PHYSICAL REVIEW E VOLUME 55, NUMBER 3 MARCH 1997

Universal density-force relations for polymers near a repulsive wall

E. Eisenriegler
Institut für Festkörperforschung, Forschungszentrum Jülich, D-52425 Jülich, Germany

(Received 19 September 1996)

The relation between the force exerted by long flexible polymer chains on a repulsive wall and the corresponding monomer density close to the wall is shown to imply a universal amplitude ratio. This is calculated in an ε expansion, and its importance in various situations is pointed out. These include a single polymer trapped between two parallel walls and a solution of polymers inducing a depletion interaction between the wall and a mesoscopic particle. Dilute and semidilute solutions in the half space are also considered. [S1063-651X(97)07003-7]

PACS number(s): 61.25.Hq, 05.70.Jk, 68.35.Rh, 82.70.Dd

I. INTRODUCTION

In a dilute or semidilute solution of long flexible polymer chains in the half space bounded by a planar repulsive wall, the *monomer density* profile has a depletion region of mesoscopic width [1]. For distances z from the wall that are small compared to this width (but large on the microscopic scale), the profile increases as $\sim z^{1/\nu}$, where ν is the Flory exponent [1]. This has been predicted by Joanny, Leibler, and de Gennes [2], who also observed that the amplitude in the power law is proportional to the repulsive *force* per unit area which the polymer solution exerts on the wall.

We recall their argument by discussing the case of a dilute polymer solution where the width of the depletion region is of the order of the chain size in bulk $\mathcal{R}_x \sim N^{\nu}$, with N the number of monomers per chain. (A precise definition of $\mathcal{R}_x$ will be given below.) Denoting the bulk densities of polymers and monomers by n_b and Nn_b, respectively, the monomer density profile is given by $\mathcal{M}(z/\mathcal{R}_x)Nn_b$, where $\mathcal{M}$ is a scaling function that tends to unity for large argument. The above mentioned behavior $\sim z^{1/\nu}$ then follows, since the monomer density profile should be independent of N if $z \ll \mathcal{R}_x$. The reason is that the monomer density close to the wall is proportional [1–3] to the force per area that the polymers exert on the wall, and the force per area equals the osmotic pressure $n_b k_B T$ of the dilute solution which is independent of N. For a semidilute solution [where the depletion width is of the order of the screening length $\xi \sim (Nn_b)^{-\mu\nu}$, with $\mu = 1/(d\nu - 1)$ and d the space dimension, and where the osmotic pressure is $\sim (Nn_b)^{\mu+1}$] the argument is quite similar [1,2]. While these arguments yield the power-law exponent $1/\nu$ of the profile they make no definite prediction about the amplitude in the density-force relationship.

In this paper a *complete* quantitative expression for the density-force relationship is given, which is free of microscopic details [3] and characterized by a *universal* number B. It is shown that the *same* number appears in a wide variety of *different* situations.

The following situations will be considered: (i) A single chain with one end (or both ends) *fixed* fluctuating in the half space bounded by a wall. (ii) A single chain *trapped* between two parallel walls. The distant wall may be either repulsive or near the threshold for adsorption [1,4]. (iii) A dilute and monodisperse solution of *free* chains in a half space or (iv) in a half space containing a mesoscopic obstacle (‘‘particle’’) of arbitrary shape and finite extent. In (iii) and (iv) the polymer density far from the wall (and from the particle) is fixed, and the difference between the forces with and without the particle yields the depletion interaction of the particle with the wall. A semidilute solution in half space (iii’) is briefly considered at the end.

In all cases it is assumed that lengths, such as the chain size $\mathcal{R}_x$ (or the screening length) and the distance from the wall to a fixed end of the chain or to the closest point of another confining boundary (which we denote collectively by $\mathcal{D}$), are much larger than the ‘‘microscopic’’ lengths a (monomer size or the ranges of the monomer potentials [3] due to a wall or particle). It is for $a \ll z \ll \mathcal{D}$ that the monomer density varies $\sim z^{1/\nu}$ and forms a universal relation with the mean repulsive force f exerted by the polymer(s) on the wall in which the number B appears.

The density-force relations are stated in Sec. II, illustrated in Secs. III and IV and derived (by means of the polymer-magnet analogy) in Sec. V. Section VI is reserved for concluding remarks.

II. DENSITY-FORCE RELATIONS

Consider a modified monomer density defined by

$$\rho(\mathbf{r})\, d\mathbf{r} = k\, d\mathcal{N}(\mathbf{r}), \tag{1}$$

where $d\mathcal{N}(\mathbf{r})$ is the number of monomers [5] located inside the volume element $d\mathbf{r}$ around the point $\mathbf{r}$. The quantity k is the nonuniversal amplitude

$$k = (\mathcal{R}_x)^{1/\nu}/N \tag{2a}$$

that relates the total number N of monomers in a single chain to the mean square

$$\mathcal{R}_x^2 = \langle R_x^2 \rangle_{\text{bulk}} = \langle \mathbf{R}^2/d \rangle_{\text{bulk}} \tag{2b}$$

of the projection R_x of the end to end distance $\mathbf{R}$ onto the x axis when the chain fluctuates in unbounded space. Here d is the space dimension. Since only the ratio $d\mathcal{N}/N$ enters ρ, it is less dependent on the monomer structure than the usual density $d\mathcal{N}/d\mathbf{r}$. The scaling dimension of ρ is (length)$^{(1/\nu)-d}$ and equals the ordinary (or ''naive'') dimension of ρ, compare [5] and Sec. V below. Similarly one may define layer densities $\rho_\lambda(z)$ by

$$\rho_\lambda(z)\ dz = k\ d\mathcal{N}_\lambda(z), \tag{3}$$

where $d\mathcal{N}_\lambda(z)$ is the number of monomers with a distance from the wall between z and $z+dz$. Thus $\rho_\lambda(z)=\int d\mathbf{r}_\parallel\ \rho(\mathbf{r})$ where the integration is over the $d-1$ components of $\mathbf{r}=(\mathbf{r}_\parallel, z)$ parallel to the wall.

In the single-chain situations (i) and (ii), the universal relation reads [6]

$$\langle \rho_\lambda(z)\rangle^{(\mathrm{as})}/z^{1/\nu} = Bf/k_BT. \tag{4}$$

Here the superscript (as) refers to the ''asymptotic'' condition $a \ll z \ll \mathcal{D}$, and B is the universal amplitude mentioned in the Introduction. For ideal (random walk) chains [7]

$$B = B_{\mathrm{id}} = 2 \tag{5}$$

independent of d, while for chains with excluded volume (EV) interaction

$$B = B_{\mathrm{EV}} = 2\{1 - b_1\varepsilon\}, \tag{6a}$$

with

$$b_1 = (\ln 2 + C_E - 2/3)/8 = 0.075 \tag{6b}$$

and $d = 4-\varepsilon$ is close to 4. Here $C_E = 0.577$ is Euler's constant.

