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End-to-End Distance of a Polymer Confined between Two Plates

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ABSTRACT: The end-to-end distance of a polymer chain confined between two plates is studied in the presence of the excluded volume interaction using the homotopy parameter expansion method proposed by Oono [*Phys. Rev.*, **A30**, 986 (1984)]. It is found that $\langle R_z^2 \rangle / \langle R_z^2 \rangle_\infty$, the reduced value of the perpendicular component of mean square end-to-end distance of a perturbed chain is almost the same as that of a Gaussian chain, where ∞ denotes the value of the unconfined chain. The parallel components, $\langle R_x^2 \rangle / \langle R_x^2 \rangle_\infty$ is expressed as $\langle R_x^2 \rangle / \langle R_x^2 \rangle_\infty = 1 + c \langle R_z^2 \rangle_\infty^{1/2} / D$, where D is the distance between the plates and c is a quantity slightly depend on $D / \langle R_z^2 \rangle_\infty^{1/2}$. The full cross-over behavior and distribution functions of the end-to-end distance for small values of $D / \langle R_z^2 \rangle_\infty^{1/2}$ are also presented.

KEY WORDS End-to-End Distance / Confined Polymer / Slit /Slab / Excluded Volume / Renormalization Group Theory / Homotopy Parameter Expansion /

The behavior of a polymer chain, confined to a restricted spatial region, is important for such practical problems as the adsorption of polymers, the steric stabilization of colloidal dispersions, and the gel permeation chromatography. In recently, these systems attract much interest theoretically in connection with scaling of finite systems. The end-to-end distance of a polymer with the excluded volume interaction, confined between two plates separated by a distance D, is one of the simple models of the confined polymer, but has been investigated theoretically by a few authors.

Daoud and deGennes[1] studied this problem using scaling theory and the blob concept. They assumed that the polymer is made up blobs of size D, and behaves as a self avoiding chain in 2-dimensional space under the confined state. They predicted that the chain dimension increases propotionally $D^{-1/4}$ with decreasing D.

Wang, Nemirovsky and Freed[2] investigated this problem using the ε expansion method. They introduce the Fourier–Laplace transformation of the end-to-end vector distribution function. They obtained the explicit form of the component of the mean squre end-to-end distance parallel to the plates, $\langle R_x^2 \rangle$ by the Laplace inversion assuming that the root of mean square end-to-end distance of an unconfined chain, $\langle R^2 \rangle_\infty^{1/2}$ is much smaller than D.

The full cross-over dependence of the end-to-end distance of a confined chain on D has not been predicted yet.

Oono[3] proposed a new expansion method, the homotopy parameter expansion method for renormalization group theory, and a model Hamiltonian for the polymer chain with the excluded volume interaction. His proposal allows us to perform the perturbative expansion calculation in 3 dimensional space. The homotopy parameter expansion method gives a more convenient way to study the chain conformation under the boundary conditions made by the confinement in 3 diemsional space than the ε expansion method does.

In this paper, we study the end-to-end distance of a polymer with the excluded volume interaction, confined between two plates, using the homotopy parameter expansion method.

MODEL

A model chain consists of N_0 free rotating bonds of the unit length. The distance between the plates, D ia much larger than the unit length. The z axis is taken perpendicular to the plates, and the x, y axes are taken parallel to the plates.

The distribution function of Gaussian chain with N_0 bonds, which starts at z' and ends at z is expressed as

$$G_{z0}(z, z', N_0)=\frac{2}{D}\sum_k \sin\left(k\pi\frac{z}{D}\right)\sin\left(k\pi\frac{z'}{D}\right) \times \exp(-k^2\pi^2 N_0/6D^2) \quad (1)$$

The z component of the end-to-end vector $\boldsymbol{R}$ is $R_z = z - z'$. The utilizable range of z is $[R_z, D]$ for $z \geq z'$, and $[0, D+R_z]$ for $z < z'$. Equation 1 is averaged with respect to z, then we have

$$G_0(\boldsymbol{R}, N_0)=\left(\frac{3}{2\pi N_0}\right) \times \exp\left(-\frac{3(R_x^2+R_y^2)}{2N_0}\right)E\left(\frac{N_0}{6D^2}, \frac{R_z}{D}\right)\frac{1}{D} \quad (2)$$

where R_x and R_y are components of $\boldsymbol{R}$ parallel to the plates. $E(x, y)$ is given as

$$E(x, y)=[\textstyle\sum_k\{(1-|y|)\cos(k\pi y) + \sin(k\pi|y|)/k\pi\}\exp(-k^2\pi^2 x)]/ [\textstyle\sum_k'(8/k^2\pi^2)\exp(-k^2\pi^2 x)] \quad (3)$$

where $\sum_k'$ denotes the sum over odd k.

The Hamiltonian proposed by Oono[3] is expressed as

$$H=\frac{1}{2}\int_0^{N_0} \mathrm{d}S\left(\frac{\mathrm{d}}{\mathrm{d}S}C(S)\right)^2+\frac{v_0}{2}\int_0^{N_0}\mathrm{d}S \times \int_0^{N_0} \mathrm{d}S'\delta(C(S)-C(S'))l(S, S')^{\theta-1/2}$$
$$|S-S'|>a \quad (4)$$

where $C(S)$ designates the conformation of the chain, v_0 is the excluded-volume parameter, $l(S, S')$ is the shortest contour length between $C(S)$ and $C(S')$ along the chain, assuming both ends are connected, and a is the cut-off which is introduced to eliminate the self interaction of segments. The first term of eq 4 corresponds to the Gaussian chain. The second term represents the contribution made by the excluded volume interaction. When $\theta = 1/2$, the second term in eq 4 is independent of l, and the Hamiltonian is the same as that proposed by Edwards.[4] When $\theta < 1/2$, the local two-body interaction is more stressed than those with a long contour distance. In other words, this model is a natural expansion of restricted self avoiding walks. When $\theta = 0$, the model chain asymptotically behaves as a Gaussian chain in the limit of $N_0 \to \infty$.

