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Interaction between irreversibly adsorbed polymer layers: Is the mean field picture really inadequate?

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We found out that the mean-field theory (MFT), if done consistently, is in good agreement with experimental observations for the force between irreversibly adsorbed polymer layers. This result is fairly unexpected in light of the conventional Cahn–de Gennes mean-field (CdGMF) theory that claims this force is zero. We reexamine the CdGMF equations and show that the consistency of the CdGMF approach is broken. This motivated us to derive an equation for the polymer density on the adsorbing surface that describes a minimum of the surface free energy. This equation replaces the conventional boundary condition used in CdGMF. The disjoining pressure is calculated by making use of the developed theory. An excellent agreement with the experimental results is indicated. We believe that our findings rehabilitate the mean-field theory as one of the most powerful tools for investigating the polymer-mediated interaction between colloids. Our result show that the unphysical predictions of CdGMF are due to its inconsistency rather than because this approach is "completely inadequate to discuss the plate-plate interactions in good solvent" [P. G. de Gennes, Macromolecules **15**, 492 (1982)].

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The aim of this paper is to bridge the gap between the results of the mean-field theory [1–3] and experimental observations [4–6] of the interaction between irreversibly adsorbed polymer layers.

The system considered in the above theory and experiments consists of two parallel plates carrying adsorbed polymer layers that are immersed into a good solvent. The main quantity of interest is the disjoining force acting between the plates due to the presence of adsorbed polymers. In the present work, we deal with the situation of the so-called restricted equilibrium. In this situation, the homopolymer chains of high molecular weight are irreversibly adsorbed onto the plates so that the polymers cannot escape from the gap between the plates. The adsorbed polymer layers are saturated: they are formed in the course of the incubation period that is long enough to ensure the thermodynamic equilibrium with the solution. This situation is described in Refs. [1,4] in great detail. Again, here we restrict ourselves to the consideration of the good solvent conditions only.

As is well known, the Cahn–de Gennes mean-field (CdGMF) theory predicts that the polymer-mediated force between the plates vanishes identically in the situation described above. This result seems to be quite unphysical, especially in the light of detailed experimental observations [4,5] of the disjoining pressure in this system. The experiments reveal that the interaction between the adsorbed layers is purely repulsive [4]. It was found that the corresponding force can be described by a simple monotonic, fast decaying function of the separation between the plates.

Our findings presented in this paper show that the mean-field approach, if carried out properly, is completely adequate for the description of the above experimental situation. We show that the reason for unphysical predictions of CdGMF is due to the fact that this approach in its standard formulation is not entirely consistent (rather than totally inadequate). More specifically, we show that the consistency of CdGMF breaks down because the boundary condition for the polymer density at the surface is defined artificially. In order to circumvent this problem, we obtain a refined equation for the surface density of the polymer by performing an accurate minimization of the *actual* surface free energy. This leads to a result for the disjoining force which is in excellent agreement with experiment.

We should note that the usual limitations of the CdGMF theory also apply to our approach [7]. Specifically, our version of the mean-field theory does not take into account the end (finite molecular weight) effects since our approach is still based on the ground state solution of the Edwards diffusion equation. In fact, the classical theories of Scheutjens, Fleer [8,9], and Semenov [10] have shown the importance of the end effects in the cases where the separation between plates is larger than the radius of gyration of the polymer. For the case of long enough polymers considered here, the end effects are found to be negligibly small [10]. In addition, the present version of our theory is limited in scope since it treats the polymer-mediated interaction between the irreversibly adsorbed, saturated layers only.

Before proceeding to the discussion of our proposed approach, it is worth making a few remarks regarding an alternative analysis of the experimental data [11] based on the scaling method of de Gennes[1,12]. This method, which was proposed in order to remedy the aforementioned unphysical behavior of the CdGMF approach, is based on the assumption that the correlation length describing the effective interaction between polymers is a spatially dependent function. The refined version of the de Gennes scaling approach was found to be in reasonably good agreement with experiment [11]. However, it should be noted that this theory employs an artificial boundary condition of the same type as that used in CdGMF. In our opinion, this fact calls for a significant refinement of the scaling approach before this theory can be

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*Email address: chervany@egor1.chem.virginia.edu compared with experiment [13]. In addition, the scaling theory operates with *four* adjustable parameters while our refined version of mean-field theory (MFT) involves only *two*.