In situation (iii) the density-force relation also has the form (4). Dividing both sides by the area A of the wall, one finds that $\langle\rho(\mathbf{r})\rangle^{(\mathrm{as})}_{(\mathrm{iii})}/z^{1/\nu}$ equals Bn_b, with n_b the polymer density in the bulk (far from the wall). Here the pressure on the wall f/A equals the pressure in the bulk, which is n_bk_BT from the ideal gas law. On denoting the bulk normalized [5] monomer density $\langle\rho\rangle_{(\mathrm{iii})}/(n_b\mathcal{R}_x^{1/\nu})$ in the scaling region $a \ll z, \mathcal{R}_x$ by $\mathcal{M}(z/\mathcal{R}_x)$, the universal relation can also be written as

$$\mathcal{M}^{(\mathrm{as})}(z/\mathcal{R}_x)/z^{1/\nu} = B/\mathcal{R}_x^{1/\nu}. \tag{7}$$

Immersing the finite particle of situation (iv) in the polymer solution in the half space changes the force on the wall by δf, where

$$\int d\mathbf{r}_\parallel\ \{[\langle\rho(\mathbf{r})\rangle^{(\mathrm{as})}_{(\mathrm{iv})}/\langle\rho(\mathbf{r})\rangle^{(\mathrm{as})}_{(\mathrm{iii})}] - 1\} = \delta f/(n_bk_BT). \tag{8}$$

Equation (8) is expected to hold for densities $\langle\rho(\mathbf{r})\rangle$ down to distances microscopically close to the wall ($z \sim a$). For a particle which repels the chains, the density deviation and thus δf are negative, i.e., the repulsive force onto the wall is reduced [8], reflecting the attractive character of the depletion interaction. Note that multiplying Eq. (8) by $\langle\rho(\mathbf{r})\rangle^{(\mathrm{as})}_{(\mathrm{iii})}/z^{1/\nu} = Bn_b$ yields a form which closely resembles Eq. (4).

It is instructive to compare (iv) with the case where the force between wall and particle is not mediated by a polymer solution but by a critical fluid, such as a binary mixture at its critical demixing point [9,10]. In this case, the order parameter profile $\langle\phi(\mathbf{r})\rangle^{(\mathrm{as})}$ and the force onto the wall satisfy [11] a relation similar to Eq (8). However, unlike the integrand in Eq. (8), the expression $[\langle\phi(\mathbf{r})\rangle^{(\mathrm{as})}_{(\mathrm{iv})}/\langle\phi(\mathbf{r})\rangle^{(\mathrm{as}}_{(\mathrm{iii})}] - 1$, which now appears on the left-hand side (lhs) is not z independent and negative, but proportional to z^d and positive (if we assume that the wall and particle surfaces have the same character). Since the right-hand side (rhs) now has [11(b)] the form $-Cz^d\delta f/k_BT$ with C a positive universal constant, the interaction is again attractive.

III. FIXED AND TRAPPED CHAINS

As a consequence of the simple universal relationships (4) and (8), the asymptotic density and the force must have the *same* dependence on the variables $\mathcal{D}$ mentioned above. We now discuss the various cases, beginning with situation (i) where an ideal chain has one end fixed at a distance z_A from the wall. Then for $a \ll z \ll z_A, \mathcal{R}_x$ (as) one finds a scaled density $\langle\rho_\lambda(z)\rangle^{(\mathrm{as})}/z^2$ given by $2\partial_{z_A}\ln \mathrm{erf}\,[z_A/(\sqrt{2}\mathcal{R}_x)]$, which is twice the repulsive force f/k_BT, compare, e.g., [4]. Thus Eqs. (4) and (5) are obeyed, and the density and the force both change from a power-law [12] behavior $\sim z_A^{-1}$ for $z_A \ll \mathcal{R}_x$ to an exponential dependence $\sim\mathcal{R}_x^{-1}\exp[-z_A^2/(2\mathcal{R}_x^2)]$ for $\mathcal{R}_x \ll z_A$. Equations (4) and (5) can also be easily checked for an ideal chain with two fixed ends at distances z_A and z_B and with $a \ll z \ll z_A, z_B, \mathcal{R}_x$. In this case f/k_BT equals $2\mathcal{R}_x^{-1}(\zeta_A+\zeta_B)/[\exp(2\zeta_A\zeta_B)-1]$, with $\zeta_A = z_A/\mathcal{R}_x$, $\zeta_B = z_B/\mathcal{R}_x$.

Consider now situation (ii) of a chain trapped in the slit between two parallel planar walls with separation D. If both walls are repulsive, one finds the scaling laws [13]

$$\langle\rho_\lambda(z)\rangle = (\mathcal{R}_x^{1/\nu}/D)X(z/\mathcal{R}_x, D/\mathcal{R}_x), \tag{9}$$

with z the distance from one of the walls, and

$$f/k_BT = D^{-1}Y(D/\mathcal{R}_x), \tag{10}$$

where X and Y are universal functions. Thus the result (4) confirms the plausible assumption [14] that for $a \ll z \ll \mathcal{R}_x, D$, i.e., close to the repulsive wall, $\langle\rho_\lambda\rangle$ and f/k_BT have the same dependence on $\mathcal{R}_x$ and D, and one can identify

$$B = \lim_{x\to 0} x^{-1/\nu}\ X(x,y)/Y(y). \tag{11}$$

We give explicit forms for $D/\mathcal{R}_x$ large and small. In the wide-slit limit $D\to\infty$ with the other variables kept fixed,

$$\langle\rho_\lambda(z)\rangle \to (\mathcal{R}_x^{1/\nu}/D)\mathcal{M}(z/\mathcal{R}_x) \tag{9$'$}$$

and

$$f/k_BT \to D^{-1}, \tag{10$'$}$$

since this limit corresponds to the half space problem (iii) with a polymer density $n_b = 1/(DA)$ in bulk, compare with the discussion leading to Eq. (7). Thus $X\to\mathcal{M}$, $Y\to 1$, and Eq. (11) reduces to Eq. (7) for $D/\mathcal{R}_x \gg 1$. In the narrow-slit limit $D/\mathcal{R}_x \ll 1$

$$Y(D/\mathcal{R}_x) \sim (D/\mathcal{R}_x)^{-1/\nu}, \tag{10$''$}$$

i.e., $f/k_BT\sim N$ [15,16], since the most important D dependence of the chain partition function comes from an exponential factor $\exp[-\text{const}(\mathcal{R}_x/D)^{1/\nu}]$.

If the wall at $z=D$ in the parallel-wall geometry is at the adsorption threshold [4] rather than repulsive, Eqs. (9)–(11) again apply. Except for the half space limits (9′),(10′), where the nature of the distant wall does not enter, the scaling functions X and Y are different from before, although the ratio (11) remains the same. This may be explicitly confirmed for an ideal chain in a narrow slit $D\ll\mathcal{R}_x$, where the results $X\rightarrow 2\{\sin^2(z\pi/D),\sin^2[z\pi/(2D)]\}$ and $Y\rightarrow(\mathcal{R}_x/D)^2\pi^2[1,1/4]$ in the two cases [repulsive-repulsive, repulsive-threshold] readily follow from ground-state dominance [1,17]. In the second case the chain favors the distant wall (the density maximum is at $z=D$), and both $\rho_\lambda^{(\text{as})}$ and f/k_BT are smaller by a factor of 1/4 than in the first case (with the density maximum in the center $z=D/2$ of the slit). If the distant wall is not precisely at the adsorption threshold but close to it (e.g., on the repulsive side), the variable describing the deviation must be included in the scaling description [4]. Also in this crossover scaling case, where X and Y in Eqs. (9) and (10) depend on an additional scaling variable, the expression corresponding to the rhs of Eq. (11) leads to the same number B given by Eqs. (5) or (6) as before.

Another interesting situation arises if one end of the chain in the slit is fixed to the wall at $z=D$. Here Eqs. (4) and (9)–(11) again apply. While B is given by Eqs. (5) or (6) as before the scaling functions X and Y are different from those in the previous cases where no end was fixed. For example, for given z and $\mathcal{R}_x$ density and force decrease for $D\rightarrow\infty$ (wide-slit limit) with exponential laws and not with the power laws (9′) and (10′). However, the leading behavior of layer density and force in the narrow-slit limit is expected to remain unchanged on fixing one end of the chain.