The calculation proceeds as follows: the Hamiltonian is first expanded around the standard state, $\theta = 0$, then physical properties are evaluated as the function of θ, and finally θ is equated to 1/2. This idea is similar to the ε expansion method, in which a Hamiltonian in the four dimensional space is perturbatively expanded with respect to $4-d$ $(=\varepsilon)$ and ε is set equal to unity in order to evaluate physical properties in the three dimension.

When Hamiltonian is expressed as eq 4, $G_b(\boldsymbol{R}, N_0)$ is expanded with respect to v_0, and the first order term in v_0 is given by

$$G_b(\boldsymbol{R}, N_0)=G_0(\boldsymbol{R}, N_0)-v_0\int \mathrm{d}S(N_0-S) \times G_0(\boldsymbol{R}, N_0-S)G_0(0, S)\{\min(S, N_0-S)\}^{\theta-1/2} \quad (5)$$

where S is the contour length of a loop.

THE MEAN SQUARE END-TO-END DISTANCE

Gaussian Chain

A simple way to calculate the mean square end-to-end distance, $\langle R^2 \rangle$ is to calculate the Fourier transform of $G(\boldsymbol{R})$ directly. For a Gaussian chain, the Fourier transform of eq 2 is expanded with respect to the scattering vector, $\boldsymbol{q}$ as follows.

$$g_0(\boldsymbol{q}, N_0) = \int \mathrm{d}\boldsymbol{R} G_0(\boldsymbol{R}, N_0) \exp(\mathrm{i}\boldsymbol{q}\boldsymbol{R})$$
$$= 1 - (N_0/3)(q_x^2 + q_y^2)/2$$
$$- F(d_0) D^2 q_z^2/2 \qquad (6)$$

where $d_0 = N_0/6D^2$ and $F(x)$ is given as

$$F(x) = [\textstyle\sum_k (-1)^{k-1}/k^2\pi^2 \exp(-k^2\pi^2 x)$$
$$- \textstyle\sum'_k (8/k^4\pi^4) \exp(-k^2\pi^2 x)]/$$
$$[\textstyle\sum'_k (8/k^2\pi^2) \exp(-k^2\pi^2 x)] \qquad (7)$$

From eq 6, components of $\langle R^2 \rangle$ are given as

$$\langle R_x^2 \rangle = \langle R_y^2 \rangle = N_0/3 \qquad (8a)$$

$$\langle R_z^2 \rangle = F(d_0) D^2 \qquad (8b)$$

In the limit of $x \to 0$, $F(x)$ tends to $2x$. For $x \geq 0.16$, the leading term of $F(x)$ is $(1-8/\pi^2)/2$. The asymptotic values of $\langle R_z^2 \rangle$ are then given by

$$\langle R_z^2 \rangle = N_0/3 \qquad \text{for} \quad N_0 \ll D^2 \qquad (8c)$$

$$\langle R_z^2 \rangle = (0.308D)^2 \qquad \text{for} \quad N_0 \geq D^2 \qquad (8d)$$

Equation 8d predicts that $\langle R_z^2 \rangle$ of a confined Gaussian chain is independent of N_0 when D is smaller than $\langle R^2 \rangle_\infty^{1/2}$ of the Gaussian chain in free space.

Bare Perturbation

For the perturbed chain, the Fourier transform of eq 5 leads to

$$\langle R_z^2 \rangle = F(d_0) D^2 \left\{ 1 + u_0 \left(\frac{N_0}{L} \right)^\theta \frac{N_0^{1/2}}{D} (J_z + K_z) \right\} \qquad (9a)$$

$$\langle R_x^2 \rangle = \frac{N_0}{3} \left\{ 1 + u_0 \left(\frac{N_0}{L} \right)^\theta \frac{N_0^{1/2}}{D} (J_x + K_x) \right\} \qquad (9b)$$

where $u_0 = (3/2\pi)^{3/2} v_0 L^\theta$ is a dimensionless interaction parameter, L is a phenomenological coarse graining length, and J_z, J_x, K_z and K_x are given by

$$J_z = \left(\frac{2\pi}{3} \right)^{1/2} \int_0^1 \mathrm{d}t \frac{E(d_0 t/(1+t), 0)}{(1+t)^{3/2+\theta} t^{3/2-\theta}} \times \left\{ 1 - \frac{F(d_0/(1+t))}{F(d_0)} \right\} \qquad (10a)$$

$$J_x = \left(\frac{2\pi}{3} \right)^{1/2} \int_0^1 \mathrm{d}t \frac{E(d_0 t/(1+t), 0)}{(1+t)^{5/2+\theta} t^{1/2-\theta}} \qquad (10b)$$

$$K_z = \left(\frac{2\pi}{3} \right)^{1/2} \int_1^\infty \mathrm{d}t \frac{E(d_0 t/(1+t), 0)}{(1+t)^{3/2+\theta} t} \times \left\{ 1 - \frac{F(d_0/(1+t))}{F(d_0)} \right\} \qquad (11a)$$

$$K_x = \left(\frac{2\pi}{3} \right)^{1/2} \int_1^\infty \mathrm{d}t \frac{E(d_0 t/(1+t), 0)}{(1+t)^{5/2+\theta}} \qquad (11b)$$

J_z and J_x represent contributions come from short loops and K_z and K_x those from long loops.