Moving now to the discussion of our proposed approach, we start with a brief outline of the main formulas of the conventional CdGMF theory. Although these formulas are well known and can be easily found in the literature[1,3], we will rederive the main results placing the emphasis on the consistency of the derivation. The calculation of the disjoining pressure Π starts from the expression for the excess free energy of the polymer solution confined in slab between two parallel plates. This energy, $2\Delta F$, takes the following form [1,3]:

$$\beta\Delta F[\psi] = -\beta\gamma\psi_s^2 + \frac{1}{2}\int_0^h\left(\frac{1}{3}(\partial_z\psi)^2 + v\psi^4\right)dz - \frac{v\mu\Gamma}{2}, \tag{1}$$

where $2h$ is the separation between the two plates, z is the distance from the plate, $\psi(z)$ is the MFT order parameter proportional to the square root of the monomer volume fraction, ψ_s is the value of the order parameter at the plate, γ is the (positive) local polymer-surface interaction energy, $\Gamma \equiv \int_0^h \psi^2 dz$ is the coverage, $\beta \equiv 1/k_B T$ is the Boltzmann factor, and v is the excluded volume parameter, which is positive for a good solvent. The monomer unit (Kuhn) length is set equal to unity. The Lagrange multiplier μ is introduced into Eq. (1) in order to satisfy the constraint that the total number of monomers in the solution does not depend on the separation h. The above constraint corresponds to the afore-described situation of the irreversible adsorption when the polymer cannot escape from the gap between the plates.

Note that $\Delta F[\psi]$ in Eq. (1) is a functional of an arbitrary function ψ that cannot be directly associated with the surface free energy F_s. The surface free energy F_s can be obtained by minimizing the free energy functional ΔF with respect to all variations of the function $\psi(z)$ subject to the above constant coverage constraint. The equation for the function $\hat{\psi}(z)$ which minimizes the functional $\Delta F[\psi]$, can be written in the following form:

$$(\partial_z\hat{\psi})^2 = 3v[\hat{\psi}(z)^2 - \hat{\psi}(h)^2][\hat{\psi}(z)^2 - \nu\hat{\psi}(h)^2], \tag{2}$$

where $\nu = \psi_m^{-2}\mu - 1$. Note that the relation between the normal derivative of the order parameter at the surface, $(\partial_z\hat{\psi})_s$, and the values $\psi_s \equiv \hat{\psi}(0)$ and $\psi_m \equiv \hat{\psi}(h)$ follows immediately from Eq. (2), taking the form

$$(\partial_z\hat{\psi})_s^2 = 3v(\psi_s^2 - \psi_m^2)(\psi_s^2 - \nu\psi_m^2). \tag{3}$$

Substituting function $\hat{\psi}(z)$ into Eq. (1), one obtains the final expression for the surface free energy of the form

$$\beta F_s(\psi_s,\psi_m,\nu) = -\beta\gamma\psi_s^2 + \sqrt{\frac{v}{3}} \times\left(\int_{\psi_m}^{\psi_s}\sqrt{(\psi^2-\psi_m^2)(\psi^2-\nu\psi_m^2)}\,d\psi - \frac{\hat{h}\nu\psi_m^4}{2}\right), \tag{4}$$

where $\hat{h} \equiv \sqrt{3v}h$ is the reduced separation.

It should be noted that F_s is an ordinary differentiable function of its arguments ψ_s, ψ_m, and ν. The latter variable, "quasichemical potential" ν, can be eliminated by substituting the equilibrium order parameter profile $\hat{\psi}(z)$ obtained from Eq. (2) into the definitions of Γ and ψ_m. This yields the "normalization conditions" of the form

$$\hat{h} = \frac{I_1\left(\frac{\psi_s}{\psi_m},\nu\right)}{\psi_m}, \quad \Gamma_0 = \psi_m I_2\left(\frac{\psi_s}{\psi_m},\nu\right), \tag{5}$$

where $I_n(y,\nu) = \int_1^y x^n[(x^2-1)(x^2-\nu)]^{-1/2}dx$. The value of the coverage Γ_0 in Eq. (5) depends on the prehistory of the polymeric layers adsorbed onto the plates before they are brought in contact. For the saturated plates considered here, Γ_0 is found to be a simple function of the surface interaction energy γ of the form $\Gamma_0 = (D\sqrt{3v})^{-1}$, where D is the characteristic length of the polymer-surface interaction defined as [1,3] $D \equiv (6\beta\gamma)^{-1}$. Note that the second equation in Eq. (5) expresses the quasichemical potential ν in terms of ψ_s and ψ_m. The first equation in Eq. (5) defines $\psi_m = \psi_m(\psi_s, \hat{h})$ as a function of ψ_s and $\hat{h}$. Therefore, these two equations make it possible to express ψ_m and ν in terms of ψ_s and $\hat{h}$.

