheta_{\parallel}$ can be calculated on the basis of $\vartheta_{\parallel}$ via the so-called Derjaguin (or proximity-force) approximation, which turns out to be rather accurate already for $z/R \lesssim 0.3$.\textsuperscript{11} In the limit of strong preferential adsorption, $\vartheta_{\parallel}$ retains the same qualitative features as $\vartheta_{\parallel}$, being negative (attractive $F$) for (sphere, substr.) = (±, ±) BCs and positive (repulsive $F$) for (±, +) BCs. The critical Casimir potential $\Phi(z) = \int_{z}^{\infty} dz' F(z')$ can be measured by monitoring the Brownian motion of a single colloidal particle close to a substrate, both immersed in a near-critical fluid.\textsuperscript{12,13} A recent experimental measurement of $\Phi(z)$ in a water-lutidine liquid mixture\textsuperscript{12} provided the first direct evidence of the critical Casimir effect, in remarkable quantitative agreement with the theoretical predictions based
on the Derjaguin approximation and on the Monte Carlo results for $\vartheta_\parallel$ in three dimensions. As in the case of wetting films, the sign of $F$ is determined by the preferential adsorptions of the surfaces of the substrate and of the colloid, whereas its range, set by $\xi$, is controlled by minute temperature changes around $T_c$. Due to this high degree of tunability this force might find concrete applications — together with the omnipresent dispersion forces — for operating parts of micro-electromechanical systems. As an illustration, Fig. 1 compares a recent measurement\(^\text{14}\) of the Casimir-Lifshitz force (data points and error bars) acting on a sphere of radius $R = 20 \mu$m, close to a substrate and immersed in a fluid at room temperature $T \simeq 300$ K, to the critical Casimir force (solid lines) expected within the same setting but in the presence of critical fluctuations with correlation length $\xi$ and of surfaces with strong preferential adsorption for the order parameter. In the former case, turning attraction into repulsion requires a change of the bulk substrate from gold (lower data set) to silica (upper set) and a careful selection of the liquid medium (bromobenzene, BB). The resulting force is not significantly affected by changes of $T$. In contrast, in the case of the critical Casimir force, the actual material properties of the medium do not play such a crucial role in determining the strength and sign of the force and they can be suitably selected in order to have a critical point (e.g., of demixing) at a convenient temperature. Moreover, the particle and the substrate can be realized with convenient materials (e.g., silica) via well-established technological processes. The adsorption preferences of their surfaces are then controlled by means of suitable surface treatments. In addition, upon
slightly varying $T$, i.e., for correlation lengths $\xi \approx 5-35$ nm, the range and the strength of the critical Casimir force can be controlled \textit{reversibly} and to a large extent, both in the case of attraction [\((-,-)\) BCs, lower set of solid curves in Fig. 1] and repulsion [\((-,+)\) BCs, upper set].

This pronounced dependence on surface properties makes rather easy to control the spatial direction of the critical Casimir force by exposing the colloid to flat substrates with a spatially varying preferential adsorption.\(^{11,13,15,16}\) This feature might have important applications to central problems in the physics of colloids such as controlling reversibly the spatial distribution and the rheology of dilute solutions, influencing aggregation, phase separation, and dynamics of colloidal mixtures etc. Most of these aspects, however, still need a proper theoretical understanding.

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\section*{References}