Since it is difficult to perform integrations in these equations, function $E(x, 0)$ and $F(x)$ are approximated by the following simple equations:

$$E(x, 0) = \begin{cases} (\pi x)^{-1/2}/2 + 0.15 + 2.5x & \text{for} \quad x < 0.16 \quad (12a) \\ \pi^2/8 & \text{for} \quad x \geq 0.16 \quad (12b) \end{cases}$$

$$F(x) = (1 - 8/\pi^2)/2 \qquad \text{for} \quad x \geq 0.16 \qquad (13)$$

For $x < 0.16$, the value of $F(x)$ at $x = d_0/(1+t)$ is evaluated by

$$F(d_0/(1+t)) = F\left(d_0 - d_0 \frac{t}{1+t} \right)$$
$$= F(d_0) - \left(\frac{\partial F}{\partial x} \right) d_0 \frac{t}{1+t} \qquad (14)$$

In Figure 1, $E(x, 0)$, $F(x)$ and their appoximate

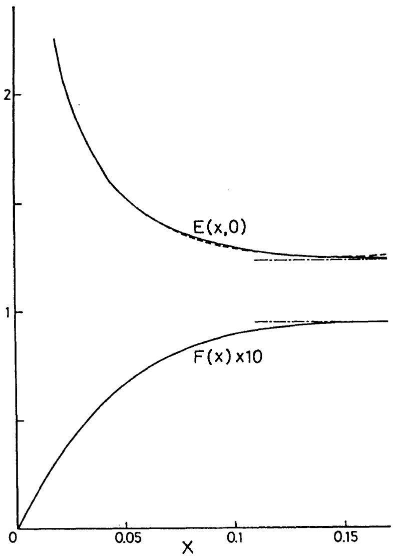

Figure 1. Dependencies of $E(x, 0)$ and $F(x)$ on x. The solid curves, exact values (the value of $F(x)$ multiplied by 10 is drawn); the dotted curve, approximated value by eq 12a; dot–dash lines, values in the limit of $x \to \infty$.

values are plotted against x. Solid curves represent exact values. The dotted curve represents eq 12a. The dot–dash lines represent eq 12b and 13. These approximate values agree very well with the exact values.

The integrations in eq 10a—11b are evaluated as follows.

1) For $d_0 < 0.16$ or $d_0 p/(1+p) < 0.16$ for all p, the integrals are evaluated using eq 12a and 14.

2) For $0.16 \leq d_0 < 0.32$ or $p = 0.16/(d_0 - 0.16) > 1$, J_z and J_x are evaluated using eq 12a and 14. The integrals contained in K_z and in K_x are split into two parts. The former is integrated over 1 to p, using eq 12a and 14, and the latter is integrated over p to infinite, using eq 12b and 13, respectively.

3) For $d_0 \geq 0.32$ or $p = 0.16/(d_0 - 0.16) \leq 1$, K_z and K_x are evaluated using eq 12b and 13. The integrals contained in J_z and in J_x are split into two parts. The former is integrated over 0 to p using eq 12a and 14. The latter is integrated over p to 1 using eq 12b and 13. We then have

$$J_z = \frac{(\partial F/\partial x) d_0}{F(d_0)} \left(\frac{D}{N_0^{1/2}} J_1 + 0.15 J_2 + 2.5 d_0 J_3 \right) \tag{15a}$$

$$J_x = \frac{D}{N_0^{1/2}} J_1 + 0.15 J_2 + 2.5 d_0 J_3 + J_4 \tag{15b}$$

$$K_z = \frac{(\partial F/\partial x) d_0}{F(d_0)} \left(\frac{D}{N_0^{1/2}} K_1 + 0.15 K_2 + 2.5 d_0 K_3 \right) \tag{16a}$$

$$K_x = \frac{D}{N_0^{1/2}} K_1 + 0.15 K_2 + 2.5 d_0 K_3 + K_4 \tag{16b}$$

with

$$J_1 = \int_0^p \mathrm{d}t (1+t)^{-2-\theta} t^{-1+\theta} \tag{17}$$

The explicit forms of J_2 to K_4 are given in Appendix A. Integrating J_1 by parts once and expanding with respect to θ, we get

$$\begin{aligned} \theta J_1 &= [(1+t)^{-2-\theta} t^{\theta}]_0^p \\ &\quad + (2+\theta) \int_0^p \mathrm{d}t (1+t)^{-3-\theta} t^{\theta} \\ &= \left(1 + \theta \ln \frac{p}{1+p} \right) \Big/ (1+p)^2 \\ &\quad + (2+\theta) \int_0^p \mathrm{d}t (1+t)^{-3} \\ &\quad \times \left(1 + \theta \ln \left(\frac{t}{1+t} \right) \right) \\ &= 1 + \theta J_R \end{aligned} \tag{18}$$

$$J_R = \ln \left(\frac{p}{1+p} \right) - \frac{p}{1+p} \tag{19}$$

J_1 is singular at $\theta = 0$. This singularity corresponds to that of the ε expansion method at point $\varepsilon = 0$. The term in [ ] diverges at $t = 0$. But the divergence can be absorbed in the renormalization constant. J_2 to K_4 are regular at $\theta = 0$.

