Long-Range Interactions in Polymer Melts: The Anti-Casimir Effect

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It is well known that small neutral particles normally tend to aggregate due to the van der Waals forces. We discover a new universal long-range interaction between solid objects in polymer media that is directly opposite the van der Waals attraction. The new force could reverse the sign of the net interaction, possibly leading to the net *repulsion*. This universal repulsion comes from the subtracted soft fluctuation modes, which are not present in the real polymer system, but rather are in its ideal counterpart. The predicted effect has a deep relation to the classical Casimir interactions, providing an unusual example of fluctuation-induced repulsion instead of normal attraction. That is why it is referred to as the *anti-Casimir* effect. We also find that the correlation function of monomer units in a concentrated solution of infinite polymer chains follows a power-law rather than an exponential decay at large distances.

Long-range forces between conducting plates in vacuum were predicted more than half a century ago by Casimir [1]. These interactions may seem to come from nowhere, but they were proven to arise from electromagnetic fluctuations in a vacuum. Since the original theoretical discovery of Casimir, a plethora of similar long-range interaction effects induced by thermal fluctuations has been predicted in various systems (ranging from critical liquid mixtures and superfluids to liquid-crystals, charged fluids, and membranes) [2–4]. There are two generic features of most long-range Casimir forces: (i) they involve fluctuations of massless fields (scale-free fluctuations, Goldstone modes), and (ii) they are normally attractive.

In this Letter we consider a novel example of universal long-range forces contradicting the above notions: We predict long-range *repulsive* interactions in polymer melts where the relevant (density) fluctuations are believed to be both weak and short range. Nevertheless we show that the effect is indeed related to the Casimir interactions, thus establishing a new bridge between the general theoretical physics and polymer physics. The predicted long-range forces in polymer systems are likely to be important in numerous physical, chemical, and technological applications.

The predicted effect is nontrivial on theoretical grounds. Polymer melts and other concentrated polymer systems have been viewed for years as ideal objects for a mean-field analysis. Since long ago it was generally believed that all correlations and interactions in these systems (with however long polymer chains) are short range, with the decay length comparable to the monomer unit size [5–10]. The concept of totally screened effective interactions of monomer units at length scales much exceeding the unit size is one of the cornerstones of the modern theory of concentrated polymer systems [5–7]. It is proved here that this opinion is not true: long-range correlations and interactions are inherent in concentrated polymer systems.

Considering importance of this issue we present several complementary theoretical arguments elucidating different physical aspects of the long-reange effects [(I),(II),(III)]:

(I) We employ the polymer-magnetic analogy [7] and argue that soft transverse Goldstone modes of n-vector spin fluctuations must generate the Casimir force multiplied by the number of these modes $(n - 1)$. Thus in the limit $n \to 0$ corresponding to linear polymers [7] we get exactly the opposite of the Casimir effect, i.e., long-range repulsion instead of attraction.

We follow the mapping between a polymer melt and a magnetic system used for lattice models [11–13]: Consider a lattice of sites $\{r_i\}$ with an n-component field $\varphi(r_i) = \{\varphi_1(r_i), \ldots, \varphi_n(r_i)\}$ defined at each site. The interaction between the sites is controlled by constants K_{ij} ($K_{ij} = 1$ for each pair of neighboring sites ij, and $K_{ij} = 0$ otherwise). The partition function of the system is [14]:

$$Z = \int \prod_{\{i\}} d\varphi(r_i) e^{-H}, \tag{1}$$

$H = \frac{1}{2} \Sigma_{\{i,j\}} \varphi(r_i)(K_{ij})^{-1}\varphi(r_j) - \Sigma_i \ln(\frac{1}{2}\varphi^2(r_i) + h\varphi_1(r_i) + \alpha)$; α and h are constant parameters, h is related to the magnetic field. Using the Wick's theorem it is easy to prove that the partition function, Eq. (1), is equal to the grand canonical partition function of a living system of self-avoiding polymers on the same lattice: $Z = \Sigma_{\mathcal{N}_e, \mathcal{N}_v} h^{\mathcal{N}_e} \alpha^{\mathcal{N}_v} C_{conf}(\mathcal{N}_e, \mathcal{N}_v)$, $\mathcal{N}_v$, $\mathcal{N}_e$ are the numbers of vacancies and chain ends, respectively, $C_{conf}(\mathcal{N}_e, \mathcal{N}_v)$ is the number of different configurations of $\mathcal{N} - \mathcal{N}_v$ monomer units forming $\mathcal{N}_e/2$ linear chains, $\mathcal{N}$ is the total number of lattice sites. Closed loop configurations have an additional factor n through the summation over the components of the fields $\varphi_\alpha(r_i)$, thus all closed loops are eliminated for $n \to 0$.

