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Casimir force in polymer blends with immersed colloids versus temperature

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Abstract

We reexamine here the computation of the Casimir force experienced by colloidal particles immersed in a binary mixture, made of two chemically incompatible polymers of high-molecular-weight. Such a force originates from the strong fluctuations of composition near the consolute point T_c , and the fact that one polymer of the mixture prefers to be attracted by colloids (critical adsorption). More precisely, we aim at a quantitative investigation of the temperature effect on the force expression, when one is far from T_c . To achieve calculations, we use the standard φ^4 -theory, where the field φ represents the composition fluctuation (*order parameter*). Combining this theory with the standard cumulant method, we first find that the effective pair-potential is the sum of two contributions, which are directly proportional to the bulk two-point correlation functions constructed with fields φ and φ^2 , respectively. Second, taking advantage of the exactly known (mean-field) correlation functions, we demonstrate that the expected force can be

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expressed in term of the modified Bessel functions $K_1(z)$ and $K_2(z)$. Third, we show that the reduced Casimir force $D.F(r)/k_B T$ is a universal two-factor scaling function of the dimensionless variables r/D and ξ/D , where r is the interparticle-distance, ξ the thermal correlation length of the free polymer mixture and D the scale-distance $D = d_0 \times N^{1/2}$, where d_0 is the particles diameter and N the polymerization degree of chains. The essential conclusion is that, for high or low temperatures, the induced force becomes *less important* than that at the critical one.

Keywords : Polymer blends - Colloids - Casimir force - Temperature effects.

I. Introduction

The induced forces generated by fluctuations of some physical entity is one of the most fundamental discoveries of the last century. Already in 1948 Casimir predicted the attraction between two parallel perfectly conducting plates at zero temperature [1]. This attraction originates from the vacuum quantum fluctuations of the electromagnetic field confined between these plates. From an experimental point of view, the electromagnetic induced force has been measured between metal surfaces in a series of recent experiments [2 – 5].

The same effect also appears in other areas of physics. Indeed, in their short theoretical note, Fisher and de Gennes [6] pointed out that a similar effect can be present in the context of Statistical and Condensed Matter Physics. More precisely, this effect is inherent to those critical systems, such as a fluid near the liquid-gas critical point, a binary liquid (or a polymer mixture) near the demixing temperature, a liquid ^4He near the λ -transition or liquid-crystals. For these systems, the critical fluctuations of the order parameter play an analog role than the vacuum quantum fluctuations, and then give rise to long-range forces between the confining walls.

Theoretically, the induced forces related to critical systems confined between two parallel walls or in the presence of immersed colloidal particles, have been the subject of a great deal of attention [6 – 23]. Very recently, one has also investigated the Casimir effect in critical polymer blends or ternary polymer solutions [24 – 28].

Experimentally, several works have been devoted to the confined critical systems [29 – 37]. For instance, one has investigated, in some experiments [29 – 33], the behavior of silica beads of diameter of the order of $0.1 \mu\text{m}$ immersed in binary liquid mixtures of lutidine and water. The experiments revealed that, in the vicinity of the consolute point of the free binary liquid, one assists to a *reversible* flocculation of colloids in the water-rich side. In fact, this aggregation is due to a preferential adsorption of lutidine on the surface of colloids.

In this paper, we consider a low density assembly of spherical colloids, which are

immersed in a mixture of two polymers A and B of different chemical nature, at a temperature not necessary close to the critical one T_c . We suppose that, near T_c , the colloids adsorb preferentially the polymer chains A as in liquid mixtures of small molecules case. As consequence, this preferential adsorption leads to a reversible aggregation of particles in the non-preferred B -rich phase. This flocculation results from a long-range induced force we want to compute. Naturally, the latter depends on interparticle-distance, temperature and bulk and surface universality classes. We restrict ourselves here to the surface universality class, which corresponds to the situation of high chemical potential exchange on the surface of the interacting colloids. This special class is attributed to the so-called *normal transition* [38, 39]. More precisely, the purpose is the determination of the variation of the induced force between colloids upon distance, when one is far from the critical temperature. The computation of this force at the critical point has been the subject of some previous work [27]. Thus, we are interested here in how temperature can affect the value of the expected force. Manifestly, the latter is increasingly *weak* as one goes far from T_c . As a matter of fact, this is due to a considerable reduction of critical fluctuations of the order parameter away from the demixing point.