Substituteion J_1 to K_4 into J_z and rearrangement gives

$$\langle R_z^2 \rangle = F(d_0)D^2\left\{1+u_0\left(\frac{N_0}{L}\right)^\theta \frac{d_0}{F(d_0)}\left(\frac{\partial F}{\partial x}\right)\right.$$
$$\times\left[\frac{1}{\theta}+J_R+K_1+\frac{N_0^{1/2}}{D}\right.$$
$$\left.\left.\times(0.15(J_2+K_2)+2.5d_0(J_3+K_3))\right]\right\} \quad (20a)$$

In the same manner, we get

$$\langle R_x^2 \rangle = \frac{N_0}{3}\left\{1+u_0\left(\frac{N_0}{L}\right)^\theta\left[\frac{1}{\theta}+J_R+K_1\right.\right.$$
$$+\frac{N_0^{1/2}}{D}(0.15(J_2+K_2)+2.5d_0(J_3+K_3)$$
$$\left.\left.+J_4+K_4)\right]\right\} \quad (20b)$$

Renormalization

The singularity in the limit of $\theta \to 0$ is absorbed in the renormalization constants. We introduce a phenomenological number of bonds N and renormalized coupling constant u. The renormalization constants are defined and expanded as

$$N = Z_N N_0\,, \qquad Z_N = 1 + Bu \quad (21)$$

$$u = Z_u u_0\,, \qquad Z_u = 1 + o(u) \quad (22)$$

Substituting these renormalization constants to eq 20a, and using the approximation

$$(N/L)^\theta = 1 + \theta \ln (N/L) \quad (23)$$

we get the following first order term in u

$$\langle R_z^2 \rangle = F(d)D^2\left\{1+u\frac{d}{F(d)}\left(\frac{\partial F}{\partial x}\right)\right.$$
$$\times\left[\frac{1}{\theta}-B+\ln\frac{N}{L}+J_R+K_1\right.$$
$$+\frac{N^{1/2}}{D}(0.15(J_2+K_2)$$
$$\left.\left.+2.5d(J_3+K_3))\right]\right\} \quad (24)$$

where $d = N/6D^2$. The divergence is absorbed in Z_N by setting $B = 1/\theta$. After rearranging eq 24, we finally find

$$\langle R_z^2 \rangle = F\left\{d\left[1+u\left(\ln\frac{N}{L}+J_R+K_1\right.\right.\right.$$
$$+\frac{N^{1/2}}{D}(0.15(J_2+K_2)$$
$$\left.\left.\left.+2.5d(J_3+K_3))\right)\right]\right\}D^2 \quad (25a)$$

In the same manner we get

$$\langle R_x^2 \rangle = \frac{N}{3}\left\{1+u\left(\ln\frac{N}{L}+J_R+K_1\right.\right.$$
$$+\frac{N^{1/2}}{D}(0.15(J_2+K_2)$$
$$\left.\left.+2.5d(J_3+K_3)+J_4+K_4)\right)\right\} \quad (25b)$$

Renormalization of Interaction

The fixed point of renormalized coupling constant, u^* can be evaluated by

$$\beta(u) = L(\partial u/\partial L)_{N_0, v_0} = 0 \quad (26)$$

We need the coupling constant up to the order u_0^2 to calculate the stable non-zero fixed point. The terms in the order u_0^2 come from the conformations, each of which contains one very tiny loop. The sizes of these loops are much smaller than D, so the contributions from these tiny loops can be assumed to be independent of the value of D. We use the relation for the unconfined chain,[3]

$$u = u_0 - (4/\theta)u_0^2 \quad (27)$$

Then we get the stable fixed point u^* as

$$u^* = \theta/4 \quad (28)$$

We can replace u by u^* at the scaling limit, *i.e.*, a suitable long chain in good solvents. Equation 28 is substituted into eq 25a. In the limit of $D \to \infty$, $\langle R_z^2 \rangle_\infty$ is given as

$$\langle R_z^2\rangle_\infty=\frac{N}{3}\left(1+\frac{\theta}{4}\left(\ln\frac{N}{L}+J_R^\infty+K_1^\infty\right)\right)$$
$$=\frac{N}{3}\left(\frac{N}{L}\right)^{\theta/4}\left(1+\frac{\theta}{4}\left(J_R^\infty+K_1^\infty\right)\right) \quad (29)$$

where J_R^∞ $(=-\ln 2-1/2)$ and K_1^∞ $(=\pi/4-1/2)$ are values of J_R and K_1 in the limit of $D\to\infty$. Equation 29 has been obtained already by Oono.[3] From eq 25 and 29, we have

$$\langle R_z^2\rangle=F\left\{d_*\left[1+\frac{\theta}{4}(J_R+K_1-J_R^\infty-K_1^\infty+(2d_*)^{1/2}(0.15(J_2+K_2)+2.5d_*(J_3+K_3)))\right]\right\}D^2 \quad (30a)$$

$$\langle R_x^2\rangle=\langle R_x^2\rangle_\infty\left\{1+\frac{\theta}{4}(J_R+K_1-J_R^\infty-K_1^\infty+(2d_*)^{1/2}(0.15(J_2+K_2)+2.5d_*(J_3+K_3)+J_4+K_4))\right\} \quad (30b)$$

where $d_*=\langle R_z^2\rangle_\infty/2D^2$.

Explicit Form of the Mean End-to-End Distance

Introducting numerical values into eq 30a and 30b, we get explicit forms of the mean square end-to-end distance as follows (here d_0 in J_2 to K_4 are repalced by renormalized value, d_*).

1. for $d_*<0.16$ (or $D/\langle R_z^2\rangle_\infty^{1/2}>1.768$),

$$\langle R_z^2\rangle=F\left(d_*\left(1+\frac{\theta}{4}C_1\right)\right)D^2 \quad (31a)$$

$$\langle R_x^2\rangle=\langle R_x^2\rangle_\infty\left(1+\frac{\theta}{4}C_1\right) \quad (31b)$$

where

$$C_1=0.752d_*^{1/2}+2.924d_*^{3/2} \quad (31c)$$

2. for $0.16\le d_*<0.32$ (or $1.768\ge D/\langle R_z^2\rangle_\infty^{1/2}>1.250$),

$$\langle R_z^2\rangle=F\left(d_*\left(1+\frac{\theta}{4}C_2\right)\right)D^2 \quad (32a)$$

$$\langle R_x^2\rangle=\langle R_x^2\rangle_\infty\left(1+\frac{\theta}{4}(C_2+2.916d_*^{1/2}e_*^{3/2})\right) \quad (32b)$$

