Fluctuation-induced long-range interactions in polymer systems

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Abstract
We discover a new universal long-range interaction between solid objects in polymer media. This polymer-induced interaction is directly opposite to the van der Waals attraction. The predicted effect is deeply related to the classical Casimir interactions, providing a unique example of universal fluctuation-induced repulsion rather than normal attraction. This universal repulsion comes from the subtracted soft fluctuation modes in the ideal counterpart of the real polymer system. The effect can also be interpreted in terms of subtracted (ghost) large-scale polymer loops. We establish the general expressions for the energy of polymer-induced interactions for arbitrary solid particles in a concentrated polymer system. We find that the correlation function of the polymer density in a concentrated solution of very long chains follows a scaling law rather than an exponential decay at large distances. These novel universal long-range interactions can be of importance in various polymer systems. We discuss the ways to observe/simulate these fluctuation-induced effects.

1. Introduction

Fluctuations in polymer melts are generally assumed to be both weak and short range. In fact, the concept of totally screened long-range interactions in concentrated polymer systems is one of the cornerstones of the modern polymer theory [1–3]. This concept is related to the well known Flory theorem concerning polymer chain statistics in a melt [3]. For example, consider a melt of infinitely long linear polymer chains which is locally perturbed by a colloidal particle. How does this perturbation decay with the distance to the source? The classical theoretical answer would be: the perturbation is short range, it decays exponentially at distances longer than the static correlation length ξ which is of the order of the monomer size. In the present paper we prove that this is not true. We demonstrate that the interactions are not totally screened, that concentration perturbations in dense polymers show a power-law rather than an exponential decay at distances larger than ξ, and that there is a long-range repulsion between

two solid particles in a dense polymer system, and a similar interaction between parallel solid plates [4].

These results obviously contradict the idea of no long-range interactions in polymer melts [5, 6]. In order to clarify the issue we present and discuss below several qualitatively different explanations of the long-range effect (all of them are backed by corresponding quantitative treatments in sections 2–4):

(i) We employ the polymer–magnetic analogy [3] 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 [3] we get an interaction which is exactly opposite to the Casimir effect, i.e. long-range repulsion instead of attraction (see section 2).

(ii) Pursuing another approach we start with a concentrated system of *non-interacting* ideal polymers, and then turn on the excluded volume interactions. There are definitely no long-range forces in the ideal system which nevertheless shows soft modes of concentration fluctuations. By turning on monomer interactions we suppress these soft modes (at $q \to 0$) and hence suppress the virtual Casimir attraction associated with these modes, thus inducing an *anti-Casimir* repulsion (see sections 3, 4). We thus elucidate the peculiar connection between the predicted long-range interactions and the fluctuation-induced (Casimir) forces: it turns out that it is not the density fluctuations in the real polymer system (polymer melt) that matter (they are in fact negligible), but rather it is the much stronger fluctuations in the ideal polymer counterpart (i.e. in the reference system of non-interacting polymer chains, before the interactions are turned on) that are relevant. That is why an anomalous opposite effect is predicted: repulsion in contrast to the normally attractive Casimir forces [7–10].

(iii) The third and, perhaps, the best view of the problem is to consider a living melt of bi-functional units (where all functional groups are reacted). At any instant the living system is a mixture of infinite polymer chains and finite cyclic polymers of all sizes. There are no long-range effects in this living system. A linear polymer melt can be derived from the living mixture by eliminating all finite cycles (including long-range ones). However this very elimination procedure also brings in long-range interactions: for example, note that cyclization is more probable in a gap between two solid plates than in the bulk. Therefore elimination of cycles in a narrow gap results in a thermodynamically less favourable state (higher free energy) as compared with a wide gap, and hence repulsion between the plates (see section 4.2).

The predicted polymer-induced long-range (PILR) forces are likely to be of importance in various physical, chemical, and technological applications. Altogether the predicted effect is rather subtle, and as such provides an experimental challenge like that of the original Casimir effect. The possible ways to observe/simulate the PILR interactions are discussed in the last section.

2. The polymer–magnetic analogy

The analogy between a polymer melt and a magnetic system with zero number of spin components is well known (see for example an excellent introduction to the subject given by de Gennes [3]). In this section for the purpose of clarity we restrict ourselves to lattice models of polymer melts and of the corresponding magnetic systems [3, 11–13]. Monomer units occupy the lattice sites; only one unit per site is permitted. The monomer units on the nearest sites are connected with the links, thus forming long chains. Most units are connected

to two other units; a very small fraction of monomer units (chain ends) are connected only to one nearest neighbour.

2.1. The mapping

Below we will follow the mapping of a polymer melt to a magnetic system proposed for lattice models [11, 12]. Consider a lattice of sites $\{r_i\}$ with the 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 neighbouring sites ij, and $K_{ij} = 0$ otherwise). The partition function of the system is [11, 12]

$$Z = \frac{\int \Pi_{\{i\}} d^n \varphi(r_i) e^{-H_0} \Pi_{\{i\}} \{\frac{1}{2}\varphi^2(r_i) + h\varphi_1(r_i) + \alpha\}}{\int \Pi_{\{i\}} d^n \varphi(r_i) e^{-H_0}} \tag{1}$$

where

$$H_0 = \frac{1}{2} \sum_{\{ij\}} \varphi(r_i)(K_{ij})^{-1} \varphi(r_j), \tag{2}$$

operator $(K_{ij})^{-1}$ is inverse to K_{ij}, and h, α are parameters. (These parameters will be used to control the density of end points of polymers and density of vacancies in the corresponding polymer system.) It is assumed that the integration in equation (1) is over appropriate multi-dimensional complex contours such that the integrals converge. This system describes a magnetic system of n-component spins in a constant magnetic field proportional to h, and with spin coupling constants defining the spin interactions proportional to K_{ij}.[3]

Using Wick's theorem (or the Stratonovich–Hubbard transformation with respect to φ) it is easy to prove that the partition function (1) is equal to that of a living system of self-avoiding polymers on the lattice (each lattice site is occupied either by a monomer unit or by a vacancy):

$$Z = \sum_{\mathcal{N}_c, \mathcal{N}_e, \mathcal{N}_v} n^{\mathcal{N}_c} h^{\mathcal{N}_e} \alpha^{\mathcal{N}_v} C_{\text{conf}}(\mathcal{N}_c, \mathcal{N}_e, \mathcal{N}_v) \tag{3}$$

where $C_{\text{conf}}(\mathcal{N}_c, \mathcal{N}_e, \mathcal{N}_v)$ is the number of different configurations of $\mathcal{N} - \mathcal{N}_v$ monomer units forming $\mathcal{N}_e/2$ linear chains and $\mathcal{N}_c$ cycles, $\mathcal{N}$ is the total number of lattice sites, $\mathcal{N}_v$ is the number of vacancies, and $\mathcal{N}_e$ is the number of chain ends. Thus each polymer chain end contributes with the factor h, each unoccupied site with the factor α (the bonds connecting the nearest sites contribute with the factor $K_{ij} = 1$).

Closed loop configurations have an additional factor n through the summation over the components of the fields $\varphi_\alpha(r_i)$. For $n \to 0$ all closed loop configurations are eliminated. Below we consider the regime when $n = 0$ and both α and h are small, which corresponds to a concentrated solution of long linear polymers.

2.2. The mean field approximation

We can rewrite equation (1) as

$$Z = \frac{\int \prod_{\{i\}} d^n \varphi(r_i) e^{-H}}{\int \prod_{\{i\}} d^n \varphi(r_i) e^{-H_0}}$$

where H_0 is defined in equation (2), and

$$H = H_0 - \sum_i \ln\left(\frac{1}{2}\varphi^2(r_i) + h\varphi_1(r_i) + \alpha\right). \tag{4}$$

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[3] Note that for $n \neq 0$ the Hamiltonian H does not necessarily correspond to a realistic magnetic lattice spin system. This is just as a mathematical trick for obtaining the free energy of a system of living polymers with cycles.

The mean field approximation is equivalent to the saddle-point evaluation of both integrals in the above expression for the partition function Z [12]: $Z \simeq e^{-H^* + H_0^*} \equiv Z_{mf}$. The saddle point for the denominator is $\varphi = 0$, $H_0^* = 0$. Assuming that the saddle point for the numerator $H^* = H\{\varphi^*\}$ corresponds to a uniform field $\varphi^*(r_i) = (\varphi_1^*, 0 \ldots 0)$ we get the following mean field equation:

$$\varphi_1^* \left(\varphi_1^{*2}/2 + h\varphi_1^* + \alpha \right) - z \left(\varphi_1^* + h \right) = 0$$

where z is the coordination number of the lattice. The mean field approximation is applicable if $z \gg 1$ [12].

For the uniform system we thus get $H^* = \mathcal{N}[\frac{1}{2z}(\varphi_1^*)^2 - \ln(\frac{1}{2}\varphi_1^{*2} + h\varphi_1^* + \alpha)]$. Since we are interested in the properties of a melt or a concentrated solution ($\alpha \ll 1$) of long polymers ($h \ll 1$), we keep only the first-order terms in h and α:

$$\varphi_1^{*2} \simeq 2z - 2\alpha - h\sqrt{2z}.$$

The free energy per site in this approximation is: $F_{mf} = \frac{H^* - H_0^*}{\mathcal{N}} \simeq 1 - \alpha/z - 2h/\sqrt{2z} - \ln z$ (here and below we assume that $k_B T$ is the energy unit; however we explicitly write $k_B T$ in some final equations). The corresponding partition function is

$$Z_{mf} \simeq (z/e)^{\mathcal{N}} \exp\left(2h\mathcal{N}/\sqrt{2z} \right) \exp\left(\alpha\mathcal{N}/z \right). \tag{5}$$

This result will be improved in the next section by including the fluctuations around the saddle point. Let us interpret Z_{mf} in terms of the number of different configurations of polymers on the lattice. Equation (3) implies that the average numbers of end points and vacancies can be calculated by taking logarithmic derivatives of the partition function with respect to the conjugate parameters: $\mathcal{N}_e = \frac{\partial \ln Z}{\partial \ln h} \simeq 2\mathcal{N}h/\sqrt{2z}$, $\mathcal{N}_v = \frac{\partial \ln Z}{\partial \ln \alpha} \simeq \mathcal{N}\alpha/z$. Thus the average length of the polymers is $N_0 = 2 (\mathcal{N} - \mathcal{N}_v)/\mathcal{N}_e - 1 \simeq \sqrt{2z}/h$. Therefore the regime we consider ($\alpha \ll 1$, $h \ll 1$) indeed corresponds to long polymer chains ($N_0 \gg 1$) and low fraction of vacancies ($\mathcal{N}_v/\mathcal{N} \ll 1$). Note that the average number of cycles is 0 in the mean field approximation since Z_{mf} does not depend on n. Using equations (5) and (3) we can estimate the number $C_{conf} (\mathcal{N}_c = 0, \mathcal{N}_e, \mathcal{N}_v)$ of different configurations of $\mathcal{N}_e/2$ polymers with $\mathcal{N}_v$ vacancies:

$$C_{conf} (\mathcal{N}_c = 0, \mathcal{N}_e, \mathcal{N}_v) \simeq \frac{Z_{mf}}{h^{\mathcal{N}_e} \alpha^{\mathcal{N}_v}} \simeq \left(\frac{z}{e} \right)^{\mathcal{N} - \mathcal{N}_e/2 - \mathcal{N}_v} \left(\frac{2e}{c_e^2} \right)^{\mathcal{N}_e/2} \left(\frac{1}{c_v} \right)^{\mathcal{N}_v} \tag{6}$$

where $c_e = \mathcal{N}_e/\mathcal{N} \simeq 2/N_0$ is the concentration of ends and $c_v = \mathcal{N}_v/\mathcal{N}$ is the concentration of vacancies. Noting that $\mathcal{N}_e/2$ is the number of polymer chains, and $\mathcal{N} - \mathcal{N}_e/2 - \mathcal{N}_v$ is the number of polymer bonds, we conclude that the statistical weights that must be attributed to each bond and each vacancy are $\frac{z}{e}$ and $\frac{1}{c_v}$ respectively. The chain statistical weight is $\frac{2e}{c_e^2} \simeq \frac{1}{2} \frac{e}{c_p} N_0$, where $\frac{1}{2}$ is the symmetry factor, $c_p = c_e/2$ is the concentration of chains, $\frac{e}{c_p}$ is the standard ideal-gas factor, and the factor N_0 (the average length of the chain) accounts for the width of the chain length distribution.

2.3. The effect of fluctuations

In order to include the order parameter fluctuations around the mean field $\varphi^*(r_i) = (\varphi_1^*, 0 \cdots 0)$ we expand the Hamiltonian, equation (4), for small deviations from this saddle point, use the quadratic approximation, and evaluate the corresponding Gaussian integrals using the steepest descent method. The denominator in equation (1) can be easily evaluated in the same way; it stays equal to 1 for $n = 0$.