To achieve the determination of the spatial variation of the induced force, use is made of a field-theoretical approach based on the standard φ^4 -theory [40, 41], where the field φ accounts for the composition fluctuation (*order parameter*). With the help of the standard *cumulant method* [40, 41], we first compute the resulting pair-potential from which we extract the induced force. *Exact* calculations reveal that the force can be expressed in term of the modified Bessel function $K_\nu(z)$ [42]. In addition, when it is correctly reduced and its variables are suitably rescaled, the force expression shows a *universal* character, independently on the chemical nature of the two polymers and colloids.

The outline of the rest of the paper is as follows. In the second section, we present the field model enabling us to compute the induced force. The determination of the latter and related discussion are the aim of the third section. We draw some concluding remarks in the last section.

II. Field model

We start with \mathcal{N} spherical colloidal particles immersed in a binary mixture made of two chemically incompatible polymers A and B . For simplicity, these particles are assumed to be identical from a physical and geometrical point of view. We will denote by R their common radius. We suppose that, near the demixing temperature T_c of the *host* mixture, these particles have tendency to attract rather the polymer A . This is the so-called critical adsorption [6, 38, 39, 43 – 53], where each colloid is clothed by a layer made of monomers A . As result, the particles located in the non-preferred B -rich phase aggregate. Therefore, these experience a long-range attractive force, which is responsible for their aggregation.

The flocculation phenomenon can be studied through the introduction of an order parameter or composition fluctuation φ . The latter is nothing else but the difference of compositions Φ_A and Φ_B of the two polymers, that is $\varphi = \Phi_A - \Phi_B$. The order parameter $\varphi(\mathbf{r})$ is a scalar field depending on the position vector \mathbf{r} of the representative point of the mixture in the presence of colloids.

The Hamiltonian governing the system is given by

$$\frac{\mathcal{H}[\varphi]}{k_B T} = \frac{\mathcal{H}_b[\varphi]}{k_B T} + c \sum_{i=1}^{\mathcal{N}} \int dS_i \varphi_i^2 - \mu \sum_{i=1}^{\mathcal{N}} \int dS_i \varphi_i, \quad (1)$$

with T the absolute temperature and k_B the Boltzmann's constant. The first term in the right-hand side of the above equality accounts for the (reduced) bulk Hamiltonian of the host mixture [54]

$$\frac{\mathcal{H}_b[\varphi]}{k_B T} = \int d\mathbf{r} \left\{ \frac{t}{2} \varphi^2 + \frac{u}{4} \varphi^4 + \kappa (\nabla \varphi)^2 \right\}, \quad (1a)$$

where $t = (\chi_c - \chi)/2$ represents the distance from the critical point. Here, χ denotes the Flory interaction parameter [54, 55], which is inversely proportional to temperature, and $\chi_c = 2/N$ its critical value. There, $u = 1/3N$ is the coupling constant, where N is the common polymerization degree of chains, and $\kappa = a^2/9$ is a constant (a being the monomer size). The first two terms in the right-hand side of formula (1a) are just the expansion to fourth order of the standard Flory-Huggins (FH) free energy [54, 55] around the critical composition, or equivalently around $\varphi = 0$. There, $(\varphi_1, \dots, \varphi_{\mathcal{N}})$ are the values of field φ on

the surfaces of colloids. The quantity dS_i accounts for the elementary surface on colloid i , c stands for the surface coupling constant [38, 39, 56], which measures the interaction strength between polymer mixture and surfaces of colloids, and $\mu = (\mu_A^s - \mu_B^s)/k_B T$ for the (reduced) surface chemical potentials difference of the two polymers [6]. In fact, φ and μ play the role of the local magnetization and surface magnetic field in the context of magnetic materials in the presence of surfaces [38, 39, 56].

It is easy to see that the order parameter satisfies the boundary conditions

$$\partial_n \varphi_i = c \varphi_i - \mu, \quad (i = 1, \dots, \mathcal{N}), \quad (1b)$$

where the notation $\partial_n \varphi_i$ means the normal derivative of field φ on the surface of colloid i .