Equation (1) can be employed to calculate the thermodynamic parameters of the living system of long ($h \ll 1$)

linear ($n = 0$) polymer chains. In the mean-field approximation the partition function $Z \simeq Z_{mf} = \exp(-H\{\varphi^*\})$, where φ^* is the relevant saddle point [12]. Assuming uniform field $\varphi^*(r_i) = \{\varphi_1^*, 0 \ldots 0\}$ we get $\ln Z_{mf} \simeq \mathcal{N} \ln z - \mathcal{N} + 2h\mathcal{N}/\sqrt{2z} + \alpha \mathcal{N}/z$, where z is the coordination number of the lattice. The mean numbers of vacancies ($\mathcal{N}_v$) and polymer chains ($\mathcal{N}_e/2$) are: $\mathcal{N}_e = \frac{\partial \ln Z}{\partial \ln h} \simeq 2\mathcal{N}h/\sqrt{2z}$, $\mathcal{N}_v = \frac{\partial \ln Z}{\partial \ln \alpha} \simeq \mathcal{N}\alpha/z$, so the average chain length is $\bar{N} = \frac{\mathcal{N} - \mathcal{N}_v}{\mathcal{N}_e/2} - 1 \simeq \sqrt{2z}/h$.

In order to include fluctuations of the order parameter around the mean field φ^* we expand the Hamiltonian H for small deviations from this saddle point, use the quadratic approximation, and evaluate the corresponding Gaussian integrals. The resultant free energy is $F \equiv -\ln Z = F_{mf} + F_{fluct}$, where $F_{mf} = -\ln Z_{mf}$ and $F_{fluct} = \frac{1}{2}\Sigma_k \ln f(k)$. Here the sum is taken over the relevant spectrum of wave vectors k determined by the system size, $f(k) \simeq [1 + (1 - 2\alpha/z - 1/\bar{N})K(k)][1 - (1 - 1/\bar{N})K(k)]^{(n-1)}$, $K(k) = \frac{1}{z}\Sigma_j K_{ij}e^{ik \cdot r_{i,j}}$, $K(0) = 1$. The term in the first square bracket stems from integration over longitudinal fluctuations of $\varphi - \varphi^*$, the second square bracket comes from $n - 1 \rightarrow -1$ transverse fluctuation modes. The latter are Goldstone modes: their gap is $1/\bar{N}$; it tends to 0 for long chains.

The above results can be applied to determine the effective interaction between two parallel infinite plates immersed in the polymer system, say, at $x_1 = 1/2$ and $x_1 = D + 1/2$. The presence of the plates imposes the reflective (Neumann) boundary conditions for the order-parameter field φ [the plates are impenetrable, i.e., polymer chains cannot cross the plates, which is formally equivalent to setting $K_{ij} = 0$ for all lattice bonds (ij) intersecting the plates]. The bulk of the mean-field free energy F_{mf} is not affected by the plates (except small regions around them) however the spectrum of fluctuations is affected. The relevant wave vectors $k = (k_1, \ldots, k_d)$ now include the discrete component perpendicular to the plates $k_1 = \pi m/D$, $m = 0, 1, \ldots, D - 1$ (d is the space dimension):

$$F_{fluct} \simeq -\frac{1}{2}A\sum_m \int \frac{d^{d-1}k}{(2\pi)^{d-1}} \ln\left(k^2 + \frac{m^2\pi^2}{D^2} + \frac{2d}{\bar{N}}\right)$$

where A is the plate area, $D \gg 1$. The regularization of this sum (subtraction of the contribution of fluctuations in the bulk melt) is similar to the procedure used in the calculation of the Casimir effect for a scalar field [15,16]. For infinitely long chains $\bar{N} \rightarrow \infty$ we get the force per unit area (for $d = 3$):

$$f = -(1/A)\partial F_{fluct}/\partial D \simeq \zeta(3)/(8\pi D^3), \quad (2)$$

i.e., the standard Casimir force for massless scalar field [15], but with the opposite sign because of the negative number (-1) of soft components. The more general result for finite $\bar{N}$ is

$$f = \frac{1}{16\pi D^3} \int_{2D/R}^{\infty} \frac{x^2 dx}{e^x - 1} \quad (3)$$

where $R = \sqrt{\bar{N}/6}$ is the typical polymer coil size. Thus $f \propto 1/D^3$ for $D \ll R$ and $f \propto e^{-2D/R}$ for $D \gg R$, and so the relevant decay (correlation) length is not the bond length, but rather the polymer coil size R.