Now we come to the crucial point of our derivation, which differs significantly from the standard implementation of the MFT approach. First, we note that the set of equations given above is not closed yet. This can be easily seen by substituting $\psi_m = \psi_m(\psi_s, \hat{h})$ and $\nu = \nu(\psi_s, \hat{h})$ calculated from Eq. (5) into Eq. (4) and recognizing the fact that F_s is still a function of an unknown variable ψ_s. The closure adopted in the standard MFT approach is obtained by postulating the "boundary condition," i.e., the relation between ψ_s and $(\partial_z\hat{\psi})_s$, which is obtained on the basis of some plausible arguments [1,14]. Equation (3) is then used to close the problem. Here we use a different approach which is based on the fact that the surface free energy has a minimum with respect to ψ_s at any fixed h and Γ if thermodynamic equilibrium is maintained. It is important to note that ψ_m and ν should be considered the functions of ψ_s when minimizing the surface energy F_s in Eq. (4). It is precisely in this respect that our approach differs significantly from the method described in Ref. [3]. In this latter work, the same approach to obtaining the boundary condition by minimizing the surface free energy is used, but the dependance of μ on ψ_s is ignored in the course of the derivation. The present work rectifies this seemingly insignificant mathematical omission so that our approach leads to a remarkably different physical result, as explained below.

Taking the derivative $(\partial F_s/\partial\psi_s)_h$ and equating the result to zero, one finds

$$\psi_s + D\left(\partial_z\hat{\psi}\right)_s + \frac{1}{2}\left(\frac{\partial\mu}{\partial\psi_s}\right)_h = 0. \tag{6}$$

Note that each term in the refined boundary condition given by Eq. (6) is directly related to the corresponding term of the surface free energy in Eq. (4). The first and the second terms in Eq. (6) originate from the local polymer interface energy and the polymer conformational entropy, respectively. The third term is due to the dependance of the quasichemical potential on the polymer-surface density ψ_s. This last term in Eq. (6), which is omitted from the boundary condition used in Ref. [3], produces significant differences between our results and those of Ref. [3].

Equations (3) and (6) can be solved simultaneously to obtain ψ_s as a function of $\hat{h}$. After that, the disjoining pressure Π can be found by differentiating F_s with respect to h. Surprisingly, the derivative $(\partial\mu/\partial\psi_s)_h$ is eliminated from the resulting expression for Π, provided the boundary condition given by Eq. (6) is satisfied. The final result for the disjoining pressure reads [15],

$$\beta\Pi = \frac{\upsilon\nu\psi_m^4}{2}. \tag{7}$$

Now we are in the position to produce a recipe for the calculation of the output value of Π given the input values of h and Γ_0. First, we define the implicit function $\phi(y)$ by

$$\int_1^y \frac{dx}{\sqrt{(x^2-1)[x^2-\phi(y)]}}\int_1^y \frac{x^2dx}{\sqrt{(x^2-1)[x^2-\phi(y)]}} = \frac{h}{D}. \tag{8}$$

The derivative $\kappa \equiv -(1/2\psi_s)(\partial\mu/\partial\psi_s)_h$ can be easily calculated through the introduced function ϕ. The result reads

$$\kappa = -\frac{\phi'(\eta) + 2[1+\phi(\eta)]\xi'(\eta)}{2\eta[1+\eta\xi'(\eta)]}, \tag{9}$$

where $\eta = \psi_s/\psi_m$, $\xi(x) = -\ln I_2[x,\phi(x)]$, and the prime denotes differentiation with respect to the argument.

Substituting Eq. (9) into Eq. (6) and solving the simultaneous Eqs. (3) and (6), one finds the equation for η of the form

$$\eta[1-\kappa(\eta)]e^{-\xi(\eta)} = \sqrt{(\eta^2-1)[\eta^2-\phi(\eta)]}. \tag{10}$$

The root of Eq. (10), η_0, defines the ratio ψ_s/ψ_m for each value of the reduced separation h/D. Substituting η_0 into Eq. (7), one obtains the final result for the disjoining pressure in the following form:

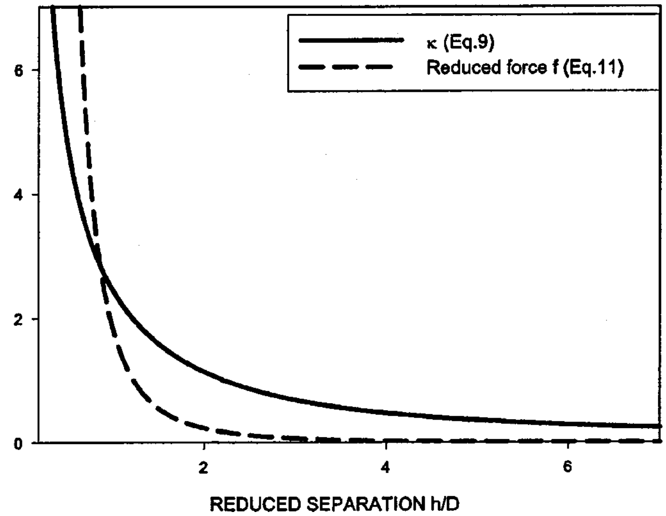

FIG. 1. Reduced force f in Eq. (11) and coefficient κ in Eq. (9) plotted against the reduced separation h/D.