For small enough particles, the Hamiltonian governing the system reduces to [27]

$$\frac{\mathcal{H}[\varphi]}{k_B T} = \frac{\mathcal{H}_b[\varphi]}{k_B T} + c \sum_{i=1}^{\mathcal{N}} \varphi^2(\mathbf{r}_i) - \mu \sum_{i=1}^{\mathcal{N}} \varphi(\mathbf{r}_i). \quad (2)$$

This total Hamiltonian then describes a critical binary polymer mixture in the presence of \mathcal{N} colloids (boundaries). Therefore, the interactions between polymer mixture and colloids depend only on two surface microscopic parameters (c, μ). We emphasize that the quadratic surface term, in Eq. (2), tends to increase the temperature parameter t appearing in the bulk Hamiltonian, relation (1a). This means that such a term reduces the chemical interactions in the host system. The surface linear term that breaks the symmetry $\varphi \rightarrow -\varphi$, is introduced in order to take into account the preference of colloidal particles for one polymer of the mixture. The critical adsorption emerges in the limit $\mu \rightarrow \infty$, at fixed $c > 0$ [38, 39].

Furthermore, it was shown [27] that the scale-invariance leads to some relations between the surface microscopic parameters (c, μ) and the amplitudes of composition profiles and bulk two-point correlation functions of the free mixture, constructed with the field φ or the composite operator φ^2 . More precisely, it was found [27] that

$$c = R^{x_2} \frac{\mathcal{A}_2}{\mathcal{B}_2}, \quad \mu = R^{x_1} \frac{\mathcal{A}_1}{\mathcal{B}_1}, \quad (3)$$

where \mathcal{A}_1 and \mathcal{A}_2 represent the amplitudes of the mean-values of fields φ and φ^2 relative to one sphere of radius R immersed in a polymer blend [27]

$$\langle \varphi(\mathbf{r}) \rangle_{sphere} \simeq \mathcal{A}_1 [R^{-1} (r^2 - R^2)]^{-x_1} , \quad (T \rightarrow T_c) , \quad (4a)$$

$$\langle \varphi^2(\mathbf{r}) \rangle_{sphere} \simeq \mathcal{A}_2 [R^{-1} (r^2 - R^2)]^{-x_2} , \quad (T \rightarrow T_c) . \quad (4b)$$

Here, $r = |\mathbf{r}|$ denotes the distance from the centre of the sphere. In these relations, x_1 and x_2 are the scaling dimensions of φ and φ^2

$$x_1 = \beta_t / \nu_t , \quad x_2 = d - \nu_t^{-1} , \quad (5)$$

with d the space dimension, and β_t and ν_t the standard critical exponents of Ising-like magnetic systems [40, 41]. Using an adequate special conformal transformation, it was found [18, 19] that the profiles relative to the one-sphere problem may be related to those in a half-space by

$$\langle \varphi(z) \rangle_{half-space} \simeq \mathcal{A}_1 (2z)^{-x_1} , \quad \langle \varphi^2(z) \rangle_{half-space} \simeq \mathcal{A}_2 (2z)^{-x_2} , \quad (6)$$

where z is the perpendicular distance, and \mathcal{A}_1 and \mathcal{A}_2 are those amplitudes appearing in Eqs. (4a) and (4b). This means that, for the determination of the value of these amplitudes, it will be sufficient to consider a polymer mixture occupying a semi-infinite space limited by a plane surface. On the other hand, \mathcal{B}_1 and \mathcal{B}_2 are the amplitudes, at small-distances compared to the bulk correlation length ξ , of the (connected) two-point correlation functions

$$\langle \varphi(\mathbf{0}) \varphi(\mathbf{r}) \rangle_{b,c} = \langle \varphi(\mathbf{0}) \varphi(\mathbf{r}) \rangle_b - \langle \varphi(\mathbf{0}) \rangle_b \langle \varphi(\mathbf{r}) \rangle_b \simeq \frac{\mathcal{B}_1}{r^{2x_1}} , \quad (7a)$$

$$\langle \varphi^2(\mathbf{0}) \varphi^2(\mathbf{r}) \rangle_{b,c} = \langle \varphi^2(\mathbf{0}) \varphi^2(\mathbf{r}) \rangle_b - \langle \varphi^2(\mathbf{0}) \rangle_b \langle \varphi^2(\mathbf{r}) \rangle_b \simeq \frac{\mathcal{B}_2}{r^{2x_2}} . \quad (7b)$$

(The subscripts b is for *bulk* and c for *connected*).