(II) The long-range effects can also be elucidated using a more traditional polymer approach: We start with a concentrated system of noninteracting ideal polymers, and then turn on the excluded-volume interactions. There are definitely no long-range forces in the noninteracting system which nevertheless shows soft modes of concentration fluctuations. By turning on monomer interactions we suppress these soft modes (at $q \rightarrow 0$) hence suppress the virtual Casimir attraction associated with these modes, thus inducing an *anti-Casimir* repulsion.

Quantitatively, the direct approach involves consideration of the energy penalty $H[c]$ for an inhomogeneous monomer distribution $c(r) = c_0 + \delta c(r)$. Once $H[c]$ is known, the concentration correlation function $G(r) = \langle \delta c(r)\delta c(0)\rangle$ and the structure factor $S(q) = \int G(r) \times \exp(ir \cdot q)d^d r$ can be calculated in a straightforward way. The standard *effective Hamiltonian* [17] for a concentrated system of long polymer chains reads [7,18]

$$H[c] = \frac{b^2}{8d} \int \frac{(\nabla c)^2}{c} d^d r + \frac{1}{2} \int \upsilon(c - c_0)^2 d^d r \quad (4)$$

where b is the polymer chain statistical length, and υ, the interaction parameter. The main feature of this $H[c]$ is that it is a *local* functional of concentration.

For a system of noninteracting Gaussian chains ($\upsilon = 0$) the structure factor is known exactly: $S_0(q) = 2c_0/(q^2a^2)$. Yet the Hamiltonian, Eq. (4) with $\upsilon = 0$, produces a different result: $S_0(q) \simeq \frac{2c_0}{q^2a^2}\{1 + \text{const} \frac{q}{c_0a^3}\}$ (for small q, $d = 3$). What about the discrepancy? Of course, it is possible to improve on $H[c]$, Eq. (4), e.g., by adding higher-order interaction terms, but this results only in negligible corrections (including trivial renormalizations). The main point is that any *local* modification of $H[c]$ could not help to fight the discrepancy: the correct correlation functions could not be obtained with a local $H[c]$. Thus $H[c]$ must be modified by adding an essentially *nonlocal* term $\Delta H \simeq \frac{1}{2^7}\frac{1}{c_0^2}\int q^3 \delta c_q \delta c_{-q} \frac{d^3q}{(2\pi)^3} = \text{const} \int \delta c(r)\delta c(r') \times \frac{1}{(r-r')^6}d^3 r d^3 r'$. The first term in Eq. (4) plus ΔH represent the conformational free energy (due to chemical bonds between monomer units rather than to their excluded-volume interactions). With $H_m[c] = H[c] + \Delta H[c]$ we get (neglecting trivial renormalizations of the parameters υ, b): $S(q) \simeq \frac{1}{\upsilon + q^2b^2/12c_0 + q^3/64c_0^2}$ for $q\xi \ll 1$; $\xi = \frac{b}{\sqrt{12\upsilon c_0}}$ is the mean-field correlation length. The last term in brackets is never dominant, yet it is very important at low q's since with this term $S(q)$ becomes weakly singular (nonanalyt-

ical) at $q = 0$ [19]. It is this singularity that generates a long-range power-law tail in the correlation function:

$$G(r) \simeq \frac{3c_0}{\pi r b^2} e^{-r/\xi} - \frac{3}{16\pi^2} \frac{1}{v^2 c_0^2} \frac{1}{r^6} \quad \text{for } r \gg \xi. \quad (5)$$

This $G(r)$ is nonmonotonic: it becomes negative for r larger than a few ξ's (i.e., *anti-correlation* at large distances). These long-range correlations are missing in the classical picture because the locality of the $H[c]$ was not questioned. The nonlocality of the conformational energy naturally stems from the structure of *long* polymer chains.

Effective interactions between solid plates or spheres in the polymer system can be also interpreted in terms of the nonlocal effective Hamiltonian. For parallel plates we thus get the result consistent with Eqs. (2) and (3). The effective energy of interaction of two solid spheres is $F_{\text{int}} \simeq \frac{5}{6} R_s^6/D^6$ for $D \gg R_s \gg \xi$; R_s, the radius of spheres, and D, the distance between their centers (the $1/D^6$ repulsion is also valid for $R_s \ll \xi$). This interaction is remarkably universal: it does not depend on any polymeric parameters. Note the same power law as for the correlation function $G(r)$ [see Eq. (5)]. This power law ($1/r^6$) is also involved in the nonlocal Hamiltonian ΔH.