IV. FREE CHAINS AND DEPLETION INTERACTION

In situation (iii) the amplitude B defined by Eq. (7) was previously introduced in Ref. [4], but its more general interpretation as the density-force amplitude for a wide class of situations was not mentioned. The ε-expansion result in [4] suffers from a bookkeeping error [18], and the correct result is given by Eq. (6).

In situation (iv) the two sides of the density-force relation [Eq. (8)] depend, apart from $\mathcal{R}_x$, on the shape of the particle and its distance from the wall. To illustrate, we quote the result for the force [19,20]

$$\delta f/(n_bk_BT)=-\mathcal{A}(\mathcal{R}_x/R)^{1/\nu}R^d\partial_{z_s}\mathcal{M}(z_s/\mathcal{R}_x) \tag{12}$$

for a spherical particle with radius R much *smaller* than its distance z_s from the wall and much smaller than $\mathcal{R}_x$. Here $\mathcal{M}$ is the density in the half space introduced above Eq. (7). The lhs of Eq. (8) can in the case considered here be calculated [21], and the result again equals the rhs of Eq. (12).

As an example of a *large* particle, consider an object with the shape of a plate [22] that is oriented parallel to the wall and with area $\hat{A}$ and linear dimension $(\hat{A})^{1/(d-1)}$ that is much larger than $\mathcal{R}_x$ and the distance D between wall and plate. Then one may disregard edge effects, $\langle\rho(\mathbf{r}_\parallel,z)\rangle_{(\text{iv})}$ between the wall and the plate is independent of $\mathbf{r}_\parallel$, and one can make contact with situation (ii). The ratio $U(D/\mathcal{R}_x)$ of the mean density between wall and plate $\int_0^D dz\langle\rho\rangle_{(\text{iv})}/D$ to the density $n_b\mathcal{R}_x^{1/\nu}$ in the bulk equals [23] the ratio of the partition function of a chain between wall and plate averaged over the distance z_A of its fixed end from the wall to the partition function of a chain with fixed end in the bulk. The first ratio implies [5] a mean number n_bUD of polymer chains per unit area between wall and plate, and the second ratio implies $Y=d\ln(yU)/d\ln y$ with the scaling function Y in Eq. (10) for the force $f=f_{(\text{ii})}$ of a trapped chain. A straightforward calculation [19,24,25] of the force exerted on the immersed plate leads to the result

$$\frac{\delta f}{k_BT\hat{A}}=-n_b\left(1-UD\frac{f_{(\text{ii})}}{k_BT}\right), \tag{13}$$

expected intuitively. For ideal chains and both walls repulsive,

$$U=\Sigma_j(8/(\pi j)^2)\exp[-(\pi j)^2\mathcal{R}_x^2/(2D^2)],$$

with $j=1,3,5,\ldots$. On inserting Eq. (10) into Eq. (13), one recovers the result of Asakura and Oosawa [25] for $-\delta f$, which decreases monotonically from $n_bk_BT\hat{A}$ to zero as $D/\mathcal{R}_x$ increases from zero to infinity. To confirm Eq. (8), note that on its lhs $\mathbf{r}_\parallel$ is confined to the interior of the slit, and one may replace $\langle\rho\rangle_{(\text{iv})}^{(\text{as})}$ by $n_bUD\langle\rho_\lambda\rangle_{(\text{ii})}^{(\text{as})}$. Then Eq. (8) follows from Eq (13) on using $\langle\rho\rangle_{(\text{iii})}^{(\text{as})}=Bn_bz^{1/\nu}$ and the relation (4) between $\langle\rho_\lambda\rangle_{(\text{ii})}^{(\text{as})}$ and $f_{(\text{ii})}$.

As a final example consider a spherical particle with radius R much *larger* than the distance z_s of its closest point to the wall and much larger than $\mathcal{R}_x$. It is then reasonable to apply the Deriagin approximation [26,27], which describes the sphere by a superposition of immersed plates with local distance $D\rightarrow\widetilde{D}(r_\parallel)=z_s+r_\parallel^2/(2R)$ from the wall. In particular $\delta f/k_BT$ is then given by the integral $\int d\mathbf{r}_\parallel$ over the rhs of Eq. (13) with D replaced by $\widetilde{D}$. Note that the second term in the parentheses in Eq. (13), which equals UY, then approaches 1 as $r_\parallel\rightarrow\infty$, and the integral converges. Since $\langle\rho(\mathbf{r}_\parallel,z)\rangle_{(\text{iv})}^{(\text{as})}$ also follows from the plate expression given above on replacing $D\rightarrow\widetilde{D}(r_\parallel)$, Eq. (8) again applies. An explicit formula for $\delta f/k_BT$ can be obtained for ideal chains and $d=3$. We note the corresponding free energy of interaction per k_BT

$$\frac{\delta F}{k_BT}=-n_bR\mathcal{R}_x^2V(z_s/\mathcal{R}_x) \tag{14a}$$

between sphere and wall, from which δf follows as $\delta f=-(d/dz_s)\delta F$. Here

$$V(\zeta)=4\pi\int\frac{d\tau}{2\pi i}e^{\tau}\tau^{-2}\,\ln[1+\exp(-\zeta\sqrt{2\tau})], \tag{14b}$$

where the integration path in the complex τ plane encircles the cut that extends from $\tau=-\infty$ to $\tau=0$ counterclockwise. While V is proportional to $\zeta^{-3}\exp(-\zeta^2/2)$ for $\zeta\rightarrow\infty$, its expansion about $\zeta=0$ is $V=4\pi(\ln 2-\sqrt{2/\pi}\zeta+\frac{1}{4}\zeta^2)$, apart from terms of order ζ^5. This should be compared with the result

[25] $(\delta F/k_BT)_{\mathrm{phs}} = -n_b R\pi(2\tilde{\mathcal{R}} - z_s)^2\Theta(2\tilde{\mathcal{R}} - z_s)$, with Θ the step function, for a model where each polymer chain interacts with the wall and with the large spherical particle like a hard sphere (phs) with an effective radius $\tilde{\mathcal{R}}$ [28].

V. POLYMER-MAGNET ANALOGY AND SHORT-DISTANCE EXPANSION

Now we derive the density-force relations (4)–(8). It is convenient to use the polymer-magnet analogy [1,4,29], since wall effects for critical Ginzburg-Landau (GL) ''magnets'' are well understood [30,31]. The partition function of a single polymer chain, with the ends fixed at $\mathbf{r}_A$ and $\mathbf{r}_B$, is related to the correlation function of the order parameter densities $\phi_1(\mathbf{r}_A)$ and $\phi_1(\mathbf{r}_B)$ [32] in a GL model by means of a Laplace transformation $\mathcal{L}$ with respect to $T-T_c$. The conjugate Laplace variable L has the dimension of length squared and is proportional to the total number N of monomers of the chain. The monomer density $\rho(\mathbf{r})$ is related to the quantity

$$\Psi(\mathbf{r}) = \mathcal{R}_x^{1/\nu}(2L)^{-1}\mathbf{\Phi}^2(\mathbf{r}), \tag{15}$$

which has identical naive and scaling dimensions (length)$^{(1/\nu)-d}$. To avoid lengthy formulas we introduce the compact notation

$$\varphi_{A,B} = \phi_1(\mathbf{r}_A)\phi_1(\mathbf{r}_B) \tag{16}$$

for the product of two order parameter densities at $\mathbf{r}_A$ and $\mathbf{r}_B$.