We recall that, as demonstrated by de Gennes [54, 57], the polymer mixtures can be correctly described using mean-field theory. This is true only for those polymer mixtures of high-molecular-weight. Indeed, the critical region around the critical point T_c , where a

non-classical behavior is expected, is very narrow (of the order of N^{-1}), so that the mean-field theory can be applied. Therefore, close to T_c , one observes trivial critical exponents, and in particular, $\beta_t = 1/2$ and $\nu_t = 1/2$. The critical behavior of a free binary polymer mixture emerges in the $d \rightarrow 4$ limit, and then, $x_1 = 1$ and $x_2 = 2x_1 = 2$. By a simple map between the sphere and a semi-infinite space, we obtain

$$\mathcal{A}_1 = \frac{4a}{3} \sqrt{\frac{1}{u}} = \frac{4a}{\sqrt{3}} \sqrt{N}, \quad \mathcal{A}_2 = \mathcal{A}_1^2 = \frac{16a^2}{3} N. \quad (8)$$

For the remaining amplitudes, we simply sketch the results

$$\mathcal{B}_1 = \frac{1}{8\pi^2\kappa} = \frac{9}{8\pi^2a^2}, \quad \mathcal{B}_2 = 2\mathcal{B}_1^2 = \frac{81}{32\pi^4a^4}. \quad (9)$$

To derive the second relation in Eq. (9), we have used the Wick theorem [40, 41].

Combining relations (3), (8) and (9), we find the desired expressions [58]

$$c = \frac{512\pi^4}{243} \frac{R^2}{a^2} N, \quad \mu = \frac{32\pi^2}{9\sqrt{3}} \frac{R}{a} \sqrt{N}. \quad (10)$$

These relations show the explicit dependence of the surface microscopic parameters upon colloids geometry, via their radius R , and chains characteristics, through the monomer size a and the polymerization degree N .

We finish this section by the following useful remark. When one is concerned with phenomena occurring at low temperature ($t < 0$), the field φ must be naturally written as

$$\varphi = \varphi_b + \psi, \quad (11)$$

where the new field ψ is the fluctuation of the order parameter φ around its bulk value φ_b

$$\varphi_b = \begin{cases} 0, & \text{for } t > 0, \\ \sqrt{-\frac{t}{u}}, & \text{for } t < 0, \end{cases} \quad (12)$$

which is the minimum of the standard FH free energy. Now, insert the decomposition (11) in the total Hamiltonian, relations (1a) and (2), and expand it to second order around $\psi = 0$, to get

$$\frac{\mathcal{H}[\psi]}{k_B T} = \frac{\mathcal{H}_b^0[\psi]}{k_B T} + c \sum_{i=1}^{\mathcal{N}} \psi^2(\mathbf{r}_i) - \hat{\mu} \sum_{i=1}^{\mathcal{N}} \psi(\mathbf{r}_i), \quad (13)$$

with

$$\frac{\mathcal{H}_b^0[\psi]}{k_B T} = \int d\mathbf{r} \left\{ \frac{\hat{t}}{2} \psi^2 + \kappa (\nabla \psi)^2 \right\} \quad (13a)$$

the new bulk Hamiltonian, which is quadratic in the field ψ . The parameters \hat{t} and $\hat{\mu}$ are

$$\hat{t} = t + 3u\varphi_b^2, \quad \hat{\mu} = \mu - 2c\varphi_b. \quad (14)$$

Explicitly, we have

$$\hat{t} = \begin{cases} t, & \text{for } t > 0, \\ -2t, & \text{for } t < 0, \end{cases} \quad (14a)$$

$$\hat{\mu} = \begin{cases} \mu_+ = \mu, & \text{for } t > 0, \\ \mu_- = \mu - 2c\sqrt{-\frac{t}{u}}, & \text{for } t < 0, \end{cases} \quad (14b)$$

where c and μ are those surface parameters given by Eq. (10). The signs (+) and (−) are for *high* and *low* temperatures, respectively.

The following step consists in the computation of the induced force away from the critical point. To this end, use will be made of the new Hamiltonian $\mathcal{H}[\psi]$, relations (13) and (13a).

III. Induced force

As we said in the beginning, the critical fluctuations of the order parameter give rise to an induced force, which is attractive and of long-range. The determination of the distance decay of such a force will be achieved through the knowledge of the pair-potential, denoted $U(r)$. Here, r is the center-to-center distance of two interacting particles. Formally, and taking advantage of the standard cumulant method [40, 41], we show that the p -body interaction energy, $U(\mathbf{r}_1, \dots, \mathbf{r}_p)$, is the connected p -point correlation function

$$\frac{U(\mathbf{r}_1, \dots, \mathbf{r}_p)}{k_B T} = \langle \mathcal{O}(\mathbf{r}_1) \dots \mathcal{O}(\mathbf{r}_p) \rangle_{b,c}, \quad (15)$$

constructed with the field operator

$$\mathcal{O}(\mathbf{r}) = -c\psi^2(\mathbf{r}) + \hat{\mu}\psi(\mathbf{r}). \quad (15a)$$