(III) The approach outlined above can be used to find the effective interaction between arbitrary objects (solid particles) in the polymer system:

$$F_{\text{int}} \simeq \frac{1}{2} \int d^d r \int_0^\infty \frac{dN}{N} G_N(\mathbf{r}, \mathbf{r}) + \text{const} \quad (6)$$

where $G_N(\mathbf{r}, \mathbf{r}')$ is the partition function of a chain of N monomers with ends at $\mathbf{r}$ and $\mathbf{r}'$; G_N satisfies the well-known Edwards equation $\frac{\partial G_N}{\partial N} = a^2 \nabla_r^2 G_N - \frac{1}{N} G_N$ with the "initial" condition $G_0(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}')$ and boundary conditions $\mathbf{n} \cdot \nabla G_N = 0$ at the solid surfaces ($\mathbf{n}$ is unit vector normal to the surface).

Interestingly, the long-range energy, Eq. (6), involves only one "polymeric" quantity $G_N(\mathbf{r}, \mathbf{r})$ which is actually the partition function of an N cycle. Why do cycles seem to play a crucial role for the system of linear chains? The interpretation is given below. Consider a living melt of bifunctional monomer units. The bond energy is high, so the units form either long linear chains or rings. The fraction of rings is proportional to the probability p that a growing chain meets its first unit, $p \sim 1/c_0 b^d$, where c_0 is concentration of units. Let us assume that $c_0 b^d \gg 1$, hence $p \ll 1$; i.e., nearly all units belong to linear chains, and just a small fraction to rings. This living system may be considered as a weak, nearly ideal "solution" of rings in the linear matrix. Its free energy is $F_{\text{liv}} = F + F_{\text{ring}}$, where F is the free energy of linear chains, $F_{\text{ring}} = -\ln Z_{\text{ring}}$, $Z_{\text{ring}} = \exp(\Sigma_N Z_N)$ is the grand partition function of the ideal system of living rings, and Z_N is the statistical weight of a ring of N units: $Z_N = \frac{1}{2N} \int G_N(r, r) d^3 r$ ($\frac{1}{2N}$ is the symmetry factor reflecting the equivalence of all N units

in a cycle, and also of the two ways of their counting, forward and backward).

The central notion is that there are no long-range interactions in the living system since its effective Hamiltonian is a *local* functional of the monomer distribution $c(r)$ (local monomer interactions plus local bonds between monomers), and it does not show any Goldstone fluctuation modes. (This conclusion can be also derived from the polymer-magnetic analogy: the weight of a cycle is proportional to the number of "spin components" n, and the amplitude of long-range interactions is proportional to $n - 1$. Therefore the interactions must be absent when the cycles are allowed with the natural weight, $n = 1$.) Hence $F_{\text{liv}} = \text{const}$ in the long-range sense, and so $F = \text{const} - F_{\text{ring}} = \text{const} + \Sigma_N Z_N$, i.e., we arrive at exactly Eq. (6) for $F = F_{\text{int}}$. We observe that F_{int} is proportional to the number of cycles in the corresponding living polymer system (neglecting the constant term). Thus the long-range interaction can be viewed as being due to subtracted living cycles. The probability of cyclization in a narrow gap between two solid plates is higher than in the bulk. Therefore elimination of cycles results in a more significant decrease of the statistical weight in the case when the plates are close to each other. An effective repulsion of the plates is thus explained. On the scaling level, the interaction energy is proportional to the number of relevant cycles (of size $\sim D$). Concentration of such cycles is $\sim 1/D^d$, so F_{int} per unit area is proportional to $1/D^{d-1}$, in agreement with the results considered above.

In summary, we show that the effective interactions between monomer units in polymer melts are not totally screened even at large length scales: concentration perturbations in dense polymers show a power law rather than an exponential decay at large distances. The total energy of polymer-induced (PI) interactions between solid objects in a polymer system involves two basic contributions: the mean-field (depletion) attraction that dominates at short distances, and the fluctuation-induced repulsion that dominates at long distances. The latter follows a power law for separations smaller than the polymer size R. The correlation function of concentrations fluctuations $G(r)$ (or, equivalently, the correlation function of vacancies) shows a similar behavior: it is positive and decreasing with r at short distances $r \lesssim \xi$ and negative and increasing for large distances, $r \gg \xi$, with a depletion minimum at an intermediate r.