The result of this calculation is: $Z \simeq Z_{mf} Z_{fluct}$, where

$$Z_{fluct} = \prod_{k} [f(k)]^{-1/2} .$$

Here the product is taken over the relevant spectrum of wavevectors k determined by the system size,

$$f(k) \simeq [1 + (1 - 2\alpha/z - 1/N_0) K(k)] [1 - (1 - 1/N_0) K(k)]^{(n-1)} ,$$

$$K(k) = \frac{1}{z} \sum_{j} K_{ij} e^{ik \cdot (r_i - r_j)} \tag{7}$$

is the Fourier transform of K_{ij}, $K(0) = 1$, and $1/N_0 \simeq h/\sqrt{2z}$. Equation (7) is valid in the first approximation for $h \ll 1$, $\alpha \ll 1$. Thus fluctuations of the order parameter produce an additional contribution to the free energy:

$$F_{fluct} = - \ln Z_{fluct} \simeq \tfrac{1}{2} \sum_{k} \log f(k). \tag{8}$$

The term in the first square brackets in equation (7) comes from the integration over longitudinal fluctuations, $\varphi_1 - \varphi_1^*$, which are associated with correlation function of the total density of monomer units. The term in the second square brackets comes from integrations over $n - 1$ transverse fluctuations of the order parameter (Goldstone modes) which are associated with end-to-end correlations of individual polymer chains. From this point on we will always consider the case $n = 0$, so the number of transverse modes is equal to -1. At small h (long polymer chains) these modes have a gap $1/N_0 \simeq h/\sqrt{2z}$ and the main contribution to Z_{fluct} comes from the terms with small $k \sim (1/N_0)^{1/2}$. In real space this corresponds to the distances up to the typical polymer coil size $\sim N_0^{1/2}$.

We are now in a position to consider the system in the presence of two parallel impenetrable plates. The plates affect the order parameter fluctuations, thereby changing the free energy. An effective interaction between the plates is thus induced. We may disregard the effects of distortion of the order parameter profile near the boundaries: this distortion decays exponentially away from the boundary, so it cannot contribute to the interaction between the plates separated by a distance larger than a few lattice units. It is convenient to consider the plates oriented normal to the x_1-axis: $x_1 = -1/2$ (plate 1) and $x_1 = D - 1/2$ (plate 2), where D is the distance between the plates (the position vector $r = (x_1, x_2, \ldots, x_d)$, where d is the space dimension). We focus on the part of the system in the gap, $-1/2 < x_1 < D - 1/2$: it is this part that determines the interaction of plates. The partition function Z of the system with plates is defined by the general equations (1), (2) with the same matrix K_{ij} except that now $K_{ij} = 0$ for all lattice bonds (ij) crossing the plates. The last condition ensures that the plates are impenetrable: the same Z corresponds to a system of living polymer chains that do not cross the plates. In order to proceed we need to establish the boundary conditions for the order parameter φ. For simplicity we first consider just one plate at $x_1 = -1/2$ and the sub-system $x_1 > -1/2$. Let us modify slightly the spin interaction matrix: $K_{ij} \rightarrow K_{ij} + \delta_{ij}\Delta_i$, where δ_{ij} is the Kronecker delta, $\Delta_i = 1$ if r_i is near the plate (at the distance $1/2$), and $\Delta_i = 0$ otherwise. This transformation for $n = 0$ does not affect at all either the statistics of the corresponding polymer system or the partition function Z. Let us compare the modified half-system and the original bulk system with no plate with the same order parameter field $\varphi(r_i)$ for $x_1 > -1/2$; for the bulk system we demand in addition that the field $\varphi(r_i)$ is symmetric with respect to the reflection in the plane $x_1 = -1/2$. It is easy to show that the Hamiltonian H for the half-system ($x_1 > -1/2$) is exactly $1/2$ of the original bulk Hamiltonian of the whole system with no plate. Hence reflective (Neumann) boundary conditions must be imposed at the plates (i.e. $\partial\varphi/\partial x_1 = 0$ in the continuous limit). In this case the mean field (saddle point)

$\varphi^*(r_i) = \{\varphi_1^*, 0 \cdots 0\}$ is not affected by the plates (i.e. φ^* remains uniform), and the mean field free energy F_{mf} is not affected by the plates either. It is the spectrum of fluctuations of φ that is defined by the plates. The relevant wavevectors $k = (k_1, k_2, \ldots, k_d)$ now include the discrete component perpendicular to the plates: $k_1 = \pi m/D$, $m = 0, \ldots, D-1$ (the parallel components $k_2, \ldots, k_d$ are continuous). Taking into account only transverse modes (i.e. order parameter fluctuations perpendicular to the unperturbed vector φ^*: it is these modes that are soft for small k) we get

$$F_{\mathrm{fluct}} \simeq A \sum_{m=-\infty}^{+\infty} \Phi(m) \tag{9}$$

where $\Phi(m) = -\frac{1}{2} \int \frac{\mathrm{d}^2 k}{(2\pi)^2} \ln(k^2 + m^2 \pi^2/D^2 + 2d/N_0)$, A is the plate area. Note that equation (9) implies that F_{fluct} is independent of α.

In order to obtain only the distance dependent contribution to F_{fluct} we can subtract from F_{fluct} the contribution of fluctuations in the bulk, where the summation over k_1 is replaced by integration. This regularization of the sum in equation (9) (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 with mass [14, 15]. For technical reasons it is convenient to calculate directly the force $f = -\frac{1}{A} \frac{\partial F_{\mathrm{fluct}}}{\partial D}$ between the plates. The final result for $d = 3$ is

$$f \simeq \frac{k_B T}{16\pi D^3} \int_{2D/R_g}^{\infty} \frac{x^2 \, \mathrm{d}x}{e^x - 1} \tag{10}$$

where $R_g \simeq \sqrt{N_0/6}$ is the polymer coil gyration radius. For $D \ll R_g$ we get the standard expression for the Casimir force with massless scalar field [14]:

$$f = k_B T \zeta(3) / \left(8\pi D^3\right), \tag{11}$$

however, with the opposite sign because of the negative number (-1) of soft components. In other words the predicted long-range *repulsion* is due to the negative number of soft Goldstone modes. For $D \gg R_g$ we get an exponential decay:

$$f \simeq \frac{k_B T}{16\pi D^3} \left(2D/R_g\right)^2 e^{-2D/R_g}.$$

The cases of cubic and body centred cubic lattices with no vacancies, $\alpha \to 0$, are somewhat special if only the nearest neighbour interactions are involved. In these cases the inverse longitudinal propagator is zero at $k = (\pi, \ldots, \pi)$ [12], leading to an oscillatory correlation function of vacancies showing a tendency towards antiferromagnetic ordering. Formally, in the limit of an extremely dense melt $\alpha \to 0$ the contribution of the longitudinal mode cancels the effect of -1 transverse modes. This cancellation effect exists only for simple cubic and bcc lattices and only with minimal number of nearest neighbours. It is easy to check that for any other generic lattice the longitudinal fluctuations are unimportant. On these two special lattices the obligatory condition for this cancellation is that the number of vacancies is much less than the number of polymer chains. Basically this means that the dense packing problem for a polymer chain (Hamiltonian path problem) on these two lattices is different from the generic dense packing problem, because of specific symmetry constraints. We will address this issue in a future publication[4].

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[4] Moreover, even for the special cubic lattices the soft longitudinal mode is likely to be a mean field effect valid in the random phase approximation (RPA). A due account of the higher order fluctuation corrections would renormalize the gap for the longitudinal mode and would then reinstall the long-range interaction even for the special lattices (note that the minimal number of nearest neighbours corresponds to the strongest fluctuations, i.e. to significant corrections to the RPA results). It is therefore likely that the 'antiferromagnetic' oscillations represent a *short-range* effect even for the special cubic lattices, and even in the limit $\alpha \to 0$.

3. The real-space analysis of the long-range fluctuation effects

In this section we consider the long-range effects using an alternative purely 'polymeric' theoretical approach. The analysis directly involves the free energy as a functional of the real-space distribution of polymer conformations.

3.1. Correlation function of polymer density fluctuations

Let us discuss the fluctuation effects for the equilibrium correlation function of density fluctuations in a polymer melt (or in a concentrated solution). The correlation function

$$\mathcal{G}(r) = \langle \delta c(r) \delta c(0) \rangle$$

is related to the scattering function (the structure factor)

$$S(q) = \frac{1}{V} \langle c_q c_{-q} \rangle = \int \mathcal{G}(r) e^{ir \cdot q} d^d r$$

where $\delta c(r) = c(r) - c_0$, $c(r)$ is the local concentration of monomer units, c_0 is its average value, $c_q = \int c(r) e^{-iq \cdot r} d^d r$ is its Fourier transform, V is the total volume, and d is the space dimension. The equilibrium probability of a fluctuation $\delta c(r)$ is proportional to $e^{-H[c(r)]}$, where $H[c]$ is the effective Hamiltonian (mesoscopic free energy) of the system [16][5]. Once $H[c]$ is known, both $S(q)$ and $\mathcal{G}(r)$ can be calculated using a standard technique, e.g. by expanding $H[c]$ as a series in δc (a melt is a weakly fluctuating system, so δc is typically small, $\delta c \ll c_0$). For example,

$$S(q) = \frac{1}{V} \int c_q c_{-q} e^{-H[c]} D[c] \bigg/ \int e^{-H[c]} D[c], \qquad q \neq 0. \tag{12}$$

The Hamiltonian can be written as

$$H[c] \simeq H_{\text{id}}[c] + H_{\text{int}}[c]$$

where H_{id} corresponds to the reference system of ideal polymer chains (with the same chemical bonds, but no excluded volume interactions), and H_{int} is essentially the free energy of monomer interactions. The well known mean field result for a dense system of non-interacting (ideal) infinitely long polymer chains reads [17, 19, 3]

$$H_{\text{id}}^{(0)}[c] = \frac{a^2}{4} \int \frac{(\nabla c)^2}{c} d^d r \tag{13}$$

where $a^2 = b^2/(2d)$, b, the chain statistical length. This equation is valid for both weak and strong inhomogeneities (i.e. in the general case $\delta c \sim c_0$) provided that the relevant length scale is larger than Λ. As for the interaction energy H_{int}, we may expand it as a series in $\delta c = c - c_0$ and keep only the dominant quadratic term assuming that $\delta c \ll c_0$:

$$H_{\text{int}} \simeq \frac{1}{2} \int v (c - c_0)^2 d^d r. \tag{14}$$

The irrelevant constant and linear terms are omitted here. The interaction parameter v is related to the bulk compression modulus of the system (osmotic modulus in the case of solution):

$$v = \frac{1}{c_0} \frac{\partial \Pi}{\partial c_0} \tag{15}$$

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[5] Note that the effective Hamiltonian is a functional of the coarse-grained (rather than microscopic) concentration distribution $c(r)$, with some coarsening scale Λ, $c_0 \Lambda^d \gg 1$.

where Π is the pressure (osmotic pressure). Thus in the general case v is not just the excluded volume of a monomer unit[6]. Adopting the quadratic approximation also for $H_{id}^{(0)}$, i.e. expanding it in δc and truncating the expansion, and using equations (12), (13), (14), we get the classical result $S(q) \simeq \frac{1}{v} \frac{1}{1+q^2\xi^2}$, where $\xi \simeq a/\sqrt{2vc_0}$ is the mean field static correlation length. It is also easy to show that higher order terms in either $H_{id}^{(0)}$ or H_{int} result in negligible corrections to the structure factor (provided that the fluctuation parameter $Gi \equiv \frac{v^{d-2}}{c_0^{4-d}b^{2d}} \ll 1$, i.e. in the mean field regime)[7]. So what is the point?

The central point is that the very basic expression for $H_{id}^{(0)}$, equation (13), must be modified, because the effective Hamiltonian $H_{id}^{(0)}$ is not exact even for the ideal polymer system! To see this we calculate $S_0(q)$, the structure factor of the ideal system using equation (13). The result for $d = 3$ is (it can be easily obtained by using the substitution $c = c_0\psi^2$)[8]

$$S^{(0)}(q) \simeq \frac{2c_0}{q^2a^2}\left\{1 + \text{const}\,\frac{q}{c_0a^2}\right\}$$

where the last term in curly brackets is a correction due to higher order terms in the δc-expansion of $H_{id}^{(0)}$. Yet the structure factor of the ideal long Gaussian chains is known to be exactly $S_{id}(q) = \frac{2c_0}{q^2a^2}$. Hence there is a correction to $H_{id}^{(0)}$:

$$H_{id} = H_{id}^{(0)} + H_{nloc}. \tag{16}$$

Demanding that H_{id} generates the correct structure factor (and higher order correlation functions characterizing the ideal system) we get

$$H_{nloc} = \frac{1}{2}\frac{\varkappa_d}{c_0^2}\int q^d \delta c_q \delta c_{-q} \frac{d^d q}{(2\pi)^d} + O\left(\frac{\delta c}{c_0}\right)^3$$

where $\varkappa_d = 2^{-2d}\pi^{\frac{3-d}{2}}\frac{1}{\cos\left(\frac{\pi(3-d)}{2}\right)\Gamma\left(\frac{d-1}{2}\right)}$. Note that H_{nloc} is essentially non-local, and it can be represented as

$$H_{nloc} \simeq \frac{C_d}{2c_0^2}\int \delta c(r)\delta c(r')\frac{1}{|r-r'|^{2d}}d^d r\,d^d r' \tag{17}$$

where $C_d = \frac{\sqrt{\pi}}{(2\pi)^d}\frac{\Gamma(d)\Gamma(1+d/2)}{\Gamma(d/2-1/2)}$. It is this fluctuation-induced non-local term H_{nloc} that is the source of all long-range effects in dense systems of interacting polymers.