Notice that for $p = 1$, the one-body potential $U(\mathbf{r}_1) = k_B T \langle \mathcal{O}(\mathbf{r}_1) \rangle_b$ is space-independent due to the spatial translation symmetry. For $p = 2$, we get the pair-potential

$$\frac{U(r)}{k_B T} = \langle \mathcal{O}(0) \mathcal{O}(\mathbf{r}) \rangle_{b,c} . \quad (15b)$$

Explicitly, we have

$$\frac{U(r)}{k_B T} = -\hat{\mu}^2 G_1(r) - c^2 G_2(r) , \quad (15c)$$

where

$$G_1(r) = \langle \psi(\mathbf{0}) \psi(\mathbf{r}) \rangle_{b,c} , \quad (15d)$$

and

$$G_2(r) = \langle \psi^2(\mathbf{0}) \psi^2(\mathbf{r}) \rangle_{b,c} = 2G_1^2(r) \quad (15e)$$

are the *connected* two-point correlation functions of fields ψ and ψ^2 , respectively. These functions are constructed with the Boltzmann weight $\exp\{-\mathcal{H}_b^0[\psi]/k_B T\}$, where $\mathcal{H}_b^0[\psi]$ is the bulk Hamiltonian, relation (13a). We note that the second equality in relation (15a) results from the Wick theorem [40, 41]. Remark the absence of the crossed coefficient $\hat{\mu}c$ in relation (15c). Indeed, this coefficient multiplies the correlation function $\langle \psi \cdot \psi^2 \rangle_{b,c}$, which is *zero*, since the bulk Hamiltonian is quadratic in the field ψ . On the other hand, the correlation function $G_1(r)$ can be computed exactly. Then, the result, in the mean-field limit ($d \rightarrow 4$), writes [59]

$$G_1(r) = \frac{\mathcal{B}_1}{r^2} \left(\frac{r}{\xi_{\pm}} \right) K_1 \left(\frac{r}{\xi_{\pm}} \right) , \quad (16)$$

where $K_1(z)$ is the modified Bessel function [42]. Here, \mathcal{B}_1 is that amplitude appearing in Eq. (9), and

$$\xi_{\pm} = \begin{cases} \xi_0^+ t^{-1/2} , & \text{for } t > 0 , \\ \xi_0^- (-t)^{-1/2} , & \text{for } t < 0 \end{cases} \quad (16a)$$

is the bulk correlation length, with amplitudes $\xi_0^+ = a\sqrt{2}/3$ (above T_c) and $\xi_0^- = a/3$ (below T_c). With these considerations, we find that, near T_c , the pair-potential writes

$$\frac{U(r)}{k_B T} = -\mu_{\pm}^2 \frac{\mathcal{B}_1}{r^2} \left(\frac{r}{\xi_{\pm}} \right) K_1 \left(\frac{r}{\xi_{\pm}} \right) - 2c^2 \frac{\mathcal{B}_1^2}{r^4} \left(\frac{r}{\xi_{\pm}} \right)^2 \left[K_1 \left(\frac{r}{\xi_{\pm}} \right) \right]^2 . \quad (17)$$

Now, the first derivative of this potential with respect to the distance r gives the expected induced force $F(r)$

$$\frac{F(r)}{k_B T} = -\mu_{\pm}^2 \frac{\mathcal{B}_1}{\xi_{\pm}^3} \left(\frac{\xi_{\pm}}{r} \right) K_2 \left(\frac{r}{\xi_{\pm}} \right) - 4c^2 \frac{1}{\xi_{\pm}^5} \mathcal{B}_1^2 \left(\frac{\xi_{\pm}}{r} \right)^2 K_1 \left(\frac{r}{\xi_{\pm}} \right) K_2 \left(\frac{r}{\xi_{\pm}} \right). \quad (18)$$

We have used some recursion formulae satisfied by the modified Bessel function $K_{\nu}(z)$ [42].