Consider first situation (i) of a chain with two fixed ends, in which case [4,19,29]

$$\langle\rho(\mathbf{r})\rangle = \mathcal{L}\langle\Psi(\mathbf{r})\cdot\varphi_{A,B}\rangle_{\mathrm{w}}/\mathcal{L}\langle\varphi_{A,B}\rangle_{\mathrm{w}}. \tag{17}$$

Here $\langle\rangle_{\mathrm{w}}$ denotes a statistical average for a GL field in the half space with the Dirichlet condition $\mathbf{\Phi}=0$ at the boundary wall [31]. The dot following Ψ denotes a cumulant average. The property [33]

$$\int_+ d\mathbf{r}\ \mathcal{L}\langle\Psi(\mathbf{r})\cdot\varphi_{A,B}\rangle_{\mathrm{w}} = \mathcal{R}_x^{1/\nu}\mathcal{L}\langle\varphi_{A,B}\rangle_{\mathrm{w}} \tag{18}$$

ensures the normalization [5] of $\langle\rho(\mathbf{r})\rangle$. Here the integral $\int_+$ extends over the half space bounded by the wall. To find the behavior $\langle\rho\rangle^{(\mathrm{as})}$ of $\langle\rho\rangle$ near the repulsive wall, one can use the short-distance expansion of $\mathbf{\Phi}^2$ near a Dirichlet wall [4,34–36], which implies [37,38]

$$\Psi(\mathbf{r}_\parallel, z) \to Bz^{1/\nu}\ T_{\perp\perp}(\mathbf{r}_\parallel, 0) \tag{19}$$

in the scaling region $a \ll z$, where B is the universal amplitude in Eqs. (5) or (6). The surface operator $T_{\perp\perp} = [\mathbf{\Phi}_\perp(\mathbf{r}_\parallel)]^2/2$ with $\mathbf{\Phi}_\perp = (\partial_z\mathbf{\Phi})_{z=0}$ is the component of the stress tensor perpendicular to the wall. In both Eqs. (4) and (8) the integral $\int d\mathbf{r}_\parallel T_{\perp\perp}(\mathbf{r}_\parallel, 0)$ of $T_{\perp\perp}$ over the surface of the wall appears, which implies a shift of the wall [4,35,39]. In the present situation (i) of a chain with two fixed ends, $\langle\rho_\lambda\rangle$ follows from Eq. (17) on integrating over $\mathbf{r}_\parallel$ and it is the shift identity [4,39]

$$\int d\mathbf{r}_\parallel\ \langle T_{\perp\perp}(\mathbf{r}_\parallel, 0)\cdot\varphi_{A,B}\rangle_{\mathrm{w}} = (\partial_{z_A} + \partial_{z_B})\langle\varphi_{A,B}\rangle_{\mathrm{w}} \tag{20a}$$

that can be used. Thus $\langle\rho_\lambda\rangle$ obeys Eq. (4) where f/k_BT is given by the derivative $(\partial_{z_A} + \partial_{z_B})\ln\mathcal{L}\langle\varphi_{A,B}\rangle_{\mathrm{w}}$ of the logarithm of the polymer partition function. This is in accordance with Ref. [6]. In the case of a chain with only one end $(\mathbf{r}_A)$ fixed $\langle\rho(\mathbf{r})\rangle$ follows from the expression in Eq. (17) on integrating in the numerator and denominator $\mathbf{r}_B$ over the half space and the validity of Eq. (4) (with f/k_BT given [6] by $\partial_{z_A}\ln\int_+ d\mathbf{r}_B\mathcal{L}\langle\varphi_{A,B}\rangle_{\mathrm{w}}$) follows from the same line of arguments [40]. Here one uses that the integration over the half space $\int_+ d\mathbf{r}_B$ of the quantity in Eq. (20a) leads to $\partial_{z_A}\int_+ d\mathbf{r}_B\langle\varphi_{A,B}\rangle$. The ∂_{z_B} term in Eq. (20a) does not contribute to the integral because of the Dirichlet boundary condition at $z_B = 0$.

Consider next the situation (iii) of a dilute polymer solution in the half space [4]. Then $\langle\rho(\mathbf{r})\rangle/n_b$ follows from the rhs of Eq. (17) on replacing the denominator by the bulk quantity $\zeta_{\mathrm{bulk}} = \mathcal{L}\int d\mathbf{r}_B\langle\varphi_{A,B}\rangle_{\mathrm{bulk}}$ and on replacing in the numerator $\langle\cdot\rangle_{\mathrm{w}}$ by the double integral $\int_+ d\mathbf{r}_A\int_+ d\mathbf{r}_B\langle\cdot\rangle_{\mathrm{w}}$. In the bulk limit $z\to\infty$ the double integral tends to $\int d\mathbf{r}_A\int d\mathbf{r}_B\langle\cdot\rangle_{\mathrm{bulk}}$ and one verifies [5] the bulk value $\mathcal{R}_x^{1/\nu}$ of $\langle\rho\rangle/n_b$ on using translational invariance and the counterpart of Eq. (18) in the bulk. The validity of the relation (7) follows on using translational invariance parallel to the wall in order to write the double integral as $\int_0^\infty dz_A\int_+ d\mathbf{r}_B\int d\mathbf{r}_\parallel\langle\cdot\rangle_{\mathrm{w}}$ and on applying [40] Eqs. (19) and (20a). Here one takes into account that the integration $\int_0^\infty dz_A\int_+ d\mathbf{r}_B$ and the Laplace transformation $\mathscr{L}$ of the quantity in Eq. (20a) yields ζ_{bulk}.

The density-force relations in situations (ii) and (iv) can be shown in essentially the same way. The reason is that Eqs. (18) and (19) apply not only for the average $\langle\cdot\rangle_{\mathrm{w}}$ in Eq. (17) but also for corresponding averages $\langle\cdot\rangle_{\mathrm{ww}}$ or $\langle\cdot\rangle_{\mathrm{pw}}$ for a GL field in the space between two walls (ww) or between a mesoscopic particle and a wall (pw). Here $\int_+$ in Eq. (18) has to be replaced by the corresponding space integral [33]. For example, consider situation (ii). In this case $\langle\rho(\mathbf{r})\rangle$ follows from the rhs of Eq. (17) on replacing the two averages $\langle\rangle_{\mathrm{w}}$ by averages $\langle\rangle_{\mathrm{ww}}$ and on integrating in the numerator and denominator z_A and z_B perpendicular to and $\mathbf{r}_{A\parallel}$ parallel to the walls. Now it is the shift identity [41]

$$\int d\mathbf{r}_\parallel\ \langle T_{\perp\perp}(\mathbf{r}_\parallel, 0)\cdot\varphi_{A,B}\rangle_{\mathrm{ww}} = (\partial_{z_A} + \partial_{z_B} + \partial_D)\langle\varphi_{A,B}\rangle_{\mathrm{ww}} \tag{20b}$$

that can be used. Note that the insertion of the integrated stress tensor increases not only the distances z_A, z_B between the wall at $z=0$ and the points $\mathbf{r}_A, \mathbf{r}_B$, but also the distance D between the two walls. Integration $\int_0^D dz_A\int_0^D dz_B$ of the quantity in Eq. (20b) leads to $(d/dD)\int_0^D dz_A\int_0^D dz_B\langle\varphi_{A,B}\rangle_{\mathrm{ww}}$, where the Dirichlet condition at $z=0$ has been taken into account. Combining this with Eq. (19) [40] and with the form of $\langle\rho(\mathbf{r})\rangle$ described above, one obtains Eq. (4) for situation (ii), where f/k_BT is given [6] by $(d/dD)\ln\mathcal{L}\int_0^D dz_A\int_0^D dz_B\int d\mathbf{r}_{A\parallel}\langle\varphi_{A,B}\rangle_{\mathrm{ww}}$. Equation (8) can be derived along similar lines [42].