With $H \simeq H_{id}^{(0)} + H_{nloc} + H_{int}$ as defined by the above equations we get[9]

$$S(q) \simeq \left(v + \frac{q^2a^2}{2c_0} + \varkappa_d\frac{q^d}{c_0^2}\right)^{-1}, \qquad q\xi \ll 1. \tag{18}$$

The last term in brackets, $\sim q^d$, is due to the fluctuation-induced Hamiltonian H_{nloc}.[10] The q^d term is not dominant, yet it is very important at low q since with this term $S(q)$ becomes non-analytical (weakly singular) at $q = 0$. This weak singularity generates a long-range power-law tail in the correlation function for $r \gtrsim \xi$:

$$\mathcal{G}(r) = \int S(q)e^{iq\cdot r}\frac{d^d q}{(2\pi)^d} \simeq \mathcal{G}_{mf}(r) - \frac{C_d}{v^2c_0^2}\frac{1}{r^{2d}} \tag{19}$$

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[6] In the general case a length scale dependence of v must be taken into account, i.e. the integrand in equation (14) must be replaced by the form $v(r, r')\delta c(r)\delta c(r')$. However normally the direct monomer (excluded volume) interactions are short range, so the dispersion can be neglected if we set the cut-off Λ to be longer than the interaction length scale.

[7] The corrections to the mean field $S(q)$ do not bring in any long-range effect even in the general case $Gi \sim 1$ when these corrections are non-negligible.

[8] We neglect the inessential terms that tend to 0 as the cut-off Λ is increased.

[9] Here we neglect trivial corrections like a renormalization of the parameter a.

[10] A similar q^3 term for the intra-chain structure factor for $d = 3$ was derived in [24].

where $\mathcal{G}_{\mathrm{mf}}(r)$ is the mean field result. For $d = 3$ we get

$$\mathcal{G}(r) \simeq \frac{c_0}{2\pi r a^2} e^{-r/\xi} - \frac{3}{16\pi^2} \frac{1}{v^2 c_0^2} \frac{1}{r^6} \qquad \text{for } r \gtrsim \xi. \qquad (20)$$

Note that $\mathcal{G}(r)$ is non-monotonic: it becomes negative for r larger than a few ξs (i.e., *anti-correlation* at large distances). Note also that equations (19), (20) are valid for almost any r in the case of sufficiently long chains. These equations are asymptotically correct for $r \gg \xi$ because the basic equation (18) is valid in the corresponding low q regime as long as the relevant fluctuation parameter (the Ginzburg parameter) is small [2, 17–19]: $\mathrm{Gi} \equiv \frac{v^{d-2}}{c_0^{4-d} b^{2d}} \ll 1$. On the other hand, the above equations for $\mathcal{G}(r)$ are also asymptotically valid for $r \sim \xi$ because the mean field term, $\mathcal{G}_{\mathrm{mf}}$, is dominant in this region (if $\mathrm{Gi} \ll 1$). In addition, the first term in equation (20) assumes Gaussian statistics which is valid for $r \gg b$. Equation (20) is also valid for polymer chains of finite length if r is smaller than the coil size $R_{\mathrm{g}} \simeq b N^{1/2}/\sqrt{2d}$, i.e. this equation is applicable in the range $b \ll r \ll R_{\mathrm{g}}$.

In practice the fluctuation parameter is often not small. This is true, for example, for lattice (Flory) models of flexible polymers, or at low enough concentrations. (In semidilute solutions $\mathrm{Gi} = \frac{v^{d-2}}{c_0^{4-d} b^{2d}}$ can formally be $\gg 1$; this marks the scaling regime of swollen blobs. In this regime we can consider concentration blobs as renormalized monomers thus bringing the fluctuation parameter back to $\mathrm{Gi} \sim 1$.) Therefore it is important to work out whether the above results are applicable when fluctuations are not weak, i.e. in the regime $\mathrm{Gi} \sim 1$. This is a more subtle issue. The higher order fluctuation corrections could considerably affect the first term in equation (20). However, this term is exponentially small for $r \gg \xi$, so only the second non-local term survives in this regime. Do fluctuations renormalize this term? To find this out we consider a coarse-grained model with large enough coarsening scale $\Lambda \gg \xi$. Then the effective Hamiltonian $H[c]$ is considered as a functional of the smoothed concentration distribution $c(\boldsymbol{r})$ which can be defined, for example, by specifying the number of monomers in each cell of size Λ. Turning to the ideal (non-interacting) system we identify the relevant fluctuation parameter as $\left(\frac{\delta c}{c_0}\right)^2 \sim \frac{1}{c_0 b^2 \Lambda}$, where the fluctuation δc is averaged over a cell (for $d = 3$). The parameter $\frac{1}{c_0 b^2 \Lambda}$ is small if $\Lambda \gg \xi$ and $\mathrm{Gi} \sim 1$; therefore fluctuations of the *coarse-grained* $c(\boldsymbol{r})$ are weak even for the ideal system (and of course they become even weaker when the monomer excluded volume interactions are turned on). In other words we consider renormalized monomers of size much larger than ξ. These monomers strongly overlap. Therefore the fluctuation effects are weak; i.e. the effective renormalized fluctuation parameter is small for length scales larger than ξ. It is in the regime of weak fluctuations that the mean field result for H_{id}, equation (13), is asymptotically exact [17], and the same conclusion applies to the non-local correction H_{nloc}. In fact, a renormalization of the cell size obviously does not affect the non-local term provided that $\delta c \ll c_0$; therefore equation (17) is asymptotically exact for $\Lambda \gg \frac{1}{c_0 b^2}$ when the typical fluctuations are indeed small ($\delta c \ll c_0$). When the excluded volume monomer interactions are turned on, the effective Hamiltonian must be modified. In the case $\Lambda \gg \xi$, $\mathrm{Gi} \sim 1$ this modification is not as simple as adding the interaction term, equation (14). The interactions can affect the polymer chain conformations at the sub-cell length scale $< \Lambda$; hence, for example, the statistical segment must be renormalized: $b \to b^*$ [26]. The square-gradient term, equation (13), is also affected by the interactions; in particular, the coefficient a^2 is renormalized: $a^2 \to \tilde{\beta}$. Note however that the two renormalizations are essentially different: in the general case $\tilde{\beta}/a^2$ is not equal to $(b^*/b)^2$! Normally $b^* > b$, meaning that a sufficiently long chain fragment is somewhat swollen relative to its unperturbed Gaussian size [26]. On the other hand, $\tilde{\beta}$ can become smaller than a^2; moreover, the square-gradient term may even become negative, i.e. $\tilde{\beta} < 0$ (this was shown for $d = 2$ [20], but can possibly be the case also for $d = 3$). Since monomer interactions are local, they do not affect the general structure of the

non-local Hamiltonian; however they can renormalize its amplitude giving rise to an additional prefactor κ^* in equation (17). This prefactor accounts for the effect of higher order fluctuation corrections (beyond the one-loop approximation). The factor κ^* is calculated in section 4.2.

Thus the effective Hamiltonian for $\Lambda \gg \xi$, $\text{Gi} \sim 1$ is $H[c] = H^{(0)} + H_{\text{nloc}}$:

$$H[c] \simeq \int \left[\frac{\tilde{\beta}}{4c_0} (\nabla c)^2 + \frac{v}{2} (\delta c)^2 \right] \mathrm{d}^d r + \frac{\kappa^* C_d}{2c_0^2} \int \delta c(\mathbf{r}) \delta c(\mathbf{r}') \frac{1}{|\mathbf{r} - \mathbf{r}'|^{2d}} \, \mathrm{d}^d r \, \mathrm{d}^d r' \qquad (21)$$

where $\delta c = c(\mathbf{r}) - c_0$, $\delta c \ll c_0$. The case $\delta c \sim c_0$ in considered in section 4.

The correlation function $\mathcal{G}(r)$ for $r \gg \xi$ can be obtained from equation (21) using its general relation to the corresponding susceptibility [16]. The result is (compare with the second term in equation (19)):

$$\mathcal{G}(r) \simeq -\frac{\kappa^* C_d}{v^2 c_0^2} \frac{1}{r^{2d}}, \qquad r \gg \xi \qquad (22)$$

where v is defined in equation (15). This result is valid in the general case, $\text{Gi} \sim 1$. For simplicity below (and until section 4.2) we assume that fluctuations are weak, $\text{Gi} \ll 1$, so that $\kappa^* \simeq 1$, i.e. the interactions of monomer units nearly do not affect the non-local Hamiltonian. The interaction energy is then simply additive: $H = H^{(0)} + H_{\text{nloc}}$, $H^{(0)} \simeq H_{\text{id}}^{(0)} + H_{\text{int}}$.

The correlation function also defines the response of the system to a weak perturbation induced, for example, by two probe monomers: their interaction potential is [2] $v^*(r) \simeq -v^2 \mathcal{G}(r)$. Using equation (20) we find

$$v^*(r) \simeq \frac{3}{16\pi^2} \frac{k_{\text{B}} T}{c_0^2} \frac{1}{r^6} \qquad \text{for } r \gg \xi. \qquad (23)$$

Note that this power law ($1/r^6$) already emerged in the non-local Hamiltonian, equation (17). Thus monomer interactions are not completely screened at $r \gg \xi$: effective long-range *repulsion* between the monomers is predicted (as opposed to the classical mean field attraction at $r \lesssim \xi$). The interaction of two oligomeric chains, each of g monomers, is g^2 times stronger (provided that the distance r between the chains is larger than their size). A similar repulsion is predicted for any particles immersed in a dense polymer system (see below, section 4.4).

The two-dimensional case is somewhat special [20]: a renormalization of the length a must be taken into account. Then we get (compare with equation (18)) $S(q) \simeq \left(v + \frac{q^2 a_0^2}{2c_0} + \frac{q^2 \ln q \xi}{8\pi c_0^2} \right)^{-1}$ for $d = 2$, where $2a_0$ is the unrenormalized statistical segment. Note that this $S(q)$ is non-monotonic: it shows a *maximum* at a finite $q = q^* \sim \xi^{-1} \mathrm{e}^{-4\pi c_0 a_0^2}$. Fourier transforming this $S(q)$ we get $\mathcal{G}(r) \simeq \frac{c_0}{\pi a_0^2} K_0(r/\xi) - \frac{1}{4\pi^2} \frac{1}{v^2 c_0^2} \frac{1}{r^4}$ (for $r \gtrsim \xi$) in agreement with equation (19).

3.2. Interaction between two solid plates in a polymer melt

Consider two parallel thin solid plates immersed in a polymer system, the separation D between the plates being much smaller than their lateral size. The effective interaction between such plates is of fundamental importance: the practically interesting case of curved surfaces can be reduced to the plain case by virtue of the Deryagin approximation [21]. As before we first assume that polymer chains are very long: their coil size R_{g} is much larger than D. It is well known that dilute polymers induce a depletion attraction between the plates [22, 23] (of course we assume a complete thermodynamic equilibrium, in particular of polymer chains in the gap between the plates and outside this gap). At higher polymer concentrations the range of this attraction becomes progressively shorter: the attraction decays exponentially at separations larger than the static correlation length, $D > \xi$. According to the mean field theory the interaction is totally suppressed in an incompressible polymer melt.

Below we elucidate the nature of a long-range universal *repulsion* between the plates at $\xi \ll D \ll R_g$. We assume that the direct plate/monomer or monomer/monomer interactions are short ranged (with the length scale comparable with the monomer size) and neglect any *direct* interactions of the plates.

For simplicity of the further consideration we assume that the monomer/plate interaction is chosen in such a way that the monomer density profile is least perturbed outside a few monolayers near the plate. This assumption does not affect the generality of our conclusions: obviously the short-range monomer/solid interaction defines the interfacial tension; however it cannot possibly affect the long-range force between the plates. In other words we consider the case of neutral solid walls with short-range attraction of monomers exactly compensating their steric repulsion from the walls. Such surfaces impose reflective boundary conditions on the monomer distribution: $u \cdot \nabla c = 0$ at the wall, where u is the unit vector normal to the wall.

As before we write the effective Hamiltonian of the system as $H = H_{id} + H_{int}$, where H_{int} is defined in equation (14). We start with the ideal system, $v = 0$. The ideal-chain problem is exactly solvable (with any boundary conditions; it is indeed trivial with 'reflective' boundaries), the result is no force at all (i.e. the free energy $F = F_0$ of ideal polymers does not depend on the separation between the walls).