where

$$C_2=-1.571+(e_*(1-e_*))^{1/2}+\operatorname{atan}\left(\left(\frac{0.16}{0.16-d_*}\right)^{1/2}\right)+0.15d_*^{1/2}(5.013-2.363e_*^{3/2})+2.5d_*^{3/2}(1.170+1.418e_*^{5/2}-2.363e_*^{3/2}) \quad (32c)$$

$$e_*=1-0.16/d_* \quad (32d)$$

3. for $d_*\ge 0.32$ (or $D/\langle R_z^2\rangle_\infty^{1/2}\le 1.250$),

$$\langle R_z^2\rangle=F\left(d_*\left(1+\frac{\theta}{4}C_3\right)\right)D^2 \quad (33a)$$

$$\langle R_x^2\rangle=\langle R_x^2\rangle_\infty\left(1+\frac{\theta}{4}(C_3+6.185d_*^{1/2}-3.499+0.187d_*^{-1/2})\right) \quad (33b)$$

where

$$C_3=-0.101-0.174/d_*-\ln(d_*) \quad (33c)$$

DISTRIBUTION FUNCTIONS OF THE END-TO-END DISTANCE

Substituting eq 2 into eq 5 and rearranging, we get

$$G_b(\boldsymbol{R}, N_0)=G_0(\boldsymbol{R}, N_0)\times\left\{1-u_0\left(\frac{N_0}{L}\right)^\theta\frac{N_0^{1/2}}{D}(J+K)\right\} \quad (34)$$

where

$$J=\left(\frac{2\pi}{3}\right)^{1/2}\int_0^1 dt\,\frac{\exp(-r_0^2t)E(d_0t/(1+t),0)}{(1+t)^{1/2+\theta}t^{3/2-\theta}}\times\frac{E(d_0/(1+t),R_z/D)}{E(d_0,R_z/D)} \quad (35)$$

$$K=\left(\frac{2\pi}{3}\right)^{1/2}\int_1^\infty \mathrm{d}t\,\frac{\exp(-r_0^2t)E(d_0t/(1+t),0)}{(1+t)^{1/2+\theta}t}\times\frac{E(d_0/(1+t),R_z/D)}{E(d_0,R_z/D)} \quad (36)$$

and $r_0^2=3R_r^2/2N_0$, $R_r^2=R_x^2+R_y^2$.

Substituting eq 12 into eq 35 and 36, and expanding around $\theta=0$, we get

$$J=-\frac{D}{N_0^{1/2}}(j_s/\theta+j_s+1+j_1)+0.15j_2+2.5d_0j_3+j_4 \quad (37)$$

$$K=\frac{D}{N_0^{1/2}}k_1+0.15k_2+2.5d_0k_3+k_4 \quad (38)$$

where

$$j_1=(1+j_p+r_0^2j_r+d_0j_d)/E(d_0,R_z/D) \quad (39)$$

The explicit forms of functions contained in eq 37—39 are given in Appendix B.

J is singular at $\theta=0$. We use the renormalization constants for N and u (eq 21 and 22). We need another renormalization constant, Z_G for the renormalized end-to-end distance distribution function, G. We introduce as

$$G=Z_GG_b\,,\qquad Z_G=1+Au \quad (40)$$

We set $A=-1/\theta$ and $B=1/\theta$ to absorb the singularity in the limit of $\theta\to0$. We get

$$G(\boldsymbol{R},N)=G_0(\boldsymbol{R},N)\times\left\{1+\frac{\theta}{4}\left(j_s\ln\frac{N}{L}+j-\frac{N^{1/2}}{D}k\right)\right\} \quad (41)$$

where

$$j=1+j_s+j_1-k_1 \quad (42)$$

$$k=0.15(j_2+k_2)+2.5d_0(j_3+k_3)+j_4+k_4 \quad (43)$$

After rearrangement eq 41 using eq 2 and exponentiation of the order u terms, we get

$$G(\boldsymbol{R},N)=\left(\frac{3}{2\pi N}\right)\exp(-r_*^2)E\left(d_*,\frac{R_z}{D}\right)\frac{1}{D}\times\exp\left\{\frac{\theta}{4}(j-j_s(J_R^\infty+K_1^\infty)-(2d_*)^{1/2}k)\right\} \quad (44)$$

where $r_*^2=R_r^2/\langle R_r^2\rangle=(R_x^2+R_y^2)/(\langle R_x^2\rangle+\langle R_y^2\rangle)$, $d_*=\langle R_z^2\rangle_\infty/2D^2$. r_0 and d_0 in eq 42 and 43 should be replaced by renormalized values, r_* and d_*, respectively.

It is difficult to perform integrations in j and k. But for $D/\langle R_z^2\rangle_\infty^{1/2}<1.25$ (or $d_*>0.32$), the value of $E(d_*,y)$ is independent of d_*. Using eq 12a and putting $E_t=E_0$, we find

$$j_s=r_*^2 \quad (45)$$

$$j_1=1+r_*^2(1-\gamma-\ln(r_*^2)-\mathrm{E_i}(r_*^2))+\left(\frac{1}{p}+r_*^2\ln(p)\right)\exp(-r_*^2p) \quad (46)$$

$$j_2=-2\left(\frac{2\pi}{3}\right)^{1/2}\left\{\frac{\exp(-r_*^2p)}{(1+p)^{1/2}p^{1/2}}+I_3(p)+2r_*^2I_1(p)\right\} \quad (47)$$

$$j_3=2\left(\frac{2\pi}{3}\right)^{1/2}I_3(p) \quad (48)$$

$$j_4=\left(\frac{\pi^5}{24}\right)^{1/2}\left\{\frac{\exp(-r_*^2p)}{(1+p)^{1/2}p^{1/2}}-\frac{\exp(-r_*^2)}{2^{1/2}}+I_3(p)-I_3(1)+2r_*^2(I_1(p)-I_1(1))\right\} \quad (49)$$