The universal amplitude B is also expected to appear in situations with overlapping chains. For example, consider situation (iii'), where the half space bounded by the repulsive wall contains a *semidilute* polymer solution [1,2,43]. In the ''equilibrium ensemble description'' of des Cloizeaux [29],

$\langle \rho(\mathbf{r}) \rangle$ is given [44] by $\langle \Psi(\mathbf{r}) \rangle_{\mathrm{w}}^{(-)}$ where $\langle \rangle_{\mathrm{w}}^{(-)}$ is a half space average with the GL temperature adjusted *below* T_c so that the GL bulk free energy density, apart from the sign, equals the bulk pressure of the polymer solution. Here we are interested in the behavior of $\langle \rho(\mathbf{r}) \rangle^{(\mathrm{as})}$ for $a \ll z \ll \xi$, with ξ the screening length [1], which corresponds to the correlation length for $\mathbf{\Phi}^2$ fluctuations in the GL model. Since the short-distance expansion (19) again applies, and since $\langle T_{\perp\perp}(\mathbf{r}_\parallel,0) \rangle_{\mathrm{w}}^{(-)}$ equals the GL bulk free energy density apart from its sign [45], one finds that $\langle \rho(\mathbf{r}) \rangle_{(\mathrm{iii}')}^{(\mathrm{as})} / z^{1/\nu}$ equals B times the bulk pressure per $k_B T$ of the semidilute solution. This relation is the same as in the dilute case (iii).

On dropping the restriction $a \ll z$ and allowing for microscopically small z, one expects a relation of the type (19), with $Bz^{1/\nu}$ replaced by a z-dependent quantity of less universal character. While this quantity still has the ''local'' property of being independent of the lengths $\mathcal{D}$ [37] and of the particular situation (i)–(iv), it does depend upon details of the wall-monomer and monomer-monomer interaction. Even for the Dirichlet boundary conditions of the ''repulsive wall fixed point'' [4,31] this quantity depends upon the actual strength of the excluded-volume interaction [4,34,36]. It is instructive to verify the local property in the case of a repulsive wall w′ characterized by an extrapolation length c^{-1} for $\mathbf{\Phi}$ which is not zero but of the order of a microscopic length. In situation (i) with two ends fixed the corresponding correlation function has a c^{-1}-correction of the form

$$\langle \Psi(\mathbf{r}) \cdot \varphi_{A,B} \rangle_{\mathrm{w}'} = [1 + c^{-1}(\partial_z + \partial_{z_A} + \partial_{z_B})] \langle \Psi(\mathbf{r}) \cdot \varphi_{A,B} \rangle_{\mathrm{w}} \; , \tag{21}$$

compare with the $1/c$ expansion in Ref. [39]. On the rhs of Eq. (21) an average for a Dirichlet wall w appears, for which one can apply the short-distance expansion mentioned above. The two contributions from ∂_{z_A} and ∂_{z_B} on the rhs of Eq. (21) can be neglected since they lead to corrections that are smaller than the leading contribution by $(cz_A)^{-1}$ and $(cz_B)^{-1}$. However, cz can now be of order 1. The nonuniversal but local quantity replacing $Bz^{1/\nu}$, in this case is $(L^R)^{-1} \mathcal{R}_x^{1/\nu} [1 + c^{-1} \partial_z] E^{(\infty)}_{\varphi_\perp^2;\varphi^2}$ in the notation [38] of Ref. [4], where $E^{(\infty)}_{\varphi_\perp^2;\varphi^2}$ depends on z and the strength of the excluded volume interaction. In this context it is also useful to discuss the monomer density right at $z=0$ for a representative w″ of the repulsive wall, corresponding to a potential for the monomers which vanishes for $z>0$ and has a large but finite value for $z<0$. Generalizing the simple wall-shift argument of Ref. [46] to GL averages which arise in situation (i), one obtains $t_+ \int d\mathbf{r}_\parallel \, \langle \mathbf{\Phi}^2(\mathbf{r}_\parallel, 0) \cdot \varphi_{A,B} \rangle_{\mathrm{w}''} = (\partial_{z_A} + \partial_{z_B}) \langle \varphi_{A,B} \rangle_{\mathrm{w}''}$, where t_+ characterizes the potential height [47]. Comparison with Eqs. (15)–(20) shows that, in this case, Eq. (4) applies, with $Bz^{1/\nu}$ replaced by the L-independent nonuniversal and local quantity $\mathcal{R}_x^{1/\nu}/(2Lt_+)$. Thus one obtains universal relations for $z \ll \mathcal{D}$, even without requiring $a \ll z$, by considering ratios such as the lhs of Eq. (8) or by taking ratios of the lhs of Eq (4) for different $\mathcal{D}$ values, since the nonuniversal local quantity then drops out. Of course, neither the $z^{1/\nu}$ dependence nor the universal amplitude B can be observed in this case.

VI. CONCLUDING REMARKS

The main results of this note are the density-force relations (4) and (8) and the values (5) and (6) of the universal amplitude B. In addition to the derivation from the field theory (in Sec. V), the relations have been verified explicitly in several cases (in Secs. III and IV). In the case of self-avoiding chains, values of B beyond the ε expansion, i.e., for $d=3$ and 2, would be desirable.

In order to observe the density-force relations in simulations or real experiments, one should distinguish between two aspects of the relations: (a) In a given situation two *different* observables, i.e., the force and the monomer density at a ''small'' distance z from the wall, have the *same* dependences on mesoscopic lengths (denoted by $\mathcal{D}$ in the Introduction), such as the Flory radius $\mathcal{R}_x$, the distance of the two walls in between which a chain is trapped, the distance from the wall of an immersed particle, etc. To observe this, one may even drop the requirement $a \ll z$ (but maintain the single inequality $z \ll \mathcal{D}$), provided one replaces $Bz^{1/\nu}$ in Eq. (4) by a nonuniversal proportionality factor which depends on z but not on $\mathcal{D}$ [48], compare the discussion at the end of Sec. V. This factor drops out on taking ratios for different values of $\mathcal{D}$, and it does not appear in the ratio on the lhs of Eq. (8). (b) If the double inequality $a \ll z \ll \mathcal{D}$ is obeyed, the proportionality factor in Eq. (4) has the form $Bz^{1/\nu}$, with the universal amplitude B. In a first attempt it would be easier to test aspect (a) implementing only the single inequality $z \ll \mathcal{D}$.

The Deriagin-type approximation for the ideal chain mediated depletion interaction between a large spherical particle and the wall as given in Eqs. (14) is presumably exact, as is argued in the Appendix.

The amplitudes B in Eqs. (5) and (6) are expected to appear also in density-force relations for the monomer density close to a *curved* repulsive wall. For example, consider a single polymer chain that is fixed with one end at a point $\mathbf{r}_A$ and exerts a repulsive force f on a spherical particle of radius R and with center at the origin $(R < r_A)$. If the chain is ideal one may use the known form of the order parameter correlation function in a Gaussian-Ginzburg-Landau model for the outer space of a sphere with Dirichlet boundary conditions (see, e.g., Ref. [19]) to explicitly show the relation [49]

$$\int dS \; [\langle \rho(\mathbf{r}) \rangle^{(\mathrm{as})} / (r-R)^{1/\nu}] \cos\vartheta = Bf/k_B T, \tag{22}$$

with $1/\nu = 2$ and with the *same* amplitude $B=2$ as for a planar wall [see Eq. (5)]. Here (as) denotes $a \ll r-R \ll r_A, R, \mathcal{R}_x$. The quantity in square brackets is then independent of $r-R$ but depends on the angle ϑ in between $\mathbf{r}$ and $\mathbf{r}_A$ and is integrated over the surface of the sphere with the projection $\cos\vartheta$ of the inward pointing surface normal onto the direction of the force. $f/k_B T$ is the derivative of the logarithm of the polymer partition function with respect to r_A. Note that Eq. (22) applies for arbitrary ratios of the three mesoscopic lengths $r_A, R, \mathcal{R}_x$ and reduces to Eq. (4) in the planar wall limit $R \to \infty$ with $\mathcal{R}_x$ and $r_A - R$ fixed. For illustration we quote [50,19] the explicit form $f/k_B T = \partial_{r_A} \ln\{1 - (R/r_A) \mathrm{erfc}[(r_A - R)/(\sqrt{2}\mathcal{R}_x)]\}$ for $d=3$ of the second factor on the rhs of (22). The density-force relation (22) also applies for a chain with excluded volume interaction [51] if one uses for B and ν, respectively, the corresponding planar-wall amplitude [see Eq. (6)] and the corresponding Flory exponent.