Next we turn on excluded volume monomer interactions, i.e. increase v keeping c_0 constant, and employ the theorem on small variations [16]: $\frac{\partial F}{\partial v} = \langle \frac{\partial H}{\partial v} \rangle = \langle \frac{1}{2} \int (c - c_0)^2 \, d^d r \rangle$. Thus $\frac{\partial F}{\partial v}$ is related to concentration fluctuations in the gap[11]:

$$\frac{\partial F}{\partial v} = \frac{DA}{2} \int \frac{d^{d-1} q'}{(2\pi)^{d-1}} \sum_m \langle |c_{mq'}|^2 \rangle \qquad (24)$$

where A is the total area of one plate, $c_{mq'}$ are normal modes of concentration fluctuations, $m = 0, 1, 2, \ldots$;

$$c(r) = \int \frac{d^{d-1} q'}{(2\pi)^{d-1}} e^{iq' \cdot r'} \left\{ c_{0q'} + \sqrt{2} \sum_{m=1}^{\infty} c_{mq'} \cos(q_m x) \right\}$$

$q_m = \frac{\pi m}{D}$; $r = (x, r')$, the x-axis is perpendicular to the plates (located at $x = 0$ and D), and r' represents $d - 1$ in-plate coordinates[12]. Next we calculate the structure factor in the gap using the RPA:

$$\langle |c_{mq'}|^2 \rangle = \frac{1}{D} \frac{1}{v + 1/S_{id}(q)} \qquad (25)$$

where $q = \sqrt{q'^2 + q_m^2}$, and $S_{id}(q)$ is the structure factor of the reference ideal system of Gaussian chains. (The term with $m = 0$ in equation (24) gives rise to a constant contribution to the free energy, and hence it does not contribute to the force and can be neglected.) Evaluating the sum in equation (24) we find the free energy $F = F_0 + \int \frac{\partial F}{\partial v} \, dv$ of the non-ideal polymer system:

$$F - F_0 \simeq \frac{A}{4} \int \frac{d^{d-1} q'}{(2\pi)^{d-1}} \widetilde{\sum_m} \ln S_{id}(q) \qquad (26)$$

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[11] Of course the external monomer pressure outside the gap also depends on v. However this pressure does not depend on D, and hence it is unrelated to the long-range interaction between the plates. Accordingly any contributions to F of the form $C_0 + C_1 D$, with constants C_0, C_1 independent of D, are neglected here and below.

[12] To get the basis functions of x, $\cos(q_m x)$, we apply the reflective boundary conditions $\frac{\partial c}{\partial x} = 0$ at the plates. In principle there is no need for the fluctuation δc to actually obey these boundary conditions. However, in order to use the bulk structure factor, we must extrapolate the concentration profile in the gap to the whole volume. This extrapolation must be performed by appropriate reflections (to keep the equivalence of the confined system and the bulk system) resulting in an even and periodic profile whose standard Fourier expansion involves precisely these basis functions, i.e. $\cos(q_m x)$.

where m is now taking all integer values both negative and positive, and the extra $1/2$ factor is compensating for this doubling of the sum[13]. This equation is similar to our previous result equation (8) obtained for the lattice model.

Defining the long-range interaction energy, $F_{lr} = F - F_0$, and evaluating the rhs of the above equation we obtain

$$F_{lr}/A \simeq B_d \frac{k_B T}{D^{d-1}} \qquad (27)$$

where $B_d = \frac{\Gamma(d/2)\zeta(d)}{2^d \pi^{d/2}}$; $B_2 = \frac{\pi}{24}$; $B_3 = \frac{\zeta(3)}{16\pi}$. This result is obviously in agreement with equation (11) obtained in the previous section using the polymer–magnet analogy (note that F_{lr} should be identified with F_{fluct}).

Equation (27) is valid for any large enough interaction parameter v such that $\xi = \frac{a}{\sqrt{2c_0 v}}$ is much smaller than D. It might seem surprising that it is enough to calculate concentration fluctuations inside the gap in the mean field approximation (RPA). One reason is that the dominant contribution to F_{lr} comes from the region of small v ($v \sim \frac{a^2}{D^2 c_0}$) where the polymer system is nearly ideal (in this regime the fluctuations are characterized by the exactly known structure factor $S_{id}(q)$); a simple analysis shows that corrections to the RPA correlation functions generate just small, subdominant contributions to F_{lr} (in particular, the singular, non-local, correction to $S(q)$ gives rise to a contribution to F_{lr} of relative order $\frac{1}{vc_0^2 D^3}$).

Note that both the dependence on D of F_{lr} and its amplitude coincide with the thermal fluctuation-induced Casimir interaction found in many systems with soft modes [8], but with the opposite sign. The physical origin of this difference was mentioned in the introduction: the long-range repulsion in the polymer melt is not due to any soft fluctuations in the melt, but rather is due to the subtracted soft fluctuations in the reference ideal polymer system (corresponding to the lower limit of integration over v). In other words the mean field ideal-chain Hamiltonian $H_{id}^{(0)}$, equation (13), involves soft fluctuation modes formally producing a sort of Casimir attraction in the ideal system. That is where the non-local term in the ideal-chain Hamiltonian comes from: it must compensate for the Casimir attraction in the reference system. In the polymer melt the fluctuation-induced attraction is suppressed, but the non-local term remains the same, and hence the net repulsion is generated as a result.

So far we assumed infinite polymer chains. With finite chains of N units we must expect the same interaction for $D \ll R_g$, and almost no (exponentially weak) interaction for $D \gg R_g$. The quantitative treatment is analogous to that given above. We consider two cases[14]:

(i) Monodisperse chains. Here the ideal structure factor is (see for example [3])

$$S_{id}(q) = c_0 N g(q^2 R_g^2), \qquad g(x) \equiv \frac{2}{x^2}\left(x - 1 + e^{-x}\right)$$

where $R_g^2 = Nb^2/(2d)$ is the mean square gyration radius of the chains. Using equation (26) with this S_{id} we get the interaction energy F_{lr}. In the general case F_{lr} could be obtained by direct numerical integration/summation in equation (26). For the three-dimensional space a

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[13] One must bear in mind that $c(r)$ is the coarse-grained function, i.e. q is bounded: $q \lesssim 1/\Lambda$. For practical purposes it is convenient to introduce the coarse graining by an appropriate cut-off factor $\Delta(q)$ in the integrand, such that $\Delta(q) = 1$ for $q < 1/\Lambda$ and $\Delta(q)$ smoothly vanishes for larger q. That sort of coarse graining is implied in replacing the sum in equation (24) by the regularized sum equal to the sum minus the corresponding integral ($\widetilde{\sum}_m = \sum_m - \int dm$). Note that the subtracted integral corresponds to the bulk free energy contribution which eventually precisely compensates for the pressure outside the gap. Therefore the excess free energy $F - F_0$ can be regarded as the energy of interaction between the plates.

[14] In the case of finite chains the long-range interactions are generated already in the mean field approximation [25]; this mean field effect is neglected here.

simpler expression for the force per unit area, $f = -\frac{1}{A}\frac{\partial F_{lr}}{\partial D}$, is obtained:

$$f = \frac{1}{4\pi^2 R_g^3}\tilde{f}\left(\frac{D}{\pi R_g}\right), \qquad \tilde{f}(y) \equiv \frac{1}{2y^3}\widetilde{\sum}_m m^2 \ln g\left(\frac{m^2}{y^2}\right)$$

where m is any integer. The reduced function $\tilde{f}(y)$ shows a power-law behaviour for small reduced distances: $\tilde{f}(y) \simeq \frac{\zeta(3)}{2\pi^2}\frac{1}{y^3}$ for $y \ll 1$, i.e. the force $f \simeq \frac{\zeta(3)}{8\pi}\frac{1}{D^3}$ for $D \ll R_g$ in agreement with equation (27). For $y \gtrsim 1$ the function $\tilde{f}(y)$ shows damping oscillations; however $\tilde{f}(y)$ is numerically very small in the regime of oscillations. The force virtually vanishes for $D \gtrsim 1.5R_g$, i.e. when the separation just exceeds the gyration radius.

A similar effective cut-off at $D \approx 1$–$1.5R_g$ is expected for the correlation function of density fluctuations, for the interaction between solid particles in the polymer system, or for the interaction between lines in the two-dimensional case.

(ii) Next we turn to the case of polydisperse living polymers with Flory molecular weight distribution: the number of chains of exactly N monomer units (per unit volume) is

$$\nu(N) = \frac{c_0}{N_0^2}e^{-N/N_0} \tag{28}$$

where N_0 is the number average of N. The general equation (26) is applicable to the monodisperse case, but with the appropriately averaged S_{id}:

$$S_{id}(q) = \int dN\, \nu(N)\Phi(N,q)$$

where $\Phi(N,q) = N^2 g(Nq^2b^2/6)$ is the form factor of one N-chain. Thus we get

$$S_{id}(q) = \frac{2c_0}{1/N_0 + q^2b^2/6}.$$

Next using the identity $\ln x = \int_0^\infty \left(\frac{1}{t+1/x} - \frac{1}{t+1}\right)dt$ we represent equation (26) as

$$F_{lr}/A = (F - F_0)/A \simeq \frac{1}{4}\int \frac{d^{d-1}q'}{(2\pi)^{d-1}}\widetilde{\sum}_m \int dt \left(\frac{1}{q^2b^2/6 + 1/N_0 + t} - \frac{1}{1+t}\right).$$

Finally, interchanging the last integration and summation we get after some algebra

$$F_{lr}/A = \frac{2^{-d}\pi^{\frac{1-d}{2}}}{\Gamma(\frac{d+1}{2})}\frac{k_B T}{D^{d-1}}h_F(D/R_g), \tag{29}$$

where $h_F(x) = \int_x^\infty dt\,(t^2 - x^2)^{\frac{d-1}{2}}\frac{2}{e^{2t}-1}$. For very long chains, $R_g \gg D$, we approximate $h_F(x)$ by $h_F(0) = 2\Gamma(d)\zeta(d)$ and thus recover the asymptotic result, equation (27). The repulsion force (per unit area) is

$$f = 2^{1-d}\pi^{\frac{1-d}{2}}\frac{1}{\Gamma\left(\frac{d-1}{2}\right)}\frac{k_B T}{D^d}h_f(D/R_g), \qquad h_f(x) = \int_x^\infty dt\,\frac{2t^2}{e^{2t}-1}(t^2 - x^2)^{\frac{d-3}{2}}.$$

In particular, for $d = 3$, $f = \frac{1}{2\pi}\frac{k_B T}{D^3}\int_{D/R_g}^\infty \frac{t^2}{e^{2t}-1}dt$, in agreement with equation (10) obtained using the polymer–magnet analogy. Thus the force is exponentially decreasing at $D \gg R_g$; however this decrease is much weaker than in the monodisperse case (note also that with living polymers the force is monotonic, i.e. no oscillations). We can speculate that in the monodisperse case the interaction at $D \gg R_g$ can be explained by rare ghost configurations in the ideal reference system. These are ideal polymers stretched to the extent that they are in contact with both plates and these configurations are exponentially rare. In the case of a polydisperse solution, these stretched configurations contribute too, but there is an additional contribution from extra long polymers present in polydisperse solution, which results in slower decay of the force with the distance.

4. Long-range interactions: the general case of arbitrary solid obstacles

4.1. The interaction energy

In this section we consider interaction between arbitrary solid objects in a polymer melt not assuming that the perturbation induced by the presence of the objects is weak (thus, in particular, the case of solid colloidal particles of any shape is included). As before we start with the case of infinitely long chains. We may assume that the monomer distribution in the presence of the particles is known:

$$\bar{c}(r) = c_0 - \sum_i c_i(r - r_i) \tag{30}$$

where r_i is the position of the ith particle, and $c_i(r - r_i)$ accounts for the monomers that have been expelled by the particle (for strictly impenetrable particles $c_i(r - r_i) = 1$ if r is inside the particle, and $c_i = 0$ otherwise). We assume (as before) that the particle/monomer interaction is short range. We also assume that the distance between the surfaces of the particles is much larger than ξ. Thus $\bar{c}$, equation (30), is a simple superposition of localized contributions $c_i(r - r_i)$ that do not overlap.