Before discussion, let us first rewrite the above expression on the following scaling form

$$\frac{F(r)}{k_B T} = -E \left[1 - \theta(-t) \frac{16}{27} \pi^2 \left(\frac{\xi_-}{D} \right)^{-1} \right]^2 \frac{D^2}{r^3} \Phi_0 \left(\frac{r}{\xi_{\pm}} \right) - H \frac{D^4}{r^5} \Phi_1 \left(\frac{r}{\xi_{\pm}} \right), \quad (19)$$

with the *universal* scaling functions

$$\Phi_0(x) = \frac{1}{2} x^2 K_2(x), \quad \Phi_1(x) = \frac{1}{2} x^3 K_1(x) K_2(x), \quad (19a)$$

and amplitudes

$$E = \frac{64}{27} \pi^2, \quad H = \frac{2048}{729} \pi^4. \quad (19b)$$

Remark that these amplitudes are *pure* numbers. There, $\theta(x)$ is the step-function. We have used the notation $D = d_0 \times N^{1/2}$, where $d_0 = 2R$ is the particles diameter. Then, the length D may be viewed as a *renormalized* particles size.

Now, let us discuss the derived expression for the induced force.

First, we emphasize that we have ignored higher order cumulants describing three-body interactions and more. In this sense, formula (18) is exact only when one is concerned with two-body interactions. Also, in the bulk Hamiltonian, we have ignored non-quadratic terms as ψ^3 and ψ^4 , which must contribute when one performs loop-expansion [41, 42], in field theory language. These terms are discarded here since the mean-field theory we consider is just the zeroth order approximation of the loop expansion.

Second, we note that in the $t \rightarrow 0$ limit, that is when one is exactly at the consolute point ($T = T_c$), we recover the previous results of Ref. [27]. Indeed, $\Phi_0(0) = \Phi_1(0) = 1$.

Third, the contribution of the surface chemical potentials difference dominates. This means that the direct interactions between the mixture and particles plays only a minor role.

Fourth, the dependence of the force on the particles size is trivial and appears through the renormalized diameter D .

Fifth, the decreasing character of the Bessel function indicates that, as it should be, the force below the consolute point is *more* important than above, when one is at the same distance from T_c . Notice that $\xi_+ > \xi_-$.

Sixth, for all temperatures around the consolute one ($T \neq T_c$) and at fixed interparticle-distance r , the force is *less* important than at $T = T_c$. This is due to the fact that the two scaling functions $\Phi_0(x)$ and $\Phi_1(x)$ are bounded from above by 1, that is $\Phi_0(x) < 1$ and $\Phi_1(x) < 1$, for all $x > 0$. Therefore, the temperature has as effect to reduce the induced force, when one goes away from the critical point.

Seventh, formula (19) tells us that the reduced force $D.F(r)/k_B T$ is a *two-factor* scaling function of the renormalized distance r/D and the ratio ξ_{\pm}/D . In addition, it is a *universal* function of these variables, independently on the chemical structure of polymers and colloids.

Eighth, at fixed distance r and very close to the critical point ($\xi_{\pm} \rightarrow \infty$), the induced force obeys an exponential decay, that is

$$\frac{F(r)}{k_B T} = -E \left[1 - \theta(-t) \frac{16}{27} \pi^2 \left(\frac{\xi_-}{D} \right)^{-1} \right]^2 \frac{D^2}{r^3} e^{-r/\xi_{\pm}} - H \frac{D^4}{r^5} e^{-2r/\xi_{\pm}} . \quad (19c)$$

We have used the standard mathematical formula [42] : $z^\lambda K_\lambda(z) \sim 2^{\lambda-1} \Gamma(\lambda) e^{-z}$ ($z = r/\xi_{\pm} \rightarrow 0$). The above formula tells us that the temperature has as effect to "screen" the induced force at $T = T_c$. The correlation length ξ_{\pm} then plays the role of the standard Debye screening length [60], but the computed induced force is much smaller than the screened Coulombian one.

Finally, we give an order of magnitude of the induced force. We consider the hydrogenated polyolefin-deuterated polyolefin mixture incorporating silicon particles of diame-

ter $d_0 = 0.1 \mu\text{m}$, for which the polymerization degree and critical temperature were found to be [61] : $N = 1570$, $T_c = 100^\circ\text{C}$. We take as values for the interparticle distance and correlation length : $r = 1 \mu\text{m}$, $\xi = 10 \mu\text{m}$. For these values, we find that the magnitude of the force is : $F = -0.28 \times 10^{-4}$ dyne. This force must be compared to that relative to the considered polymer mixture confined to two parallel plates separated by the same distance $L = 1 \mu\text{m}$. The magnitude of the latter is $F = -0.56 \times 10^{-4}$ dyne. Thus, the force between parallel plates is *two times* more important than that between a pair of colloids. Also, the same force must be compared to the electromagnetic one, which is of the order of 0.01×10^{-4} dyne (for $L = 1 \mu\text{m}$).