ACKNOWLEDGMENT

It is a pleasure to thank T.W. Burkhardt for discussions and for a critical reading of the manuscript.

APPENDIX: DERIAGIN APPROXIMATION AND CONFORMAL TRANSFORMATION

The free energy δF of interaction that a dilute polymer solution induces between wall and particle is proportional to the integral $\int d\mathbf{r}_A \int d\mathbf{r}_B$ over all space of the combination $\delta Z_{\rm pw}(\mathbf{r}_A,\mathbf{r}_B)=Z_{\rm pw}-Z_{\rm w}-Z_{\rm p}+Z_{\rm bulk}$ of partition functions of a single chain with two ends fixed that coils around the particle in half space ($Z_{\rm pw}$), in the half space ($Z_{\rm w}$), around the particle in infinite space ($Z_{\rm p}$), and in infinite space ($Z_{\rm bulk}$). In the case of a spherical particle with z_s, $\mathcal{R}_x \ll R$, there are only contributions if $\mathbf{r}_A$ and $\mathbf{r}_B$ are in a region $\mathcal{K}$ in space that is essentially given by $\Lambda_{\rm w}\cap\Lambda_{\rm p}$ where $\Lambda_{\rm w}$ and $\Lambda_{\rm p}$ are layers of width of the order of $\mathcal{R}_x$ that are centered around the wall and the particle surface, respectively, and the size of $\mathcal{K}$ is much smaller than R. For a better understanding of the local parallel-wall approximation, which is the basis of the Deriagin procedure, one may use the GL representation described in Sec. V and apply a conformal transformation [11] $\mathbf{r}\rightarrow\bar{\mathbf{r}}$, which maps wall and particle onto two *concentric* spheres $\bar{\rm w}$ and $\bar{\rm p}$, with center at $\bar{\mathbf{r}}=0$. For $z_s \ll R$ the concentric spheres have nearly equal size with a relative difference $(2z_s/R)^{1/2}$ of the radii. To be definite we choose the absolute difference of the radii equal to the distance z_s of the particle from the planar wall. For ideal chains the corresponding GL Hamiltonian for the concentric system has a position-dependent [52] coefficient $\bar{t}=b^2t$ in front of the $\mathbf{\Phi}^2$ term. Here $t\sim T-T_c$ is the position-independent coefficient in the original Hamiltonian, and $b=b(\mathbf{r})=|\partial\mathbf{r}/\partial\bar{\mathbf{r}}|^{1/d}$ is the local scale factor of the transformation (which diverges at that point of $\bar{\rm w}$ corresponding to $\mathbf{r}=\infty$). However, in the region $\bar{\mathcal{K}}$ of the concentric geometry corresponding to $\mathcal{K}$, the quantities b and $\bar{t}$ are slowly varying on the scale of the width of the enclosed slit, and one may make a local approximation to $\int d\bar{\mathbf{r}}_A\int d\bar{\mathbf{r}}_B[b(\mathbf{r}_A)b(\mathbf{r}_B)]^{(d+2)/2}\delta G_{\overline{\rm p\,w}}(\bar{\mathbf{r}}_A,\bar{\mathbf{r}}_B)$, which is the GL expression corresponding to $\int d\mathbf{r}_A\int d\mathbf{r}_B\delta Z_{\rm pw}$ when written in terms of correlation functions $G_{\overline{\rm p\,w}} =\langle\phi_1(\bar{\mathbf{r}}_A)\phi_1(\bar{\mathbf{r}}_B)\rangle_{\overline{\rm p\,w}}$, etc. in the concentric geometry. On fixing the angle of the vector $\bar{\mathbf{r}}_A$ so that it points to a given surface element $d\bar{S}_A$ of the sphere $\bar{\rm w}$ and integrating over the magnitude of $\bar{\mathbf{r}}_A$ and over $\bar{\mathbf{r}}_B$, one uses expressions for $G_{\overline{\rm p\,w}}$, etc. which are taken from the geometry of two infinite planar parallel walls with distance $\bar{z}_s$, with a space-independent coefficient $\bar{t}$ given by $\bar{t}=b^2(\mathbf{r}_{A\|},0)t$ in the Hamiltonian. Replacing $b(\mathbf{r}_B)$ by $b(\mathbf{r}_{A\|},0)$ leads to the form $\int d\bar{S}_A[b(\mathbf{r}_{A\|},0)]^{d+2}4(\bar{t})^{-3/2}/\{1+\exp[z_s(\bar{t})^{1/2}]\}=\int d\mathbf{r}_{A\|}\,4t^{-3/2}/\{1+\exp[\tilde{D}(r_{A\|})t^{1/2}]\}$ of the double integral. Here we have used $d\bar{S}_A[b(\mathbf{r}_{A\|},0)]^{d-1}=d\mathbf{r}_{A\|}$ and the explicit expression $b(\mathbf{r}_\|,0)=1+r_\|^2/(2z_sR)$, which imply $z_s(\bar{t})^{1/2}=\tilde{D}(r_{A\|})t^{1/2}$. This form of the double integral leads to the Deriagin expression for δF.

---

[1] P.G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University, Ithaca, 1979).

[2] J.F. Joanny, L. Leibler, and P.G. de Gennes, J. Polym. Sci. Polym. Phys. Ed. **17**, 1073 (1979).

[3] If the wall acts on the monomers with a short-range repulsive potential $v(z)$ the force per area follows [2] from the monomer density on multiplying by $-dv/dz$ and on integrating over z. Note that v is a ‘‘nonuniversal’’ quantity that depends on microscopic details characterizing the monomers and the wall. For potentials v that *repel* long polymer chains the ‘‘universal’’ quantities such as the density profile exponent and the density-force amplitude are independent of these details and have definite values $1/\nu$ and B, respectively. However, for potentials that characterize an *attractive* wall or a wall at the *adsorption threshold* [1,4] and for which $-dv/dz$ changes sign on varying z, the argument [1,2] for proportionality between the osmotic pressure and the monomer density close to the wall (just out of the potential range) breaks down and the profile exponent is different from $1/\nu$ [1,4].

[4] E. Eisenriegler, *Polymers Near Surfaces* (World Scientific, Singapore, 1993).

[5] In situations (i) and (ii) there is only one chain, and the integrals $\int d\mathbf{r}\rho$ and $\int dz\rho_\lambda$ are equal to $\mathcal{R}_x^{1/\nu}$. In the many-chain situations (iii) and (iv), monomers of *all* the chains contribute to $d\mathcal{N}$, and for $\mathbf{r}$ far from wall and particle, $\langle\rho\rangle$ tends to its bulk value $n_b\mathcal{R}_x^{1/\nu}$, with n_b the polymer density in the bulk.

[6] In the single-chain situations (i) and (ii), the mean repulsive force f exerted on the wall is, of course, defined as k_BT times the derivative with respect to the position of the wall (in the direction perpendicular to its surface and away from the polymer chain) of the logarithm of the polymer chain partition function.

[7] In this case $1/\nu=2$.