The effective Hamiltonian of the system can be written as $H[c] = H^{(0)}[c] + H_{\text{nloc}}[c]$, where the functional $H^{(0)}[c] \simeq H_{\text{id}}^{(0)} + H_{\text{int}}$ can be represented as an integral of the energy density depending only on c and its gradients, and the non-local term $H_{\text{nloc}}[c]$ is the rest. As we discussed in the previous sections the non-local term is due to fluctuations and hence it is relatively small if either Gi $\ll 1$ or the cell size $\Lambda \gg \xi$ (the latter condition implies that the sizes of the particles are $\gg\xi$). Applying the theorem on small variations [16], we get the free energy $F = -\ln Z$, where Z is the partition function of the system for the given positions of the solid particles:

$$F \simeq F^{(0)} + \langle H_{\text{nloc}} \rangle \tag{31}$$

where $\langle \cdots \rangle$ means averaging over the ensemble generated by $H^{(0)}$. The first term $F^{(0)}$ coming from the main Hamiltonian term $H^{(0)}[c]$ can be written as $F^{(0)} \simeq H^{(0)}[\bar{c}] + F^{(\text{fluct})}$, where $H^{(0)}[\bar{c}]$ is the mean field result, and $F^{(\text{fluct})}$ is the fluctuation correction. Further, the averaged H_{nloc} is nearly equal to its value for the averaged monomer profile: $\langle H_{\text{nloc}} \rangle \simeq H_{\text{nloc}}[\bar{c}]$. Thus

$$F \simeq H^{(0)}[\bar{c}] + F^{(\text{fluct})} + H_{\text{nloc}}[\bar{c}]. \tag{32}$$

For a concentrated system of interacting polymer chains $H^{(0)}[\bar{c}]$ does not depend on the positions of the solid particles, since $H^{(0)}$ is local, and the relevant correlation length ξ is larger than the distances between the solid surfaces: $H^{(0)} \simeq$ const. The same is true for $F^{(\text{fluct})}$: it is also a local functional of $\bar{c}$ since there are no soft modes in the concentrated system. Therefore the (long-range) effective (polymer-induced) interactions between the solid particles are defined by the last term in equation (32):

$$F_{\text{lr}} \simeq H_{\text{nloc}}[\bar{c}]. \tag{33}$$

Next we recall that H_{nloc} nearly does not depend on interactions, i.e. it is nearly the same for the real system and for the reference ideal system of fictitious non-interacting chains because interactions of monomer units are local (see the discussion at the end of section 3.1). Therefore H_{nloc} can be obtained by analysing the reference ideal system (compare with the approach used for the system of two solid plates; see equations (25), (26)). Equation (32) for the ideal system can be rewritten as

$$F_{\text{id}} \simeq H_{\text{id}}^{(0)}[\bar{c}] + F_{\text{id}}^{(\text{fluct})} + H_{\text{nloc}}[\bar{c}].$$

The important simplification here comes from the fact that $H_{id}^{(0)}[\bar{c}]$ as defined in the Lifshitz theory [17, 19] is exactly equal to F_{id}: $Z_{id} = \exp(-F_{id}) = \exp(-H_{id}^{(0)}[\bar{c}])$. Therefore

$$H_{nloc}[\bar{c}] \simeq -F_{id}^{(fluct)}. \tag{34}$$

It is convenient to consider the ideal polymer system in the presence of an external field $U(r)$ inducing (on the average) the inhomogeneous monomer distribution $\bar{c}(r)$, $U(r) \to 0$ as $r \to \infty$ (physically $U(r)$ is due to interactions of monomer units with the solid particles). The ideal effective Hamiltonian is

$$H_{id}^{(0)} = \frac{a^2}{4} \int \frac{(\nabla c)^2}{c}\, \mathrm{d}^d r + \int U(r)c(r)\, \mathrm{d}^d r$$

(compare with equation (13)). The field $U(r)$ is related to $\bar{c}(r)$ by the standard equations of the ground state theory [17] which are exact for an ideal system of infinite Gaussian chains:

$$\bar{c}(r) = \psi^2(r), \qquad -a^2\nabla^2\psi + U\psi = 0. \tag{35}$$

Taking into account that $\bar{c}$ is a sum of non-overlapping contributions, we can write

$$\psi = \psi_0 + \sum_i (\psi_i(r - r_i) - \psi_0)$$

where $\psi_0 = \sqrt{c_0}$, and $\psi_i(r) = \sqrt{c_0 - c_i(r)}$. Note that $\psi_i(r) \to \psi_0$ as $r \to \infty$. Accordingly we can represent $U(r)$ as a similar sum of non-overlapping contributions:

$$U(r) = \sum_i U_i(r - r_i),$$

where $U_i(r)$ is defined by the Edwards–Lifshitz ground state equation: $-a^2\nabla^2\psi_i + U_i\psi_i = 0$; note that $U_i \to 0$ as $r \to \infty$.

The fluctuation free energy formally corresponding to the ideal Hamiltonian $H_{id}^{(0)}$ is $F_{id}^{(fluct)} = -\ln Z_{id}^{(fluct)}$. The fluctuation partition function $Z_{id}^{(fluct)}$ is defined as

$$Z_{id}^{(fluct)} = \int \mathrm{e}^{-\Delta H_{id}^{(0)}[c']} D[c']$$

where $c' = c(r) - \bar{c}$, $\Delta H_{id}^{(0)}[c'] = H_{id}^{(0)}[c] - H_{id}^{(0)}[\bar{c}]$ (note that $\bar{c}(r)$ is minimizing the functional $H_{id}^{(0)}[c]$: $H_{id}^{(0)}[\bar{c}] = \min_c H_{id}^{(0)}[c]$).

Taking into account that fluctuations are weak, $|c'| \ll c_0$, and using the quadratic approximation we get

$$\Delta H_{id}^{(0)}[c'] \simeq \frac{1}{2} \int K(r, r')c'(r)c'(r')\, \mathrm{d}^d r \, \mathrm{d}^d r'.$$

Therefore $Z_{id}^{(fluct)} \simeq \mathrm{const}(\det \hat{K})^{-1/2}$, where $\hat{K}$ is the operator corresponding to $K(r, r')$: $\hat{K} = (\hat{\mathcal{G}}_0)^{-1}$, and the operator $\hat{\mathcal{G}}_0$ corresponds to the pair correlation function $\mathcal{G}_0(r, r') = \langle c'(r)c'(r') \rangle$. Hence $F_{id}^{(fluct)} \simeq -\frac{1}{2} \ln \det \hat{\mathcal{G}}_0 + \mathrm{const}$. Now using equations (33), (34) we get the following general expression for the long-range energy:

$$F_{lr}[\bar{c}] \simeq \frac{1}{2} \ln \det \hat{\mathcal{G}}_0 + \mathrm{const} = \frac{1}{2} \mathrm{Tr} \ln \hat{\mathcal{G}}_0 + \mathrm{const}. \tag{36}$$

That is, F_{lr} is related to the concentration correlation function in the reference ideal polymer system.

For infinitely long ideal chains the correlation function is

$$\mathcal{G}_0(r, r') = 2\psi(r)\psi(r')G(r, r') \tag{37}$$

where

$$G(r, r') = \int_0^\infty G_N(r, r')\, \mathrm{d}N \tag{38}$$

and $G_N(r, r')$ is the partition function of an ideal chain of N monomer units with ends at r and r'. The function G_N satisfies the well known Edwards equation [17]

$$\frac{\partial G_N}{\partial N} = -\hat{L} G_N$$

with initial condition $G_0(r, r') = \delta(r - r')$, and

$$\hat{L} = -a^2 \nabla^2 + U(r). \tag{39}$$

Note that in the case of solid obstacles (with short-range surface/monomer interactions) the definition of U, equation (35), implies that a reflective boundary condition ($u \cdot \nabla G_t = 0$) must be imposed at the solid surfaces as discussed in the previous section. The solution to this equation for the corresponding operator is $\hat{G}_N = e^{-N\hat{L}}$. Therefore the operator $\hat{G}$ corresponding to the function $G(r, r')$ defined in equation (38) is $\hat{G} = \hat{L}^{-1}$. Substituting $\mathcal{G}_0$, equation (37) in (36), and taking into account that

$$\text{Tr} \ln \hat{\mathcal{G}}_0 = \ln \det \hat{\mathcal{G}}_0 = \text{Tr} \ln \hat{G} + \int [2 \ln \psi + \ln 2] \, d^d r / \Lambda^d,$$

we get

$$F_{\text{lr}} \simeq -\tfrac{1}{2} \text{Tr} \ln \hat{L} + \text{const} \tag{40}$$

where $\int \ln \psi \, d^d r$ is adsorbed in the const since it does not depend on the distances between the particles, and $\hat{L}$ is defined in equation (39) with $U(r) = a^2 \bar{c}^{-1/2} \nabla^2 \bar{c}^{1/2}$; see equations (35). It is interesting to compare the overall structure of F_{lr}, equation (40), with equations (8), (7).

4.1.1. Weakly inhomogeneous system. As a simple application of the above equations let us calculate the energy of long-range interactions for the case when the concentration perturbations induced by the particles are weak, $|\bar{c} - c_0| \ll c_0$. Then we can consider $U(r)$ as a perturbation related to $\delta c = \bar{c}(r) - c_0$: $U(r) \simeq \frac{a^2}{2c_0} \nabla^2 \delta c(r)$, and write $\hat{L} = \hat{L}^{(0)} + \delta \hat{L}$, where $\hat{L}^{(0)} = -a^2 \nabla^2$, $\delta L(r, r') = U(r) \delta(r - r')$. Expanding the rhs of equation (40) as a series of $\delta \hat{L}$, noting that the linear term does not contribute to the interaction forces, and thus keeping only the second-order term, we obtain

$$F_{\text{lr}} \simeq \tfrac{1}{4} \text{Tr} \left(\left(\delta \hat{L} \hat{G}^{(0)} \right)^2 \right) + \text{const} \tag{41}$$

where $\hat{G}^{(0)} = [\hat{L}^{(0)}]^{-1}$, i.e. $G^{(0)}(r, r') = \frac{1}{4\pi a^2 |r-r'|}$ for $d = 3$. Using the above equations we get

$$F_{\text{lr}} \simeq \frac{\sqrt{\pi}}{(2\pi)^d} \frac{\Gamma(d) \Gamma(1 + d/2)}{\Gamma(d/2 - 1/2)} \frac{1}{2c_0^2} \int \delta c(r) \delta c(r') \frac{1}{|r - r'|^{2d}} \, d^d r \, d^d r'$$

in agreement with equation (17) (we omit the inessential constant term). In particular, the energy of interaction of two particles at a distance D (D is much larger than the particle size) in the three-dimensional space is

$$F_{\text{lr}} \simeq \frac{3}{16\pi^2} \frac{V_1 V_2}{D^6} \tag{42}$$

where $V_i = \int c_i(r) \, d^3 r$ is the effective volume of the particle i, $i = 1, 2$. The last equation is in agreement with the results of section 3.1 (see equation (23)). The result, equation (42), has a remarkable analogy with the van der Waals interactions [21], except that the sign is opposite.

4.1.2. Further generalizations.   Equation (40) can be further simplified using the identity

$$-\ln \hat{L} = \int_0^\infty \frac{\mathrm{d}t}{t} \left(\mathrm{e}^{-\hat{L}t} - \mathrm{e}^{-t} \right).$$

Taking into account that $\mathrm{e}^{-\hat{L}t} = \hat{G}_t(r, r')$ is the Green function, we get

$$F_{\mathrm{lr}} \simeq \frac{1}{2} \int \mathrm{d}^d r \int_0^\infty \frac{\mathrm{d}t}{t} G_t(r, r) + \mathrm{const.} \tag{43}$$

Applying this equation to the interaction of parallel solid plates we recover the previously obtained result, equation (27).

So far in this section we have assumed that polymer chains are infinite. Let us now consider the general case of finite chains. Then the long-range forces (with the range of the order of the typical coil size) are generated already in the reference ideal system [25], i.e. $H_{\mathrm{id}}^{(0)}[\bar{c}] \neq \mathrm{const}$, $H^{(0)}[\bar{c}] \neq \mathrm{const}$. Thus

$$F_{\mathrm{lr}} \simeq F_{\mathrm{lr}}^{(0)} + F_{\mathrm{lr}}^{(1)}.$$

Here $F_{\mathrm{lr}}^{(0)}$ stands for the mean field non-local free energy due to the chain ends (i.e. $F_{\mathrm{lr}}^{(0)}$ comes from the non-local part of $H_{\mathrm{id}}^{(0)}$; see [25]). The second term $F_{\mathrm{lr}}^{(1)} = -F_{\mathrm{id}}^{(\mathrm{fluct})}$ accounts for the fluctuation-induced long-range interactions; $F_{\mathrm{lr}}^{(1)}$ is defined in equation (36). The derivation of this equation is obviously also valid in the general case, for any distribution of chain length:

$$F_{\mathrm{lr}}^{(1)} \simeq \tfrac{1}{2} \operatorname{Tr} \ln \hat{\mathcal{G}}_0 + \mathrm{const.}$$

The problem is thus reduced to calculation of the ideal-chain correlation function $\mathcal{G}_0(r, r')$. This is a classical problem; however there is no explicit general solution even for a monodisperse system if it is not uniform (i.e. $U \neq \mathrm{const}$). Fortunately, the problem is simpler in the case of a Flory distribution; equation (28). In this case, the 'infinite-chain' equations (37), (38) are applicable once G_N is replaced by $G_N \mathrm{e}^{-N/N_0}$. This is also formally equivalent to replacing $\hat{L}$ by $\hat{L} + 1/N_0$. Thus the general equations (40), (43) are modified to (compare to equations (7), (8))

$$F_{\mathrm{lr}} \simeq -\tfrac{1}{2} \operatorname{Tr} \ln \left(\hat{L} + 1/N_0 \right) + \mathrm{const} \tag{44}$$

$$F_{\mathrm{lr}} \simeq \frac{1}{2} \int \mathrm{d}^d r \int_0^\infty \frac{\mathrm{d}t}{t} G_t(r, r) \mathrm{e}^{-t/N_0} + \mathrm{const.} \tag{45}$$

Note the analogy between equation (44) and equations (7), (8): $1/N_0$ plays the same role in equation (44) as the magnetic field h in the magnetic formalism. These equations define the fluctuation-induced interaction energy for a concentrated system of polymers with a Flory distribution of the molecular weight, N_0 being the number average polymerization degree. Calculating the energy of the polymer-induced interaction between two parallel solid plates using the last equation we get a result which is identical to equation (29).