$$\beta\Pi = \frac{f\left(\frac{h}{D}\right)}{18\upsilon D^4}, \quad f(x) = \phi(\eta_0(x))e^{4\xi[\eta_0(x)]}, \tag{11}$$

where we introduced a universal function $f(h/D)$ which describes the reduced force acting on the plates versus the separation between them.

Equation (10) was solved numerically and the result for η_0 was used to calculate the reduced force $f(h/D)$ in Eq. (11) and κ in Eq. (9). The results are shown in Fig. 1. As can be seen from Fig. 1, the value of κ is positive for any value of h. In addition, κ is found to be a decreasing function of the separation. This function is of the order of unity for $h/D \lesssim 1$ and larger than unity for $h/D \lesssim 1$. This allows us to conclude that the new (third) term in Eq. (6) included by us into the boundary condition for ψ is especially important for small separations between the plates. This term makes a crucial contribution to the total value of the disjoining pressure and cannot be neglected for any finite value of h/D, except for the "single plate" limit $h/D \to \infty$.

The reduced force $f(h/D)$ depicted in Fig. 1 can be fitted with the function $f_{fit} = 1.867D^3/h^3$ within the accuracy $|f_{fit} - f| < 0.042$ in the considered range of h/D. Note that this result is quite close to the exact expression $f(x) = 1.2x^{-3}$ obtained from Eq. (11) in the "narrow gap" limit $h/D \ll 1$. The obtained fit of the numerical results for f gives a simple scaling law for the disjoining pressure written as follows: $\beta\Pi \sim \gamma\upsilon^{-1}h^{-3}$. This result shows that the force between the plates is always repulsive. This force is proportional to the local energy of the polymer-surface interaction and inversely proportional to the excluded volume parameter. This is because the smaller the value of γ and the better the quality of the solvent, the smaller the coverage, i.e., the amount of polymer adsorbed onto the plates. This explains the above scaling relation, since the osmotic pressure is proportional to the density of the polymer confined between the plates.

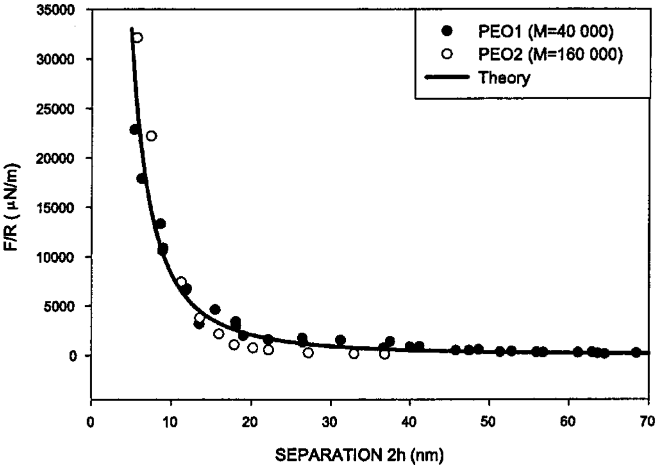

FIG. 2. Comparison of the presented theory with experiment. The solid line presents the disjoining force calculated by Eq. (12) plotted against the reduced separation. The circles present the experimental force vs separation profiles (F/R vs h/D) between mica surfaces bearing adsorbed poly-ethylene oxide across an aqueous medium ($0.1M\mathrm{KNO}_3$). Open (filled) circles correspond to the degree of polymerization $M = 160\,000$ ($M = 40\,000$). Data were taken from Ref. [11].

In Fig. 2 we compare our theoretical results with the experimental data for the force between two smooth mica surfaces immersed in poly(ethylene oxide)-water solution [11]. Note that the experimental measurements provide the force acting between the surfaces of two crossed cylinders of the radius R, rather than between two parallel plates. In order to compare the experimental results for this force with our theoretical predictions, we follow the method described in Ref. [11]. Namely, we employ Derjaguin approximation in order to relate the force between cylinders to the disjoining pressure [16]. Adopted for our result for Π, this relation reads

$$\frac{F(2h)}{R} = 6\pi\beta^{-1}\Gamma^3 v^2 \int_{3\Gamma vh}^{\infty} f(x)dx. \tag{12}$$

Note that Eq. (12) contains two phenomenological parameters (excluded volume parameter v and coverage Γ measured in the monomer units). These parameters are typically known for most polymer solutions.