[8] The amount $-\delta f=|\delta f|$ by which the force onto the wall is reduced (below n_bk_BTA) is the same as the force which the polymer solution exerts onto the particle, pushing it towards the wall.

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

[10] P.G. de Gennes, C.R. Acad. Sci. Ser. B **292**, 701 (1981).

[11] (a) T.W. Burkhardt and E. Eisenriegler, Phys. Rev. Lett. **74**, 3189 (1995); (b) E. Eisenriegler and U. Ritschel, Phys. Rev. B **51**, 13 717 (1995).

[12] We note that there is a power-law behavior $\sim z_A^{-1}$ for both sides of Eq. (4) for $z_A\ll\mathcal{R}_x$, even in the presence of excluded-volume interaction, compare Sec. 5.6.3 in Ref. [4].

[13] These apply for $\mathcal{R}_x$, D, z and $D-z$ much larger than a and follow from renormalization-group equations for polymers, which are an extension from the half space [4] to the parallel-wall geometry. Compare, e.g., K. Symanzik, Nucl. Phys. B **190** [FS3], 1 (1981) and Ref. [31] for a critical field theory bounded by two parallel plates. Note that the ratio

$\langle \rho_\lambda(z) \rangle / (f/k_B T)$ has the scaling dimension $(\text{length})^{1/\nu}$. This fundamental property which is consistent with Refs. [5,6] is not restricted to the present situation, compare the discussion in Sec. V.

[14] Together with the scaling laws (9), (10) this assumption implies the $z^{1/\nu}$ dependence of $\langle \rho_\lambda \rangle^{(\mathrm{as})}$ and an amplitude ratio of the form of the rhs of Eq (11). From Eqs. (4)–(8) one sees that from the density-force ratio (11) one may predict the corresponding ratios in the other situations (i)–(iv), since all these ratios are the *same* (compare the introductory remarks and Ref. [37]). For the behavior at $z \sim a$ see the last paragraph of Sec.V and Ref. [47].

[15] M. Daoud and P.G. de Gennes, J. Phys. (Paris) **38**, 85 (1977).

[16] On increasing N for fixed D in the blob picture of Ref. [15], the number of blobs increases $\sim N$, and each blob contributes the same N independent amount to the force. Within the polymer-magnet analogy the exponential factor in the partition function can be traced back to a suppression $\Delta T_c \sim -D^{-1/\nu}$ of the critical temperature of the magnet confined between parallel plates with separation D.

[17] The exponential prefactors mentioned above are given by $\exp\{-(\mathcal{R}_x/D)^2 \pi^2 \cdot [1/2, 1/8]\}$ in the two cases, and the factors multiplying $\mathcal{R}_x^2$ are essentially the ground-state energies [1].

[18] In the last expression (5.B.25) in Ref. [4] the term $-3/2$ inside the square brackets should be replaced by $-1/2$. Thus in the result (5.157c) for $\mathcal{B}_\infty \equiv B$ the term $-2/3$ inside square brackets should be replaced by 1/3 and the factor 0.325 multiplying $-\varepsilon$ inside curly brackets by 0.075. In addition, the three factors L^R occurring in the main lines of Eqs. (5.B.24) and (5.B.25) should be replaced by $(L^R)^{-1}$. We also note that the explicit low-order calculation of the quantities κ and λ in Eqs. (5.B.22)–(5.B.23b), while correct, is not necessary, since the ratio of the Laplace transforms of κ and λ on the rhs of Eq. (5.B.17) equals $(L^R)^{-1}$ to all orders in ε and in the interaction strength u^R, because λ is the derivative of κ with respect to the temperature variable t^R in the field theory.

[19] E. Eisenriegler, A. Hanke, and S. Dietrich, Phys. Rev. E **54**, 1134 (1996).

[20] Here $\mathcal{A} = -\widetilde{\mathcal{A}}_K \, d^{(1/(2\nu))-1}$, with $\widetilde{\mathcal{A}}_K$ introduced in [19], can be related to a half space amplitude [11]. For ideal chains in $d=3$, $\mathcal{A} = 2\pi$.

[21] In addition to the short-distance expansion and the shift identity discussed below, one needs a ‘‘small radius expansion’’ explained in Refs. [11] and [19]. The ‘‘small radius expansion’’ involves the universal amplitude of [20] and applies also to other problems where a polymer interacts with a small repulsive sphere. Compare P. G. de Gennes, C. R. Acad. Sci. Ser. B **288**, 359 (1979) and T. Odijk, Macromolecules **29**, 1842 (1996).

[22] To be precise we consider a plate of microscopic thickness. However, most of our conclusions are independent of the thickness.

[23] The equality follows since for **r** between the wall and plate one may replace the average $\langle \cdot \rangle_{\mathrm{pw}}$ in the numerator of the GL expression [42] for $\langle \rho \rangle_{(\mathrm{iv})}$ by $\langle \cdot \rangle_{\mathrm{ww}}$ and $\int_0^D dz \Psi(\mathbf{r})$ by $\mathcal{R}_x^{1/\nu}/\hat{A}$, compare the counterpart of the normalization (18) discussed in front of Eq. (20b) and Ref. [33].

[24] The counterpart of $\delta Z_L^{(K,W)}$ in Eq. (4.16) of Ref. [19] is given by the product of $\hat{A} D (U-1)$ and the partition function of a chain with one end fixed in the bulk.

[25] S. Asakura and F. Oosawa, J. Chem. Phys. **22**, 1255 (1954). The quantities P and f in Eqs. (3.1), (3.2) and Fig. 3 of this reference correspond to our quantities δf and U.

[26] B.V. Deriagin, Kolloid Z. **69**, 155 (1934).

[27] Compare the Appendix.

[28] $\widetilde{\mathcal{R}}$ may be adjusted to $\mathcal{R}_x$ by comparing the free energy change on immersing the large spherical particle in the unbounded solution [19], which leads to $\widetilde{\mathcal{R}} = \sqrt{2/\pi}\,\mathcal{R}_x$. Thus the interaction free energy per $k_B T$ at vanishing distance $z_s = 0$ in the phs model is $-8 n_b R \mathcal{R}_x^2$ which is only slightly less negative than the Deriagin expression $-4\pi (\ln 2) n_b R \mathcal{R}_x^2$. The phs and Deriagin expressions for the force, up to and including terms of order z_s^4 are identical and given by $\delta f / k_B T = -n_b R (4\sqrt{2\pi}\,\mathcal{R}_x - 2\pi z_s)$.

[29] J. des Cloizeaux and G. Jannink, *Polymers in Solution: Their Modelling and Structure* (Clarendon, Oxford, 1990).

[30] K. Binder, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J.L. Lebowitz (Academic, London, 1983), Vol. 8, pp. 1–144.

[31] (a) H.W. Diehl, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J.L. Lebowitz (Academic, London, 1986), Vol. 10, pp. 75–267; (b) H.W. Diehl, in *Proceedings of the Third International Conference ‘‘Renormalization Group–96,’’* Dubna, Russia, August 25-September 1, 1996 (World Scientific, Singapore, 1997, in press).

[32] ϕ_1 is the first of the n components of the order parameter density (or GL field) $\mathbf{\Phi}$. The formal limit $n \to 0$ [1,4,29] is taken after the calculation of the GL averages.

[33] The property (18) follows on generating $\int d\mathbf{r}\, \mathbf{\Phi}^2(\mathbf{r})/2$ in the cumulant average by differentiation with respect to $T - T_c$, which inside $\mathcal{L}$ may be converted to a factor L by partial integration.

[34] S. Dietrich and H.W. Diehl, Z. Phys. B **43**, 315 (1981).

[35] J.L. Cardy, Phys. Rev. Lett. **65**, 1443 (1990).