4.2. The role of cycles

The general result, equation (43), can be interpreted in the following 'geometrical' way (for simplicity we assume a three-dimensional system, $d = 3$): consider a living melt of bi-functional monomer units. If all bonds are saturated then monomers can form either infinitely long linear chains or rings. The fraction of rings is proportional to the probability p that a growing chain of monomers will meet its first monomer, $p \sim 1/(c_0 b^3)$, where c_0 is mean monomer concentration. Let us assume that $c_0 b^3 \gg 1$, and hence $p \ll 1$, i.e. nearly all monomers belong to linear chains, and just a small fraction to rings. The interaction between

rings is then nearly totally screened by the linear chains, i.e. the 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, $F_{\text{ring}} = -\ln Z_{\text{ring}}$, and $Z_{\text{ring}} = \exp(\sum_N Z_N)$ is the grand partition function of the ideal system of rings. Here Z_N is the statistical weight (*a priori* probability) of a ring of N monomers. Now we note 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 any soft modes are suppressed by monomer interactions. Hence $F_{\text{liv}} = $ const in the long-range sense, and so $F = \text{const} - F_{\text{ring}} = \text{const} + \sum_N Z_N$. Thus, taking into account that $Z_N = \frac{1}{2N} \int G_N(r, r) \, d^3r$ ($\frac{1}{2N}$ is the symmetry factor reflecting equivalence of all N monomers in a cycle, and also equivalence of the two ways of counting them, forward and backward) we arrive at exactly equation (43) for $F_{\text{lr}} = F + \text{const}$. Neglecting the constant term we observe that F_{lr} is equal to the number of cycles in the corresponding living polymer system (times $k_B T$).

It is important to stress that the above derivation of F_{lr} in terms of ghost cycles is rigorous. Moreover, it is more general than the derivations considered in the previous sections since the picture of ghost cycles is applicable also when fluctuations are not weak, i.e. when $\text{Gi} = \frac{v}{c_0 b^6} \sim 1$. The assumption $c_0 b^3 \gg 1$ is actually not essential (note that this condition also guarantees that the mean field theory is quantitatively applicable in the melt). The reason is that only long enough rings contribute to the long-range force, and the weight fraction of such rings is always small, even if $c_0 b^3 \sim 1$. In this case we introduce an appropriate (large enough) coarsening length scale Λ, $\Lambda \gg \xi$ (see the discussion at the end of section 3.1), and forbid any cycles of size smaller than Λ. Thus the weight fraction of the allowed (large) cycles can be made however small, so that the cycles do not interact with each other. However they do interact with the 'sea' of linear chains. Taking also into account that the statistics of each chain fragment (of an intermediate size, larger than ξ, but smaller than the characteristic length of the inhomogeneities $c_i(r)$ of the overall concentration distribution $\bar{c}(r)$, equation (30)) is nearly Gaussian, we can write the energy of a coarse-grained ring configuration $r(n)$ as

$$H[r(n)] \simeq \int \left[\frac{1}{4\beta} \left(\frac{\partial r}{\partial n} \right)^2 + U(r(n)) + \frac{3}{2} \ln(4\pi\beta) \right] dn$$

where n counts the monomers along the ring, $U = U(r)$ is the energy of interaction of a ring unit with surrounding chains and with immersed objects ($U(r) \to 0$ as $r \to \infty$), and $\beta = (b^*)^2/6$. Here b^* is the renormalized (the actual) statistical segment. In the general case, $\text{Gi} \sim 1$, b^* depends on the concentration: $b^* = b^*(c)$, and therefore β is position dependent: $\beta = \beta(r) = [b^*(\bar{c}(r))]^2/6$ (we assume that the function $b^*(c)$ is known). The partition function of an N-fragment with ends at r and r' is $G_N(r, r')$ corresponding to the operator $\hat{G}_N = e^{-N\hat{L}}$, where

$$\hat{L} = -\nabla \beta(r) \nabla + U(r). \tag{46}$$

Obviously the last equation is generalizing equation (39). It is important that exactly the same monomer–monomer correlation function $G_N(r, r')$ is applicable to fragments of both rings and linear chains. Since the linear chains are long, their monomer distribution is $\bar{c}(r) = \psi^2(r)$, where $\psi(r)$ must satisfy the generalized Edwards equation $\hat{L}\psi = 0$. The last two equations serve to specify $U(r)$ for a given $\bar{c}(r)$:

$$U(r) = \bar{c}^{-1/2} \nabla \beta \nabla \bar{c}^{1/2}. \tag{47}$$

Thus equation (43) for the long-range interaction energy is applicable in the general case, $Gi \sim 1$, if $G_t(r, r)$ is defined as the partition function of a ring: $G_t(r, r) = \langle r|e^{-t\hat{L}}|r\rangle$, where $\hat{L}$ is defined in equation (46). Therefore

$$F_{lr} \simeq \frac{1}{2} \text{Tr} \int_0^\infty e^{-\hat{L}t} \frac{dt}{t} + \text{const.}$$

The last equation can be transformed to equation (40), but with $\hat{L}$ now defined in equation (46). Thus equations (40), (46), (47) define the energy of long-range interactions in the most general case, when fluctuations are not weak, $Gi \sim 1$. This approach is also valid for finite chains with a Flory distribution of molecular weights; equation (44) should be used instead of equation (40) in this case.

Let us find the non-local energy for a weakly perturbed system of infinite polymers in the regime of fluctuations, $Gi \sim 1$. Following the approach outlined in section 4.1.1 we write: $\bar{c}(r) = c_0 + \delta c(r)$, $\beta(r) = \beta_0 [1 - \lambda \delta c/c_0]$, where

$$\lambda = -2 \frac{\partial \ln b^*(c)}{\partial \ln c} \qquad \text{at } c = c_0.$$

Using equations (46), (47) we split the transfer operator as

$$\hat{L} = \hat{L}^{(0)} + \delta\hat{L}$$

where $\hat{L}^{(0)} = -\beta_0 \nabla^2$, $\delta\hat{L} \simeq \frac{\beta_0 \lambda}{c_0} \nabla \delta c(r) \nabla + U(r)$, and $U(r) \simeq \frac{1}{2c_0} \nabla^2 \delta c(r)$. Using then equation (41) we get for $d = 3$

$$F_{lr} \simeq \frac{3}{(4\pi)^2} \frac{1 - 2\lambda + 2\lambda^2}{2c_0^2} \int \delta c(r) \delta c(r') \frac{1}{|r - r'|^6} \, d^3r \, d^3r'.$$

This result agrees with the last term in equation (21) and provides the unknown prefactor:

$$\kappa^* = 1 - 2\lambda + 2\lambda^2.$$

We stress that the above equation is exact: in effect it incorporates the fluctuation corrections of all orders. Thus the long-range correlation function of concentration fluctuations for $d = 3$ is (see equation (22))

$$\mathcal{G}(r) \simeq -\frac{3}{(4\pi)^2} \frac{\kappa^*}{v^2 c_0^2} \frac{1}{r^6}, \qquad r \gg \xi.$$

The prefactor in the last equation is thus related to the osmotic compressibility of the system and to the slope of the concentration dependence of the effective statistical segment. The latter dependence was calculated by Edwards [26] in the regime of weak fluctuations ($Gi \ll 1$). For a semidilute solution in the good solvent regime the coil size (and therefore b^*) follows a scaling law: $R_g \propto c^{-\frac{2v-1}{2(3v-1)}}$, where $v \approx 0.6$ is the Flory exponent. Then $\lambda = \frac{2v-1}{3v-1} \approx 0.25$, and $\kappa^* \approx 5/8$. Possibly much larger values of κ^* can be attained in polyelectrolyte solutions where the coil size can strongly depend on the concentration. Therefore charged polymer systems (where electrostatic interactions are well screened beyond the Debye radius) can be the best candidates for providing experimental verification of the predicted long-range correlation effects.

Let us now turn to the polymer-induced interactions of large solid particles of size $\gg \xi$. Then to a good approximation the mean concentration $\bar{c}$ is defined by just two values: $\bar{c} = 0$ inside a particle, and $\bar{c} = c_0$ outside. Thus the concentration is constant in the region accessible for the chains, and therefore the chain statistical segment is constant. In this case the transfer operator, equation (46), coincides with that for ideal chains, equation (39), provided that the statistical segment is renormalized, $b \to b^*$. Therefore the expressions for the long-range

interaction energy derived for Gi $\ll$ 1 stay valid also in the general case (Gi $\sim$ 1) if the renormalization is performed. For example, if R_g in equation (29) is defined as the actual rms gyration radius of a chain with the mean molecular weight, then this equation is generally valid. In the case of infinite chains the long-range energy does not depend on b; therefore the long-range interaction between large solid particles is universal when the relevant length scales are much larger than the mean field correlation length ξ, but are much smaller than the typical chain size. In particular, equations (27), (51) are universal, i.e. they are asymptotically valid for any Gi.

The above interpretation of the long-range effect in terms of subtracted cycles is also supported by the consideration based on the polymer–magnetic analogy. In fact, in section 2 we showed that the amplitude of long-range interactions is proportional to the number of transverse (Goldstone) modes, $n - 1$, where n is the number of 'spin' components, which is simultaneously equal to the extra weight of a cyclic polymer chain. Therefore it is clear that the cycles do contribute to the long-range force which linearly depends on their concentration. The special case $n = 1$ corresponds to the living system of bi-functional units, where cycles form with the natural weight $= 1$. This corresponds to the universality class of the Ising model. In this case the number of modes of long-range interaction is $n - 1 = 0$, i.e. the long-range effects of linear chains and of cycles cancel each other, in agreement with what was deduced just above.

4.3. Non-local pressure and stress tensor

Consider a polymer melt (or a concentrated solution) with solid (colloidal) particles in it. As before we assume for simplicity that all direct interactions (monomer/monomer, monomer/solid, etc) are short range. The free energy F of the system is a sum of the local free energy that depends on the total volume and the total surface area of the particles (the typical particle size is assumed to be much larger than the polymer static correlation length ξ) and non-local contribution F_{lr}. The total pressure exerted on the solid surface is then $\Pi = \Pi_0 + \Pi_{lr}$, where Π_0 is a constant pressure due to the local energy (i.e. Π_0 characterizes the polymer system with suppressed non-local free energy, so Π_0 is basically the classical mean field pressure), and Π_{lr} is generated by the non-local interactions. Below we focus on the non-local pressure, omitting the constant Π_0 which is irrelevant for what follows[15].

The non-local pressure can be defined in the following way (the subscript 'lr' is omitted below). Let a solid surface shift a bit towards the polymer ($A' \to A$). The corresponding free energy increment δF_{lr} must be equal to the work against pressure: $\delta F_{lr} = \int \Pi \delta h \, dA$, where dA is the surface area element, and $\delta h = \delta h(r)$ is the normal displacement of the surface. Using equation (43) we get

$$\delta F_{lr} = \frac{1}{2} \int d^d r_1 \int \frac{dt}{t} \delta G_t(r_1, r_1) - \frac{1}{2} \int dA \int \frac{dt}{t} G_t(r, r) \delta h$$

where integration over the whole system in assumed in the first integral. In order to find δG_t we note that a surface shift is equivalent to a change of the boundary conditions: the 'flux' $J = -a^2 u \cdot \nabla_r G_t(r, r_1) \, dA$ across the *shifted* surface element dA was non-zero before the surface shift and it is zero after it (u is the unit vector normal to the surface A). Therefore

$$\delta G_t(r_1, r_1) = a^2 \int dA \, \delta h \int_0^t dt' \, \nabla_r \left[G_{t-t'}(r_1, r) \nabla_r G_{t'}(r, r_1) \right].$$

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[15] In the case of a polymer solution one should distinguish between total pressure and osmotic polymer pressure; however this distinction only affects the constant term, i.e. there is no difference between the non-local osmotic pressure and non-local total pressure since the solvent as such does not produce any long-range forces between solid objects immersed in the melt.

Thus after some vector algebra we get[16]

$$\Pi = \frac{a^2}{2} \text{div} \left[\nabla_r G(r, r') \right]_{r'=r}$$

where $G(r, r') = \int_0^\infty G_t(r, r') \, dt$ is defined in equation (38).