Although of considerable theoretical interest, the mean-field result for the disjoining pressure given by Eq. (12) is not well suited for practical use by experimentalists and engineers. Keeping this in mind, we found empirically that function $f_{fit}(x) = 1.867x^{-3}$ provides a good approximation for the actual reduced force $f(x)$. Replacing $f(x)$ with $f_{fit}(x)$ in Eq. (12), one obtains the following simplified result for the disjoining pressure:

$$\frac{F(2h)}{R} = \frac{1.96\beta^{-1}Aa^2}{mh^2}, \tag{13}$$

where $A = ma^{-3}\Gamma$ is the absorbance, m is the monomer mass, and a is the Kuhn length.

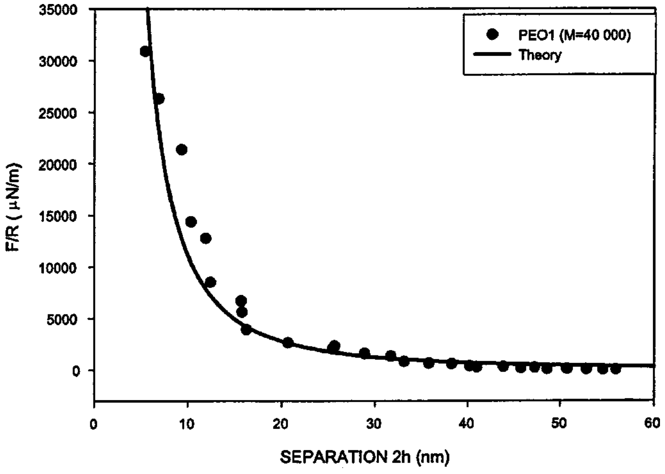

FIG. 3. Comparison of the presented theory with experiment. The solid line presents the disjoining force calculated by Eq. (12) plotted against the reduced separation. The circles present the experimental force vs separation profiles (F/R vs h/D) between mica surfaces bearing adsorbed poly-ethylene oxide across toluene. Data were taken from Ref. [6].

Note that the excluded volume parameter v does not enter the simplified expression for the disjoining force given by Eq. (13). However, this force does depend on the quality of solvent through the absorbance A, which is proportional to v^{-1}.

The accuracy of the above approximate formula for the disjoining force can be verified by fitting F/R from Eq. (13) to the experimental data reproduced in Fig. 2. Treating the reduced absorbance $\hat{A} = Aa^2m^{-1}$ as an adjustable parameter, the best fit is obtained with the value $\hat{A} = 24.4$. Given the values $m = 44$ a.m.u. and $\Gamma = 4.0 \pm 1.5$ nm [4], this yields the mesh size $a = 0.67 \pm 0.18$ nm, which is quite close to the estimate reported in the literature [17,18].

The solid line in Fig. 2 shows the disjoining force calculated from the exact expression given by Eq. (12) using the value of the reduced absorbance $\hat{A}$ given above. The excluded volume parameter v is obtained from $v = a^3(1 - 2\chi)$, where $\chi = 0.48$ is the polymer-solvent interaction parameter for the poly(ethylene oxide)/$0.1M\mathrm{KNO}_3$ system [19]. As can be seen from Fig. 2, our theoretical curve is in excellent agreement with the experimental data.

It is generally expected that the Flory-type mean-field theory described here should work well in the nearly "theta" ($\chi \sim 0.5$) solvent conditions. This point is confirmed by the above comparison with the experimental results for the disjoining force acting between polymer layers in the solvent of moderate quality ($\chi = 0.48$). It is instructive to test the validity of our theory for the solvent of intermediate quality with lower values of χ. Figure 3 shows our result for the disjoining force F calculated from Eq. (12) using the values $\chi = 0.39$ and $\hat{A} = 28.7$. The theoretical curve for F/R is plotted against the experimental points for the disjoining force measured in the poly(ethylence oxide)/toluene system ($\chi = 0.39$). As can be seen from this figure, the presented theory works reasonably well in the case of a good solvent having intermediate values of χ.

In summary, the refined CdGFT theory properly describes the above experimental results for the disjoining force, once the consistency of this approach is remedied. The refined version of the mean-field theory described here can readily be employed for the analysis of the polymer-mediated interaction between colloids in good solvent conditions.

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