$$k_4=\left(\frac{\pi^5}{96}\right)^{1/2}\int_1^\infty \mathrm{d}t\,\frac{\exp(-r_*^2t)}{(1+t)^{1/2}t} \quad (50)$$

$$k_1=k_2=k_3=0$$

where $p=0.16/(d_*-0.16)$, γ is Euler's constant $(=0.5572\cdots)$

$$I_1(x)=\int_0^{x^{1/2}}\mathrm{d}t\exp(-r_*^2t^2)/(1+t^2)^{1/2} \quad (51)$$

$$I_3(x)=\int_0^{x^{1/2}}\mathrm{d}t\exp(-r_*^2t^2)/(1+t^2)^{3/2} \quad (52)$$

and $E_i(x)$ is integrated exponential function defined by

$$E_i(-x)=\int_x^{\infty} dt \exp(-t)/t \qquad (53)$$

These relations show that the last term in eq 44 is independent of R_z. Then the distribution of R_z of the perturbed chain is predicted to be the same as that of a Gaussian chain if $D/\langle R_z^2\rangle_\infty^{1/2}<1.25$.

DISCUSSION

The values of $\langle R_z^2\rangle/\langle R_z^2\rangle_\infty$, $\langle R_x^2\rangle/\langle R_x^2\rangle_\infty$ and $\langle R^2\rangle/\langle R^2\rangle_\infty$ are plotted against $D/\langle R_z^2\rangle_\infty^{1/2}$ in Figure 2. The value of θ is put at 1/2. The effect of confinement on the end-to-end distance is remarkable in a wide range of $D/\langle R_z^2\rangle_\infty^{1/2}$. The value of $\langle R_z^2\rangle/\langle R_z^2\rangle_\infty$ is about 0.9 at $D/\langle R_z^2\rangle_\infty^{1/2}=6$, and decreases rapidly with decreasing $D/\langle R_z^2\rangle_\infty^{1/2}$. The value of $\langle R_z^2\rangle/\langle R_z^2\rangle_\infty$ is prportional to D^2 in the range of $D/\langle R_z^2\rangle_\infty^{1/2}<2$. The curve of $\langle R_z^2\rangle/\langle R_z^2\rangle_\infty$ *vs.* $D/\langle R_z^2\rangle_\infty^{1/2}$ is graphically indistingishable from that of a Gaussian chain. The dependency of $\langle R_z^2\rangle$ on D for the perturbed chain seems similar to that of an unperturbed chain, if these quantities are scaled by $\langle R_z^2\rangle_\infty$. The contribution from the excluded volume interaction changes the value of $\langle R_z^2\rangle_\infty$.

The values of $\langle R_x^2\rangle/\langle R_x^2\rangle_\infty$ are almost independent of $D/\langle R_z^2\rangle_\infty^{1/2}$ in the range of $D/\langle R_z^2\rangle_\infty^{1/2}>4$, but increase rapidly with decreasing $D/\langle R_z^2\rangle_\infty^{1/2}$ in the range of $D/\langle R_z^2\rangle_\infty^{1/2}<1$. The physical interpretations are as follows. The segment density in a polymer chain is very dilute, so the number of segment-segment contacts does not increase in the slightly compressed chain. In the range of $D/\langle R_z^2\rangle_\infty^{1/2}<2$, the value of $\langle R_z^2\rangle$ mainly depends on D instead of on N. The segments are squeezed for the direction parallel to the plates by compression of the chain in this region.

The values of $\langle R^2\rangle/\langle R^2\rangle_\infty$ decrease with decreasing $D/\langle R_z^2\rangle_\infty^{1/2}$ in large $D/\langle R_z^2\rangle_\infty^{1/2}$ region. This is caused by decreasing $\langle R_z^2\rangle/\langle R_z^2\rangle_\infty$. But the values of $\langle R^2\rangle/\langle R^2\rangle_\infty$ increase with decreasing $D/\langle R_z^2\rangle_\infty^{1/2}$ in the small $D/\langle R_z^2\rangle_\infty^{1/2}$ region, which is mainly due to increasing $\langle R_x^2\rangle/\langle R_x^2\rangle_\infty$.

The coefficient c in the eq 54 is plotted against $D/\langle R_z^2\rangle_\infty^{1/2}$ in Figure 3.

$$\langle R_x^2\rangle/\langle R_x^2\rangle_\infty=1+c\langle R_z^2\rangle_\infty^{1/2}/D \qquad (54)$$

The value of c increases with decreasing $D/\langle R_z^2\rangle_\infty^{1/2}$, from 0.0665 in the ∞ limit, to 0.547

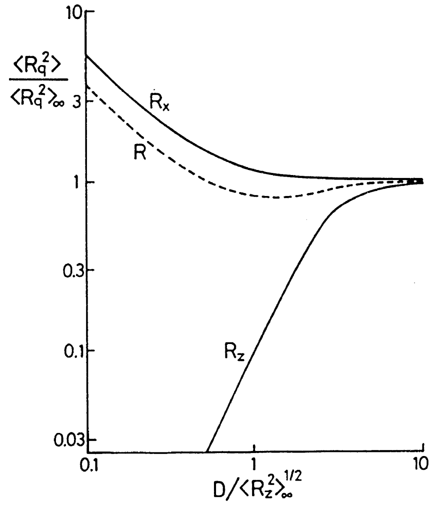

Figure 2. Reduced mean square end-to-end distance as function of $D/\langle R_z^2\rangle_\infty^{1/2}$. The symbols denoted as R_x, component parallel to the plates; R_z, component perpendicular to the plates; R, total end-to-end distance.