Taking into account that

$$u \cdot \nabla_r G(r, r') = 0 \tag{48}$$

for any r on A and for any r', we may rewrite the pressure as

$$\Pi = \frac{a^2}{2} \nabla_r \cdot \nabla_{r'} G(r, r')|_{r'=r+0} \tag{49}$$

where $\mathbf{0}$ is an infinitesimal vector.

We are now in a position to define the (non-local) stress tensor $\sigma_{\alpha\beta} = -\Pi_{\alpha\beta}$ by demanding two obvious conditions: (i) $\Pi = u_\alpha u_\beta \Pi_{\alpha\beta}$ at the solid surfaces, i.e. $\Pi_{\alpha\beta}$ generates the correct surface pressure, and (ii) $\frac{\partial}{\partial r_\beta} \Pi_{\alpha\beta} \equiv 0$ in the bulk, i.e. mechanical equilibrium. Assuming the general form

$$\Pi_{\alpha\beta} = C_1 \delta_{\alpha\beta} \nabla_r \cdot \nabla_{r'} G(r, r') + C_2 \frac{\partial}{\partial r_\alpha} \frac{\partial}{\partial r'_\beta} G(r, r')$$

we obtain

$$\Pi_{\alpha\beta} = \frac{a^2}{2} \delta_{\alpha\beta} \nabla_r \cdot \nabla_{r'} G(r, r') - a^2 \frac{\partial}{\partial r_\alpha} \frac{\partial}{\partial r'_\beta} G(r, r') \tag{50}$$

where $r' = r + \mathbf{0}$. Using the general relations $G(r, r') = G(r', r)$, $-\nabla_r^2 G(r, r') = 0$ for $r \neq r'$, and the boundary condition, equation (48), it is easy to prove that $\Pi_{\alpha\beta} = \Pi_{\beta\alpha}$ is symmetric as it should be, and that the stress vector $-\Pi_{\alpha\beta} u_\beta$ at a solid surface is always normal to it.

An analysis also shows that the first isotropic term in equation (50) corresponds to the *local* pressure increment ($\delta \Pi_{\text{local}} \simeq \frac{\partial \Pi_{\text{local}}}{\partial c} \delta c \simeq vc\delta c$) due to the small concentration inhomogeneity $\delta c = c - c_0$ generated by non-local interactions.

So far in this section we assumed that polymer chains are infinite. For finite chains with a Flory molecular weight distribution we start with equation (45) instead of equation (43). This substitution is equivalent to replacing $G_t(r, r')$ by $G_t(r, r')e^{-t/N_0}$ in all the equations. In particular, equations (49), (50) are valid also for finite chains provided that $G(r, r')$ is redefined as

$$G(r, r') = \int_0^\infty G_t(r, r')e^{-t/N_0} \, dt$$

(compare with equation (38)).

4.4. Interaction of two spherical particles

Consider two spherical colloidal particles of radius R_s ($R_s \gg \xi$) at the distance D ($D \gg R_s$, but the polymer coil size is much larger than D). Using either equation (49) or (50) we can calculate the interaction force (and hence the interaction energy) between the two spheres by integrating the pressure force either at the surface of one sphere or at the mid-plane between the spheres. The result for the interaction energy F_{lr} for $d = 3$ is

$$F_{\text{lr}} = \frac{5}{6} k_B T \frac{R_s^6}{D^6} = \frac{15}{32\pi^2} k_B T \frac{V_s^2}{D^6}, \tag{51}$$

[16] There is a subtlety about this derivation: one should exclude a narrow surface layer (of thickness $l \to 0$) from the region of integration over r_1 in order to avoid certain singularities.

where V_s is the sphere volume. Equation (51) is essentially in agreement with equation (42), with the additional 'form factor' of a solid sphere equal to $5/2$.

For completeness we also consider the case of small solid particles of size $R_s \ll \xi$ at the distance $D \gg \xi$, with short-range interactions between the monomer units and the particle surfaces. We start with the non-adsorbing case, i.e. hard-core (steric) repulsion. Then the energy of the effective (polymer-induced) interaction between the particles is proportional to the correlation function $\mathcal{G}(D)$ [27]:

$$F_{\mathrm{lr}} = -k\mathcal{G}(D). \tag{52}$$

The factor k is [27]

$$k = (F_1/c_0)^2 \tag{53}$$

where F_1 is the free energy cost for the particle insertion in the bulk of solution. We consider two cases:

(i) Mean field regime (Gi $\ll 1$). Then F_1 is mainly coming from the square-gradient (ideal-chain) free energy, equation (13), concentrated in the region $r - R_s \sim R_s$ (here r is the distance to the particle centre). Minimizing the rhs of equation (13) with boundary conditions $c = 0$ on $r = R_s$, $c \to c_0$ for $r \to \infty$, we get

$$F_1 \simeq 4\pi a^2 R_s c_0.$$

With equation (20) we obtain

$$F_{\mathrm{lr}} \simeq \frac{1}{12} \frac{b^4 R_s^2}{v^2 c_0^2} \frac{1}{D^6}, \qquad \xi \gg D \gg b.$$

(ii) Scaling regime (semidilute solution with swollen concentration blobs). In this case $F_1/c_0 \sim R_s^{3-1/\nu} b^{1/\nu}$ (see [27]), and $vc_0 \sim (c_0 b^3)^{\frac{1}{3\nu-1}}$, so

$$F_{\mathrm{lr}} \sim R_s^{6-\frac{2}{\nu}} b^{\frac{2}{\nu}-\frac{6}{3\nu-1}} c_0^{-\frac{2}{3\nu-1}} \frac{1}{D^6}.$$

Finally let us turn to the case of critically adsorbing particles in the mean field regime (Gi $\ll 1$). Here the short-range attraction between the monomer units and the particles compensates the hard-core repulsion so that the monomer concentration profile outside the particles is unperturbed (the so-called 'neutral' solid boundaries). Then equation (51) is applicable also for $R_s \sim \xi$ and for $b \ll R_s \ll \xi$ since it is the local concentration profile that defines the amplitude of the long-range interaction[17].

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[17] Note that equations (52), (53) are *not* applicable in the latter case. To see this we have to recall why these equations are valid at all, i.e. why the interaction is defined by the unperturbed linear response function which is proportional to $\mathcal{G}(r)$. The basic idea is that a small particle just weakly perturbs the polymer system; i.e. the typical energy of interaction between the particle and a relevant interaction blob of size ξ is small, $\ll k_B T$. This is true with hard-core particle/monomer repulsion if $R_s \ll \xi$. This is also true for critically adsorbing small particles; however in this latter case there is a subtle balance between the hard-core repulsion and the attraction, so that the net energy is zero in the first approximation, and therefore higher order corrections become important: for example, triple interactions (particle + 2 blobs) in addition to the pairwise interaction (particle + 1 blob). For that same reason equation (53) can also lead to incorrect results for the interaction of two probe monomers (see equation (23)) since a probe monomer is virtually equivalent to a small critically adsorbing sphere.

5. Discussion

(1) Polymer melts and other concentrated polymer systems have been viewed for years as ideal objects for a mean field analysis. For a long time it was generally believed that all correlations and interactions in these systems (with however long polymer chains) are short range, the decay length being comparable to the monomer unit size [1–3, 5, 6, 25]. It is proved in this paper that this is not true: long-range correlations and interactions are inherent in concentrated polymer systems. We emphasize that the earlier theoretical analysis [5, 6] was based upon *mean field* arguments, while we predict a new type of *fluctuation-induced* long-range force. Note that the predicted long-range interactions are weak enough that they do not much affect the polymer conformations: the chains remain nearly Gaussian in a melt in accordance with the Flory theorem [3].

We show that the novel long-range effect is related to the fluctuation-induced (Casimir) interactions [7]. There are two generic features of most long-range Casimir forces [8–10]:

 (i) they are due to fluctuations of massless fields (scale-free fluctuations, Goldstone modes); and
(ii) they are essentially attractive.

In view of these features the long-range *repulsion* in homopolymer *melts* (that do not show any soft fluctuation modes) predicted in the present paper may seem to be really unexpected. We thus introduce a major new concept that widens the theoretical understanding of polymer statistical physics.

Several complementary theoretical arguments elucidating different physical aspects of the predicted long-range effects are proposed: employing the polymer–magnetic analogy [3] we relate the polymer-induced long-range (PILR) forces to the Casimir effect due to $n - 1$ transverse Goldstone modes of the relevant n-vector order parameter fluctuations with $n = 0$. The number of Goldstone modes is negative and hence repulsive interaction is predicted, i.e. the 'anti-Casimir' effect.

The second way to derive the same effect is to consider a system of non-interacting chains as a reference system, and to note that the long-range force due to soft concentration fluctuation modes in the reference ideal system must be exactly balanced by a 'polymeric' contribution that is independent of excluded volume interactions. The long-range repulsive forces in polymer melts are thus related to the subtracted Casimir attraction induced by the fluctuations in the reference ideal system.

Finally we attribute the long-range interactions to the effect of large polymer rings that must be eliminated from a living polymer system: the large loops as such introduce long-range effects, and therefore the subtracted (ghost) loops must be responsible for the long-range forces of the opposite sign. This hints at a relation between the fluctuation-induced Casimir force and large-scale geometrical cycles.

(2) We show that in the general case the total energy of PILR 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_g. For example the energy of long-range interaction of two solid spheres R_s scales as $k_B T (\frac{R_s}{D})^6$ if the distance D is much larger than R_s, and the interaction energy of two parallel solid plates (per unit area) is $\sim \frac{k_B T}{D^2}$. The energy of interaction of two solid spheres is of the order $k_B T$ if D (the distances between their surfaces) is comparable to their size; the energy is larger if $R_s > D$.

The predicted long-range interactions are due to the linear chain structure of polymers. Yet they are insensitive to the details of this structure, showing remarkable universality (see equations (27), (51)). For example, the interaction nearly does not depend on concentration: the same interaction is predicted in a melt and in a semidilute solution; it is only the range of validity of the long-range power laws ($\xi \ll D < R_g$) that depends on the concentration.

(3) The long-range repulsion between solid plates, see equation (27), can be easily interpreted in terms of ghost cycles. In fact, the probability of cyclization in a gap D between the plates is higher than in the bulk: a linear chain with Gaussian size $> D$ is 'compressed' in the gap, so its ends meet each other more frequently. Hence the partition function of cycles is higher in the gap than in the bulk, leading to a negative contribution to the free energy proportional to the number $\mathcal{N}_c$ of the relevant 'compressed' cycles, i.e. those of size $\gtrsim D$. When the cycles are removed the free energy therefore *increases* by the same amount, $F_{lr} \sim \mathcal{N}_c$. The concentration of cycles of N units (with size $R \sim N^{1/2}b$) is $c_N \sim \frac{1}{N}\frac{1}{R^3}$. Therefore $\mathcal{N}_c \sim AD \sum_{R>D} c_N \sim AD\frac{1}{D^3}$, and the interaction energy per unit area is $\frac{F_{lr}}{A} \sim \frac{1}{D^2}$ in agreement with equation (27).

(4) The long-range interaction between the two plates (or between any solid objects immersed in the polymer) is insensitive to short-range wall–monomer forces. In particular, equation (11) is valid both for absolutely repulsive and for 'neutral' walls. The change of the wall–monomer interaction from neutral to repulsive is equivalent to an effective shift of the wall position to the correlation length ξ towards the bulk of polymer, i.e. to an unimportant renormalization of the effective distance: $D \rightarrow D - \xi$.

Note also that the monomer density profile near a single solid wall is perturbed: $c = c_0 + \delta c(x)$. The long-range perturbation $\delta c(x)$ is positive and decays as $1/x^3$ with the distance x to the plate. δc is also not sensitive to the wall–monomer interactions: a change from neutral to repulsive interactions is equivalent to introducing an additional repulsive layer of thickness ξ near the wall (we assume that the range of wall–monomer interactions is shorter than ξ). The *additional* perturbation $\delta c^{(a)}$ due to this repulsive layer is proportional to the bulk response function $\mathcal{G}(r - r')$ integrated over the layer: $\delta c^{(a)}(r) \sim \int \mathcal{G}(r - r')\,\mathrm{d}^3r'$. Using equation (20) we get $\delta c^{(a)}(x) \sim \xi/x^4$. Thus the monomer density perturbation changes from $\delta c \sim 1/x^3$ to $\sim 1/x^3 + \xi/x^4$, which is equivalent to changing x to $x - \xi$; i.e. the effect of the wall–monomer interactions is indeed small for $x \gg \xi$.

(5) Polymer-induced long-range repulsion between solid walls and other objects in concentrated or semidilute polymer solutions was predicted in [25]. The two long-range effects considered in the present paper and in [25] should not be mixed. The most important differences are:

 (i) The interactions considered in [25] are due to the polymer chain ends: the long-range force is inversely proportional to the polymer molecular weight, i.e. it is vanishing in the limit of very long chains ($N \rightarrow \infty$) when ends are suppressed. On the other hand the effect considered in the present paper becomes stronger as N is increased.
 (ii) The long-range force of [25] is inversely proportional to the bulk osmotic modulus of the system, so it is null for an incompressible polymer melt. This is in contrast to the *universal* repulsion, equation (11), predicted also for melts.
(iii) The long-range interaction [25] is a *mean field* effect, while the effects considered in the previous sections are due to fluctuations.