[36] E. Eisenriegler, M. Krech, and S. Dietrich, Phys. Rev. B **53**, 14377 (1996).

[37] Note that only the surface operator $T_{\perp\perp}$ in Eq. (19) leads to a behavior of $\langle \rho \rangle^{(\mathrm{as})}$ that depends on the particular situation (i)–(iv). The prefactor $B z^{1/\nu}$ always remains the same (as long as the wall at $z=0$ is repulsive) and is independent of the variables $\mathcal{D}$ introduced in Sec. I. This is a well known feature of short-distance expansions.

[38] In terms of the short-distance function $E^{(\infty)}_{\varphi_\perp^2;\varphi^2}$ and the renormalized Laplace variable L^R introduced in Ref. [4], the amplitude B is given [18] by the product of $E^{(\infty)}_{\varphi_\perp^2;\varphi^2} z^{-1/\nu}$ and $(L^R)^{-1} \mathcal{R}_x^{1/\nu}$, where the ϕ^4 coupling constant is to be taken at its fixed-point value.

[39] H.W. Diehl, S. Dietrich, and E. Eisenriegler, Phys. Rev. B **27**, 2937 (1983).

[40] Inside correlation functions with $\varphi_{A,B}$ Eq. (19) also holds when $\mathbf{r}_A$ and/or $\mathbf{r}_B$ are integrated around $(\mathbf{r}_\parallel, 0)$.

[41] The interested reader may wish to verify Eq. (20b) for the case of a Gaussian GL model [31], which describes an ideal chain and where, for $z_A < z_B$, $\int d\mathbf{r}_{A\parallel} \langle \varphi_{A,B} \rangle_{\mathrm{ww}} \exp[i\mathbf{p}(\mathbf{r}_{A\parallel} - \mathbf{r}_{B\parallel})] = \sinh(z_A \kappa)\, \gamma(z_B) / [\kappa \gamma(0)]$, with $\gamma(z_B) = \exp[(z_B - D)\kappa] + [(\kappa + \hat{c})/(\kappa - \hat{c})] \exp[-(z_B - D)\kappa]$ if the wall at $z = D$ is characterized by an extrapolation length $1/\hat{c}$. Here $\kappa = (p^2 + t)^{1/2}$, with $t/2 \sim T - T_c$ the prefactor of the $\mathbf{\Phi}^2$ term in the Hamiltonian [31].

[42] We note the relation to GL theory in case (iv): $\langle \rho(\mathbf{r}) \rangle / n_b$ follows from the rhs of Eq. (17) on replacing the denominator by

ζ_{bulk} and on replacing in the numerator $\langle\cdot\rangle_{\text{w}}$ by $\int_{+}d\mathbf{r}_A\int_{+}d\mathbf{r}_B\langle\cdot\rangle_{\text{pw}}$. Note that $\langle\rangle_{\text{pw}}$ and $\langle\cdot\rangle_{\text{pw}}$ vanish if either $\mathbf{r}$, $\mathbf{r}_A$, or $\mathbf{r}_B$ are inside the particle. Finally $\delta f/(n_b k_B T)$ is given by $(\zeta_{\text{bulk}})^{-1}(d/dz_p)\mathcal{L}\int_{+}d\mathbf{r}_A\int_{+}d\mathbf{r}_B\{\langle\varphi_{A,B}\rangle_{\text{pw}}-\langle\varphi_{A,B}\rangle_{\text{w}}\}$, where z_p is the distance of the particle from the wall, compare, e.g., Sec. 4 D in Ref. [19].

[43] E. Eisenriegler, J. Chem. Phys. **79**, 1052 (1983).

[44] The z dependence of $\langle\rho\rangle$ is proportional to that of $\langle\mathbf{\Phi}^2\rangle_{\text{w}}^{(-)}$, and the prefactor can be obtained from the bulk limit $z\rightarrow\infty$. In the bulk $\langle\rho\rangle$ is a grand canonical average of $\Sigma_Q\mathcal{R}_{x,Q}^{1/\nu}/\Omega=(\mathcal{R}_x^{1/\nu}/L)\Sigma_Q L_Q/\Omega$ and equals $\langle\Psi\rangle_{\text{bulk}}^{(-)}$. Here Q labels the polymer chains in a macroscopic volume Ω. Compare, e.g., Eq (A.12) in Ref. [43].

[45] This relation is quite general (see, e.g., Ref. [35] and references contained therein) and has been verified for the case we are considering in Appendix B 3 of Ref. [43].

[46] T.W. Burkhardt and H.W. Diehl, Phys. Rev. B **50**, 3894 (1994).

[47] Corresponding relations for $\mathbf{\Phi}^2$ right at the wall w″ exist in all the situations (i)–(iv). For example, the relation for the averages of situation (ii) follows on replacing $\partial_{z_A}+\partial_{z_B}$ on the rhs by $\partial_{z_A}+\partial_{z_B}+\partial_D$, which leads to the analog of the rhs of Eq. (20b) and confirms, within the polymer-magnet analogy, that the monomer density at the wall and the force of a trapped chain have the same dependence on $\mathcal{R}_x$ and D.

[48] For a given model, e.g., self-avoiding walks on the cubic lattice which may not cross the plane $z=0$, the nonuniversal factor replacing $Bz^{1/\nu}$ is also independent of the particular situation, e.g., the ratios $\langle\rho_\lambda(z)\rangle/(f/k_BT)$ for (i) and (ii) and $\langle\rho(\mathbf{r})\rangle_{\text{(iii)}}/n_b$ are equal functions of z for $z\ll\mathcal{D}$.

[49] The corresponding cumulant average $\langle\Psi(\mathbf{r})\cdot\phi(\mathbf{r}_A)\int d\mathbf{r}_B\phi(\mathbf{r}_B)\rangle$ in the one-component Gaussian-Ginzburg-Landau model equals $2\,G(r,r_A;\cos\vartheta)\,\chi(r)$, where G and χ denote, respectively, the order parameter correlation function and its integral over one of the two position vectors (i.e., the local susceptibility). Equation (22) may thus be shown, for arbitrary space dimension d, by expanding both factors to first order in $r-R$ and by using the property $\int dS\{[\partial_r G(r,r_A;\cos\vartheta)][\partial_r\chi(r)]\}_{r=R}\cos\vartheta=\partial_{r_A}\chi(r_A)$ which readily follows from the expressions for G and χ given in Ref. [19].

[50] R. Lipowsky, Europhys. Lett. **30**, 197 (1995).

[51] For the short-distance expansion of $\mathbf{\Phi}^2$ near a smoothly curved surface with Dirichlet boundary conditions one expects that the leading surface operator is again the stress tensor component $(\mathbf{\Phi}_\perp)^2/2$, with the subscript $\perp$ denoting a spatial derivative perpendicular to the surface, and that the amplitude is the same as for a planar surface [Eq. (19)]. For the particular case of a spherical surface, which can be conformally mapped onto a plane, this is consistent with the conformal invariance of the Ginzburg-Landau model at the critical point. Thus in the cumulant average corresponding to the lhs of Eq. (22) there appears the quantity $\int dS[(\mathbf{\Phi}_\perp)^2/2]\cos\vartheta$ (which by assuming $\mathbf{r}_A$ in the z direction can be written as $\Sigma_l\int dS_l T_{l,z}$ with $d\mathbf{S}=dS\;\mathbf{r}/r$ and T the stress tensor) and generates a shift of the point $\mathbf{r}_A$ away from the center of the sphere.

[52] This complication is, of course, absent for the case of a GL system describing a critical fluid right at the critical point [11], where $t=0$. In this case proving the asymptotic validity of the Deriagin approximation for the free energy of interaction is completely straightforward [11].