In Fig.1, we report the reduced induced forces $D.F(r)/k_B T_c$ versus the dimensionless distance r/D , for two temperatures $T = T_c$ and $T = T_1 \neq T_c$. In Fig.2, we superpose two reduced induced forces relative to two temperatures T_1 and $T_2 > T_1$ away from T_c , as functions of the dimensionless distance r/D . These curves reflect the above deductions.

IV. Conclusions

We recall that the purpose of the present paper was the determination of the spatial variation of the induced force between colloidal particles immersed in a binary polymer mixture, at temperatures far from the critical one. The colloidal aggregation is due to a preferential attraction of one polymer by the particles.

All calculations were done in the framework of the standard φ^4 -theory, where the field φ is simply the composition fluctuation (order parameter). Applying this theory and using the cumulant method, we first showed that the resulting pair-potential is the sum of two contributions, which are proportional to bulk two-point correlation functions constructed with fields φ and φ^2 , respectively. Second, for polymer mixtures of high molecular weight, these (mean-field) correlation functions are known exactly, and we found that the expected force can be expressed in term of the modified Bessel function $K_\nu(z)$. When it is adequately reduced, the force becomes a universal two-factor scaling function of the dimensionless variables r/D and ξ_\pm/D , where r is the interparticle-distance, ξ_\pm the

correlation length and D the renormalized diameter $D = 2R \times N^{1/2}$.

We emphasize that the force expression we obtained can be extended to two particles of different radii R_1 and R_2 . For this case, we state that the new expression would be similar to that relative to a monodisperse colloidal system, by making the following change of the renormalized diameter : $D \rightarrow 2\sqrt{R_1 R_2} \times N^{1/2}$.

We note that the above calculations make sense only for relatively high separations, that is for $\Delta > R$, with Δ the surface-to-surface distance between two spheres of the same radius R . When $\Delta < R$ (very small-distances), however, the colloids can be viewed as two parallel plates. For this case, the induced force decays rather as Δ^{-4} [25, 26].

Finally, the main conclusion is that, in any case, the temperature has tendency to reduce the value of the expected force (at fixed interparticle-distance) as one moves outside the critical region.

Further works, in relation with the subject, are in progress.

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Figure captions

Fig. 1 : The reduced Casimir forces $D.F(r)/k_B T_c$ upon renormalized distance r/D , for two temperatures $T = T_c$ and $T = T_1 = 1.001 \times T_c$.

Fig. 2 : The reduced Casimir forces $D.F(r)/k_B T_c$ upon renormalized distance r/D , for two temperatures $T_1 = 1.1 \times T_c$ and $T_2 = 1.2 \times T_c$.