(6) The repulsive interactions of origin other than that considered in our paper were discussed before [29, 30]. In particular, interactions between solid objects (colloidal particles or solid walls) in polymer solutions were considered for the following two typical cases:

(i) Semidilute polymer solution at nearly theta conditions and close to the coil overlap concentration [29]. The repulsion force discussed in [29] is most probably related to the end effects [25] considered in the previous clause; i.e. its origin is qualitatively different to the long-range mechanism considered in the present paper. In fact, all the basic conditions adopted in [29] (θ solvent, overlap concentration, separation $\sim R_g$, monodispersity) work to enhance the end effects.

(ii) Adsorbed polymer layers formed at the solid surfaces [30]. The layers can repel each other when they start to overlap and thus can prevent aggregation of colloidal particles. This repulsion can be either a non-equilibrium effect (due to constrained relaxation of adsorbed polymer chains because of high effective monomer/solid friction), or it can be due to interactions of tail segments of adsorbed chains [31]. Again, these effects have nothing to do with long-ranged non-mean field forces analysed in the present paper.

(7) We show that the correlation effects in a polymer melt (or in a concentrated solution) are not totally screened beyond a few monomer sizes (correlation length ξ), but rather they extend up to a much longer length scale, the polymer coil size R_g. The correlation function of concentrations fluctuations $\mathcal{G}(r)$ (which can also be interpreted as a correlation function of vacancies for a lattice model) shows a similar behaviour: it is positive and decreasing with r at short distances $r \lesssim \xi$ (ξ is the mean field correlation length) and negative and increasing for large distances, $r \gg \xi$, with a depletion minimum at an intermediate r. $\mathcal{G}(r)$ follows the $\frac{1}{r^6}$ power law for $\xi \ll r \ll R_g$ in three dimensions ($d = 3$). The effective monomer interaction potential $v^*(r)$ follows the same power law. The correlation functions show a genuine exponential decay only at large distances exceeding the polymer coil size R_g. Thus the genuine correlation length in a polymer melt is always of the order of the polymer coil size R_g, i.e. it is much larger than the mean field static correlation length ξ.

(8) We predict that the coherent structure factor $S(q)$ of a polymer melt shows a weak singularity at $q \rightarrow 0$ due to a non-classical q^d term in the denominator (see equation (18)). The q^3 correction term in the inverse intra-chain structure factor (for $d = 3$) was also obtained in the one-loop approximation in [24]. A similar term for the *inter*-chain structure factor and its relation to the Goldstone singularity are discussed there as well. This is in agreement with the results of the present paper, equation (18).

(9) Back in the 1980s when the polymer–magnet analogy was intensively discussed, it was noticed [13, 28] that the magnetic susceptibility χ is negative in the 'polymeric' limit of zero spin components, $n \rightarrow 0$. This effect is also due to the negative number ($n - 1$ per spin) of transverse modes. Hence the following question is rather natural: whether the two effects, the negative χ and the long-range interaction, are related. The point is clarified below. Firstly, we note that the fact that magnetic χ is negative does not cause any problems for the corresponding polymer system [13, 28], but rather merely gives rise to a correction term in the free energy of a polymer melt (or a concentrated solution):

$$\mathcal{F}(N_0) = \mathcal{F}_\infty + \mathcal{F}_{id} - 2\epsilon/N_0 + \text{const}/N_0^{3/2}. \tag{54}$$

Here $\mathcal{F}$ is the free energy per monomer unit, $\mathcal{F}_\infty$ is its limit for infinite chains, $N_0 \rightarrow \infty$, $\mathcal{F}_{id}$ is the ideal-gas contribution, $-\epsilon$ is the excess free energy per chain end, $2/N_0$ is the fraction of ends, and the last term is related to the magnetic susceptibility χ which is both singular and negative. In fact, by the theorem on small variations the last term is also involved in the magnetic energy $\tilde{\mathcal{F}}(h) \simeq \tilde{\mathcal{F}}_{reg}(h) + \text{const } h^{3/2}$, where $\tilde{\mathcal{F}}_{reg}(h)$ is the regular part of the magnetic energy, and $h \sim 1/N_0$ is the magnetic field. Therefore $\chi = -\frac{\partial^2 \tilde{\mathcal{F}}}{\partial h^2} \simeq -\text{const } h^{-1/2}$ [32, 33].

The dependence $\mathcal{F}(N_0)$ can be deduced from the results of the present paper. For example, note that $F^{(0)}$ in equation (31) must be a regular function of the end concentration. Therefore

a singular term may only come from the non-local energy F_{lr}. Thus, using equation (45) for the uniform system, we get (for $d = 3$)

$$\mathcal{F}(N_0) = \frac{F}{c_0 V} = \langle \text{regular part} \rangle + \frac{1}{2c_0} \frac{1}{\left(4\pi b^2/6\right)^{3/2}} \Gamma(-3/2) \frac{1}{N_0^{3/2}}$$

where $\Gamma(-3/2) = \frac{4}{3}\sqrt{\pi}$. This is in agreement with equation (54), and we also provide the prefactor. Therefore the singular free energy term is a part of the total non-local energy. Physically this term is due to the weak effective repulsion between the chain ends: the total free energy increases when two ends (perhaps of different chains) come close to each other. This interaction is similar to the interaction of micelles in a block-copolymer melt [34]; in particular, it also follows the Coulomb law: $F_{int} \sim 1/r$ for $r \ll R_g$, where r is the distance between the ends. We conclude that although the singular free energy term (related to the negative magnetic susceptibility) is also related to the non-local free energy, this term as such is not responsible for the long-range forces considered in this paper: the singular term is related to the long-range interactions of chain ends that disappear in the limit of infinite chains, $N_0 \to \infty$. On the other hand, the long-range effects considered in sections 2–4 do not disappear, but rather are enhanced in this limit.

(10) It is remarkable that the polymer-induced repulsion is rather similar to the van der Waals (VdW) interaction: the same power law and, in fact, the same magnitude in the case of the thermal VdW forces. Hence we arrive at the exciting possibility of reversing the sign of the effective long-range interaction, i.e. the possibility of net repulsion instead of the usual VdW attraction.

It is well known that many colloidal systems can be stabilized against aggregation by adding polymers (in the regime of overlapping coils) [29]. The universal long-range interaction elucidated in this paper can significantly contribute to the stabilization. In fact, the polymer-induced repulsion between solid walls (see equation (27)) is practically *always* stronger than the thermal (zero-frequency) VdW attraction (the VdW interaction energy for solid walls is [21] $F_{VdW}/A \simeq -A_H/(12\pi D^2)$, where $A_H \approx (3/4)k_B T(\epsilon_1 - \epsilon_2)^2/(\epsilon_1 + \epsilon_2)^2$ is the Hamaker constant, ϵ_1 and ϵ_2 are the dielectric constants of the solid and solution respectively). Note that the thermal VdW force is proportional to the *square* of dielectric contrast of the media; thus it can be further suppressed by matching the dielectric properties of colloidal particles and polymer solution.

Thus the PILR 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).

(11) Turning to possible experimental verifications of the predicted long-range effects and their practical implications, we note that the VdW forces are thermally induced at scales larger than $\lambda_T = \frac{\hbar c}{k_B T} \simeq 10$ μm. At shorter length scales the VdW interaction is enhanced by quantum effects, and hence the VdW forces would then typically mask the polymer-induced repulsion. However there are some special cases where the repulsion could dominate. One possibility is to reduce the VdW attraction by selecting polymer/colloidal (or polymer/polymer) pairs with matching refractive indices. Another possibility is to study phase separation in a binary polymer *solution* with soluble but incompatible polymer components, A and B (a typical example is an emulsion of A droplets in the B matrix with solvent penetrating both A and B). The long-range repulsion is independent of concentration, while the VdW contrast between the components must be proportional to the concentration, so the repulsion must dominate at low enough concentrations (dilution to about 20% of polymer is expected to be enough). A third approach is to consider the long-range effects in thin films, i.e. essentially in two dimensions: the polymer-induced 2D repulsion energy scales as $1/r^4$, i.e. it must dominate over the VdW

attraction at large enough distances (the latter still scales as $1/r^6$ since polymer confinement does not affect the 3D nature of electromagnetic fluctuations).

Measuring the equilibrium polymer-induced force between nearly parallel solid walls at short separations can be complicated because of dynamical effects: decreasing the separation requires that polymer must flow out of the gap, this process is opposed by strong polymer/wall friction. A possible way to enhance the relaxation is to resort to thin plates with holes that would allow for faster polymer exchange between inside and outside regions. Of course the fraction of holes must be small enough that the very long-range interaction between the plates is not affected. Let us clarify the latter requirement assuming holes of diameter $\delta \ll D$, occupying the fraction w of the plates. It can be formulated as: Consider a chain fragment of the relevant length (of $N_D \sim D^2/b^2$ monomers); the interaction is not affected by the holes if the probability p of the fragment penetration through a hole is negligible, $p \ll 1$. The fragment N_D can be considered as a chain of blobs of size δ, with the number of such blobs $\sim D^2/\delta^2$. With Gaussian statistics the number of blobs near the surface is $\sim D/\delta$, and the probability of meeting of a blob and a hole is $p \sim wD/\delta$. Thus the relevant conditions are: $wD \ll \delta \ll D$.

(12) An investigation of the predicted effects by computer modelling is also invited. The major advantage here is that VdW interactions can be easily switched off in simulations. Another obvious advantage is that simulations can be faster in two dimensions where the predicted long-range effects are stronger. Note that in two dimensions a certain amount of crossings between fragments of polymer chains must be allowed since

 (i) the long-range interactions in 2D are predicted just for that sort of model with an energy penalty for each crossing [20];
(ii) with possible crossings the simulation dynamics is simpler.

The following simulation studies seem reasonable in this regard:

(a) To consider concentration fluctuations in polymer solutions, and to obtain the correlation function $\mathcal{G}(r)$ for $\xi < r < R_g$. The additional advantage here is the possibility of modelling a macroscopically homogeneous system (with periodic boundary conditions) which is convenient for gathering the statistics since every pair of monomers (at a given distance r) contributes to the result. The 'signal to noise' ratio (s/n) is then inversely proportional to square root of the total number of monomer units in the system, and in addition it is proportional to $\frac{1}{c_0^2 r^6 (\partial \Pi/\partial c_0)^{3/2}}$. In the semidilute regime (when the polymer volume fraction is small, $\phi \ll 1$) the ratio s/n is small; it is proportional to $\phi^{5/8}$ for $r \sim \xi$. s/n is also small in the melt ($\phi = 1$) because of its high compression modulus $\frac{\partial \Pi}{\partial c_0}$. Thus the optimum can be achieved for the intermediate case, i.e. in a concentrated solution (say, for $\phi \sim 1/4$).

Both off-lattice and lattice simulations are possible. In the lattice case $\mathcal{G}(r)$ can be interpreted as the correlation function of vacancies. In the case of off-lattice simulation, explicit solvent monomers (tracers) could be added and their correlations analysed. There is another interesting possibility for simulating correlations between small solid spheres immersed in a polymer melt. The idea is first to do simulations without spheres, but then in each resulting polymer configuration to determine the void regions, to randomly place solid spheres in these regions, and to study the correlation function of these spheres.

(b) To consider interaction of two solid plates in a polymer melt (or a solution). The advantage here is that the total interaction energy may be high since it is proportional to the plate area (i.e. eventually to the simulation box size). That sort of simulation was already carried out [22]; however the precision of the data for the force (around 10% relative to the total

pressure) was not good enough to allow for an unambiguous conclusion (though a hint of repulsion at rather short distances can be noted from the data for the concentrated case). The disadvantage of the scheme employed is the necessity to simulate a large amount of polymer solution outside the plates in order to imitate the 'bulk' properties. We suggest performing simulation in a small simulation box with periodic boundary conditions. We can then estimate the PILR force between the plates inside the box and the same force between these plates because of the periodic boundary condition, and check the simulation results against the predicted difference of the two forces.

In order to improve the force resolution we suggest considering *free* (rather than fixed) parallel solid plates, i.e. a fluctuating gap between the plates. One problem is allowing for an efficient relaxation of the polymer amount between the plates when the separation changes. This could be achieved by resorting to a living polymer system (but without cycles) where the monomer units can appear and disappear constantly and everywhere.

An off-lattice simulation of that kind seems straightforward. A lattice brings in another problem: for a plate to move, the whole layer on one side of the plate must be empty. A solution might be to consider a $\llcorner$-shaped plate (in two dimensions) with one defect bond normal to all other bonds (one kink). The kink diffusion along the plate (which requires at each step that just one neighbouring lattice site is empty) would result in a global plate motion in the normal direction.

Acknowledgments

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