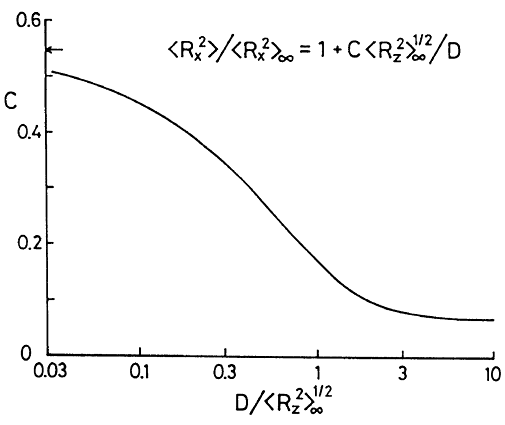

Figure 3. The dependence of the coefficient c in eq 54 on $D/\langle R_z^2\rangle_\infty^{1/2}$. The arrow at left hand side indicates the value in the limit of $D/\langle R_z^2\rangle_\infty^{1/2}\to 0$.

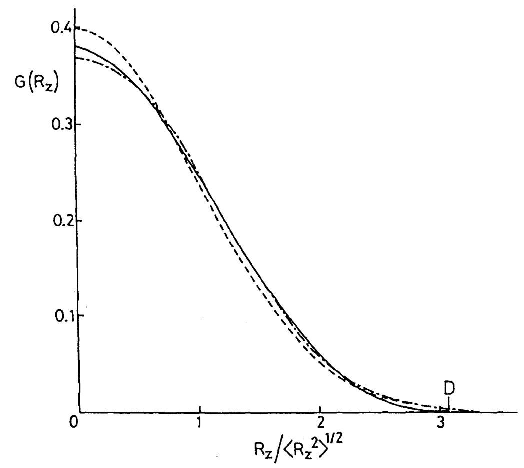

Figure 4. The normalized distribution function of end-to-end distance perpendicular to the plates. The solid curve, the confined chain under $D/\langle R_z^2\rangle_\infty^{1/2}<1.25$; the dotted curve, the unconfined Gaussian chain; the dot- dash curve, the unconfined perturbed chain.

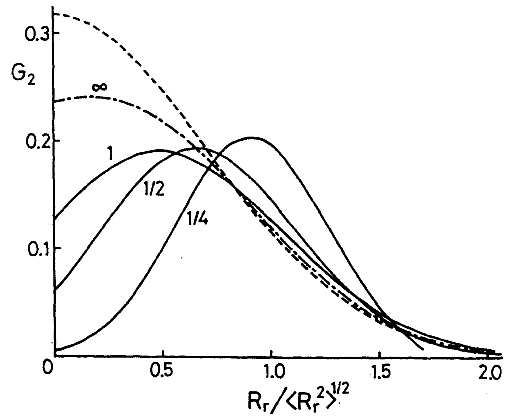

Figure 5. The normalized distribution function of the end-to-end distance parallel to the plates. The solid curves, the confined perturbed chains for indicated values of $D/\langle R_z^2\rangle_\infty^{1/2}$; the dotted curve, the unconfirned Gaussian chain; the do-dash curve, the unconfined perturbed chain.

at 0 limit. The functional form of eq 54 is consistent with the results by Wang *et al.*[2] The numerical coefficient differs from the value given by them, 0.620. Equation 54 predicts the relation, $\langle R_x^2\rangle \sim D^{-1}$ in the $D/\langle R_z^2\rangle_\infty^{1/2}\rightarrow 0$ limit. The exponent on D differs from the prediction with scaling argument by Daoud and deGennes,[1] $-1/2$. The reason for this difference is not clear at present.

The normalized density distribution function for the end-to-end distance perpendicular to the plates is shown in Figure 4. The solid curve represents $D/\langle R_z^2\rangle_\infty^{1/2}<1.25$. The excluded volume interaction is taken in $\langle R_z^2\rangle_\infty^{1/2}$, as predicted by eq 44. Then the distribution function of the perturbed chain and that of a Gaussian chain are indistinguishable, if these functions are rewritten in the terms of $R_z/\langle R_z^2\rangle_\infty^{1/2}$. The arrow indicates the value at which $R_z=D$ in the limit of $D/\langle R_z^2\rangle_\infty^{1/2}\rightarrow 0$. The dot-dash curve represents the normalized distribution function of the unconfined perturbed chain. The maximum of this curve at the origin is flatter than that of a Gaussian chain (dotted curve), because the ends of a chain are prevented from approaching by the excluded volume interaction.

In Figure 5, the normalized distribution functions for end-to-end distance parallel to the plates are shown. The solid curves represent those for small values of $D/\langle R_z^2\rangle_\infty^{1/2}$ (1, 1/2 and 1/4, respectively). These curves are vastly different from that of a Gaussian chain (dotted curve). Each of these curves has a minimum at the origin. The depth of the minimum increases with decreasing $D/\langle R_z^2\rangle_\infty^{1/2}$. These minima come from the exclusion of end-to-end contacts by the excluded volume interaction. The dot–dash curve represents the density distribution of an unconfined perturbed chain. The curve shows a shallow minimum at the origin as shown by confined chains.