$DF/k_B T_c$

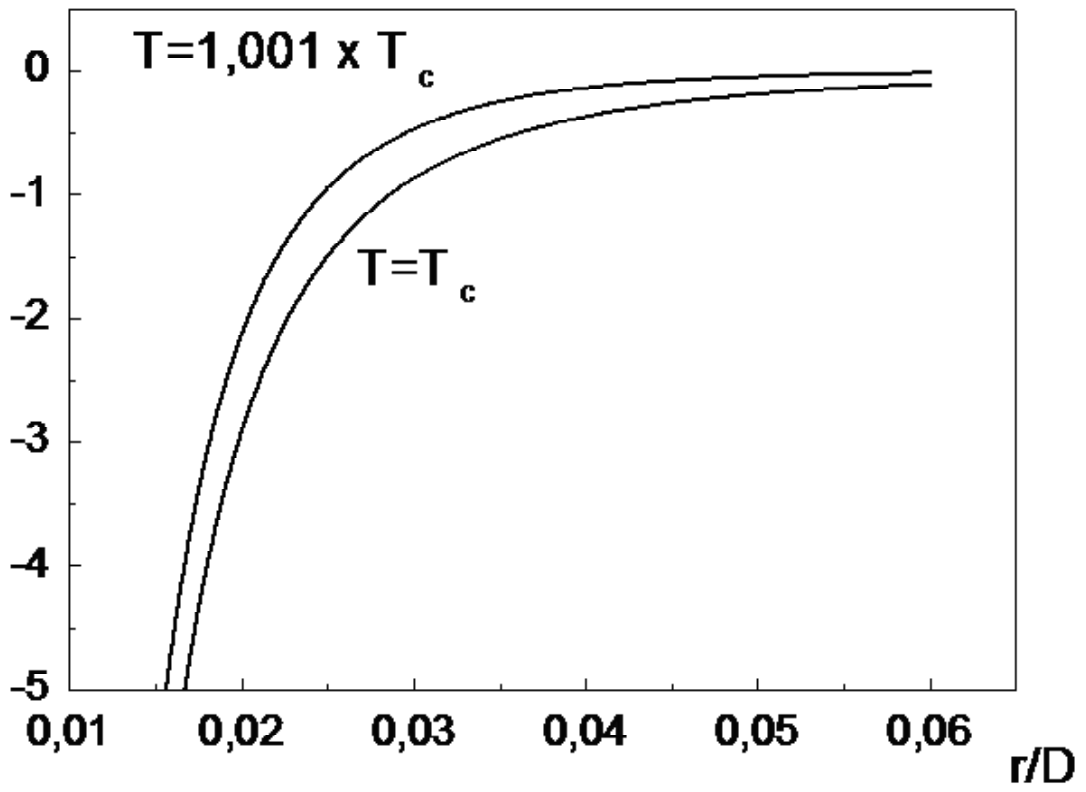


Figure 1

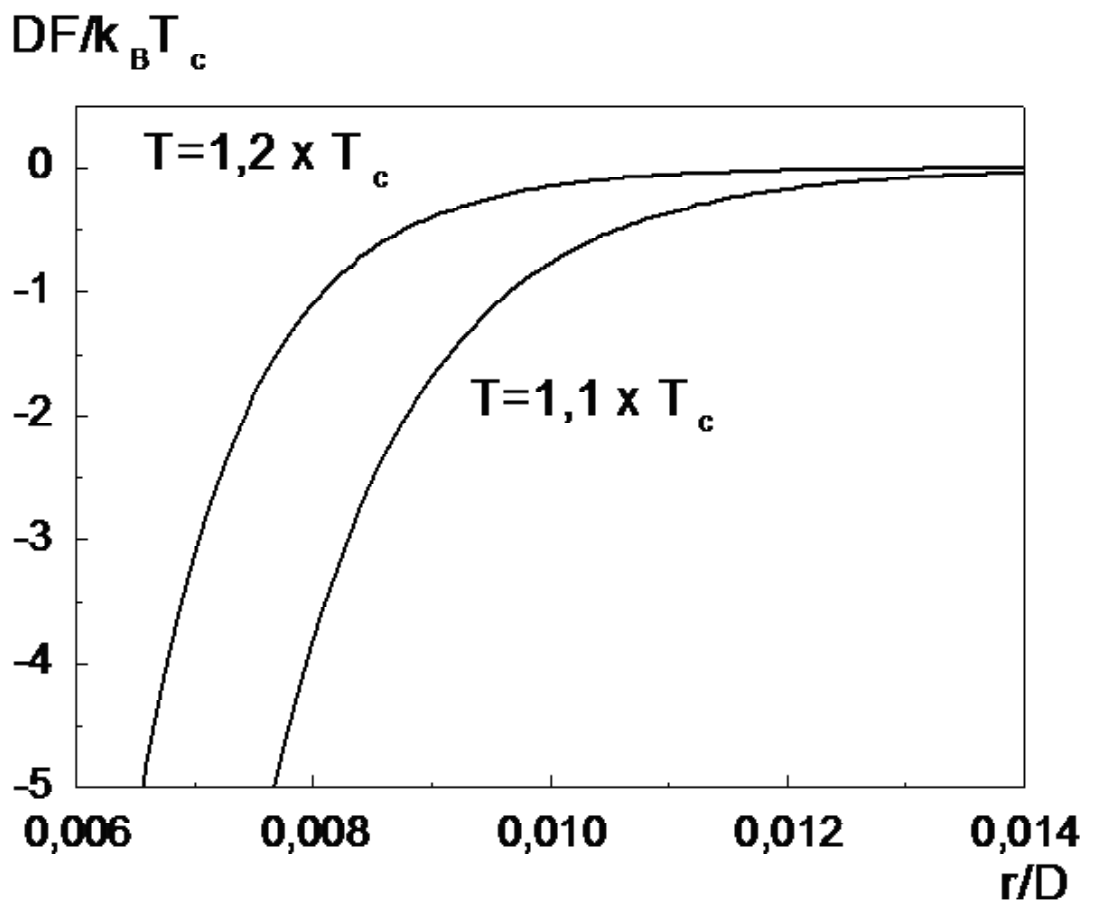


Figure 2