The predicted long-range interactions are due to the linear-chain structure of polymers. Yet they are insensitive to any details of this structure showing remarkable universality. For example, the interaction nearly does not depend on concentration, i.e., nearly the same effect in a polymer melt and in a semidilute solution. We thus introduce a major new concept expanding the theoretical understanding of polymer statistical physics.

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The following qualitative interpretations of these long-range effects are proposed: Employing the polymer-magnetic analogy we relate the long-range interactions to the Casimir effect due to $n - 1$ transverse Goldstone modes of the relevant fluctuations of an n-vector order parameter with $n = 0$. The number of Goldstone modes is negative hence repulsive interaction is predicted, i.e., an "anti-Casimir" effect. This long-range effective repulsion can be also interpreted as a specific polymeric interaction which is exactly balanced by the Casimir force induced by soft modes of concentration fluctuations in the reference system of noninteracting polymers. In the melts the soft modes are suppressed by excluded-volume interactions, hence the anti-Casimir repulsion is unmasked. Finally we interpret the long-range forces as being due to living large-scale polymer rings, but with the opposite sign (subtracted loops). This hints at a relation between the fluctuation-induced Casimir forces and large-scale geometrical loops.

It is remarkable that the PI repulsion is rather similar to the van der Waals (VdW) interaction: the same power law and comparable magnitudes in the case of thermal VdW forces. This notion opens up an exciting possibility of reversing the sign of the effective long-range interaction (i.e., net repulsion instead of the usual VdW attraction). Such a repulsion may serve to stabilize colloidal suspensions, or it may arrest phase separation in binary polymer systems at an intermediate stage (yielding kinetically stable emulsions). The predicted long-range polymer effect is rather subtle, and as such provides an experimental challenge likewise the original Casimir effect. The following systems seem to be favorable for observation of that sort of effects: (a) Emulsion of one polymer in an immiscible polymer with low dielectric contrast (the ratio of VdW to PI forces may be further decreased by adding a nonselective solvent: VdW interactions can be suppressed by dilution that, however, nearly does not affect the PI forces). (b) Thin polymer film (the PI repulsion in the 2-dimensional system scales as $1/r^4$, hence it can dominate over the VdW attraction that is proportional to $1/r^6$). Two-dimensional polymer systems also seem to be ideal candidates for computer investigations of the predicted long-range effects, in particular, (i) of the correlation function of either monomer units or vacancies, and (ii) of interaction between two solid lines in a 2d melt (in order to improve the resolution for the force it may help to consider free rather than fixed parallel lines and living polymer chains with a free exchange of monomer units between the regions inside and outside the gap).

[1] H. B. G. Casimir, Proc. K. Ned. Akad. Wet. **51**, 793 (1948).

[2] M. Kardar and R. Golestanian, Rev. Mod. Phys. **71**, 1233 (1999).

[3] M. E. Fisher and P. G. de Gennes, C.R. Seances Acad. Sci., Ser. B **287**, 207 (1978).

[4] A. Ajdari, L. Peliti, and J. Prost, Phys. Rev. Lett. **66**, 1481 (1991).

[5] P. J. Flory, *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, NY, 1971).

[6] S. F. Edwards, Proc. R. Soc. Vic. **88**, 265 (1966).

[7] P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, NY, 1985).

[8] P.-G. de Gennes, C.R. Acad. Sci., Ser. II: Mec., Phys., Chim., Sci. Terre Univers. **305**, 1181 (1987).

[9] D. Ausserre, J. Phys. (France) **50**, 3021 (1989).

[10] A. N. Semenov, J. Phys. II **6**, 1759 (1996).

[11] E. S. Nikomarov and S. P. Obukhov, Sov. Phys. JETP **53**, 328 (1981).

[12] H. Orland, C. Itzykson, and C. de Dominicis, J. Phys. Lett. **46**, L-353 (1985).

[13] P. D. Gujrati, Phys. Rev. A **24**, 2096 (1981).

[14] We assign $k_B T$ to be the energy unit.

[15] J. Ambjorn and S. Wolfram, Ann. Phys. (N.Y.) **147**, 1 (1983).

[16] K. Milton, hep-th/9901011.

[17] L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon Press, Oxford, 1998).

[18] I. M. Lifshitz, A. Yu. Grosberg, and A. R. Khokhlov, Rev. Mod. Phys. **50**, 683 (1978); A. Grosberg and A. Khokhlov, *Statistical Physics of Macromolecules* (American Institute of Physics, New York, 1994).

[19] A similar singularity was identified in the intrachain and interchain structure factor in semidilute solutions; it was also related to Goldstone modes [20].

[20] M. Müller, K. Binder, and L. Schäfer, Macromolecules **33**, 4568 (2000).