APPENDIX A

The explicit forms of J_2 to K_4 are given as

$$J_2=\left(\frac{2\pi}{3}\right)^{1/2}\int_0^p \mathrm{d}t(1+t)^{-5/2}t^{-1/2}$$

$$=\left(\frac{2\pi}{3}\right)^{1/2}\left\{2\left(\frac{p}{1+p}\right)^{1/2}-\frac{2}{3}\left(\frac{p}{1+p}\right)^{3/2}\right\}$$

$$J_3=\left(\frac{2\pi}{3}\right)^{1/2}\int_0^p \mathrm{d}t(1+t)^{-7/2}t^{1/2}$$
$$=\left(\frac{2\pi}{3}\right)^{1/2}\left\{\frac{2}{3}\left(\frac{p}{1+p}\right)^{3/2}-\frac{2}{5}\left(\frac{p}{1+p}\right)^{5/2}\right\}$$
$$J_4=\left(\frac{2\pi}{3}\right)^{1/2}\frac{\pi^2}{8}\int_p^1 \mathrm{d}t(1+t)^{-5/2}t^{-1/2}$$
$$=\left(\frac{\pi^5}{96}\right)^{1/2}\left\{\frac{5\sqrt{2}}{6}-2\left(\frac{p}{1+p}\right)^{1/2}+\frac{2}{3}\left(\frac{p}{1+p}\right)^{3/2}\right\}$$
$$K_1=\int_1^p \mathrm{d}t(1+t)^{-2}t^{-1/2}$$
$$=\frac{p^{1/2}}{p+1}+\operatorname{atan}(p^{1/2})-\frac{1}{2}-\operatorname{atan}1$$
$$K_2=\left(\frac{2\pi}{3}\right)^{1/2}\int_1^p \mathrm{d}t(1+t)^{-5/2}$$
$$=\left(\frac{2\pi}{3}\right)^{1/2}\frac{2}{3}(2^{-3/2}-(p+1)^{-3/2})$$
$$K_3=\left(\frac{2\pi}{3}\right)^{1/2}\int_1^p \mathrm{d}t(1+t)^{-7/2}t$$
$$=\left(\frac{2\pi}{3}\right)^{1/2}\left\{\frac{7\sqrt{2}}{120}+\frac{2}{5}(p+1)^{-5/2}-\frac{2}{3}(p+1)^{-3/2}\right\}$$
$$K_4=\left(\frac{2\pi}{3}\right)^{1/2}\frac{\pi^2}{8}\int_p^\infty \mathrm{d}t(1+t)^{-5/2}$$
$$=\left(\frac{\pi^5}{216}\right)^{1/2}(p+1)^{-3/2}$$

where we put $\theta=0$ because these integrals are regular at $\theta=0$.

APPENDIX B

Functions appearing in eq 37 and 38 are expressed as follows.

$$j_s=r_0^2+d_0E'_0/E_0$$
$$j_p=\exp(-r_0^2p)\left(E_p/p+(r_0^2E_p+d_0E'_p/(1+p)^2)\ln\left(\frac{p}{1+p}\right)\right)$$
$$j_r=\int_0^p \mathrm{d}t\frac{\exp(-r_0^2t)}{1+t}E+\int_0^p \mathrm{d}t\left\{r_0^2E+\frac{d_0E'}{(1+t)^2}\right\}\exp(-r_0^2t)\ln\left(\frac{t}{1+t}\right)$$
$$j_d=\int_0^p \mathrm{d}t\frac{\exp(-r_0^2t)}{(1+t)^3}E'+\int_0^p \mathrm{d}t\left\{\left(\frac{2}{(1+t)^3}+\frac{r_0^2}{(1+t)^2}\right)E'+\frac{d_0}{(1+t)^4}E''\right\}\times\exp(-r_0^2t)\ln\left(\frac{t}{1+t}\right)$$
$$j_2=-2\left(\frac{2\pi}{3}\right)^{1/2}\frac{1}{E_0}\left\{\frac{\exp(-r_0^2p)E_p}{(1+p)^{1/2}p^{1/2}}+\frac{1}{2}\int_0^p \mathrm{d}t\frac{\exp(-r_0^2t)E}{(1+t)^{3/2}t^{1/2}}+r_0^2\int_0^p \mathrm{d}t\frac{\exp(-r_0^2t)E}{(1+t)^{1/2}t^{1/2}}+d_0\int_0^p \mathrm{d}t\frac{\exp(-r_0^2t)E'}{(1+t)^{5/2}t^{1/2}}\right\}$$
$$j_3=\left(\frac{2\pi}{3}\right)^{1/2}\frac{1}{E_0}\int_0^p \mathrm{d}t\frac{\exp(-r_0^2t)E}{(1+t)^{3/2}t^{1/2}}$$
$$j_4=\left(\frac{\pi^5}{96}\right)^{1/2}\left\{\frac{2\exp(-r_0^2p)}{(1+p)^{1/2}p^{1/2}}-2^{1/2}\exp(-r_0^2)-\int_p^1 \mathrm{d}t\frac{\exp(-r_0^2t)}{(1+t)^{3/2}t^{1/2}}-2r_0^2\int_p^1 \mathrm{d}t\frac{\exp(-r_0^2t)}{(1+t)^{1/2}t^{1/2}}\right\}$$
$$k_1=\frac{1}{E_0}\int_0^p \mathrm{d}t\frac{\exp(-r_0^2t)E}{t^{3/2}}$$

$$k_2=\left(\frac{2\pi}{3}\right)^{1/2}\frac{1}{E_0}\int_1^p \mathrm{d}t\,\frac{\exp(-r_0^2 t)E}{(1+t)^{1/2}t}$$

$$k_3=\left(\frac{2\pi}{3}\right)^{1/2}\frac{1}{E_0}\int_1^p \mathrm{d}t\,\frac{\exp(-r_0^2 t)E}{(1+t)^{3/2}}$$

$$k_4=\left(\frac{\pi^5}{96}\right)^{1/2}\int_p^\infty \mathrm{d}t\,\frac{\exp(-r_0^2 t)}{(1+t)^{1/2}t}$$

Here we put $E=E(d_0/(1+t), R_z/D)$. E_p is E at $t=p$. E' and E'' mean $\partial E/\partial x$ and $\partial^2 E/\partial x^2$, respectively.

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