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Monte-Carlo studies of a polymer between planes, crossover between dimensionalities (*)

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Résumé. — Nous décrivons les résultats des calculs de Monte-Carlo sur des chaînes polymériques caractérisées par une interaction de volume exclu confinées dans une plaque de largeur D. Nous avons étudié spécifiquement $R^2(N, D)$, le carré moyen de la longueur d'une chaîne à N liens. Pour N grand et D constant, $R^2(N, D) \sim R_2^2(N)$, la longueur carrée d'une chaîne confinée sur un plan. Nous trouvons $R_2^2(N) \equiv R^2(N, 0) \propto N^{2\nu}$ où $2\nu = 3/2$ en accord avec une prédiction de Flory. Avec $R_3^2(N) \equiv R^2(N, \infty)$, la longueur d'une chaîne non confinée à trois dimensions, nous examinons la loi d'échelle de *crossover* de $R^2(N, D)/R_3^2(N)$ en fonction $f(x)$ de $x \equiv D/R_3(N)$. Quand $x \leqslant 0{,}45$, $f(x) \propto x^{1/2}$ ce qui s'accorde avec les prévisions de Daoud et de Gennes. Nous discutons aussi les propriétés d'une chaîne sans volume exclu dans la même géométrie de confinement.

Abstract. — We describe the results of Monte-Carlo calculations of polymer chains with excluded volume interactions which are confined within a slab of width D. We studied, in particular, $R^2(N, D)$, the mean square of the end-to-end distance of a chain with N links. For large N and fixed D, $R^2(N, D) \sim R_2^2(N)$, the squared end-to-end distance of a chain constrained to a plane. We find $R_2^2(N) \equiv R^2(N, 0) \propto N^{2\nu}$ with $2\nu = 3/2$ in agreement with the prediction of Flory. Letting $R_3^2(N) \equiv R^2(N, \infty)$, the end-to-end distance for an unconstrained three dimensional chain, we examine the crossover scaling of $R^2(N, D)/R_3^2(N)$ as a function $f(x)$ of $x \equiv D/R_3(N)$. For $x \leqslant 0.45$, $f(x) \propto x^{-1/2}$, in agreement with predictions of Daoud and de Gennes. The behaviour of a chain without excluded volume interactions in the same constraining geometry is also discussed.

1. **Introduction.** — The change in the properties of a polymer molecule when confined to a restricted spatial region is an interesting theoretical and practical question, relevant for the behaviour of biological macromolecules in cell membranes and in other fields such as gel permeation chromatography and in oil recuperation. Some aspects of this problem such as thermodynamic properties have been studied analytically for random walk models (with no excluded volume interactions) [1-3]. Monte-Carlo simulation of walks on lattices several layers deep were carried out by Wall *et al.* [4, 5] and conformational properties reported. In this note we describe results on Monte-Carlo simulations for a continuum beads-on-a-string model with excluded volume interactions in which the chains are confined to a slab of width D. We study in particular the variation of the size of the polymer as a function of D and of N the number of links.

Many current theoretical studies exploit the analogy between a very long polymer chain and a thermodynamic system close to its critical temperature [6, 7] — both systems exhibit long range correlations. Consequently the variation of chain properties with D may be considered as an example of a crossover of a critical system between two dimensionalities. As D varies from $D > R_3(N)$, the size of an unconstrained chain in three dimensions, to $D \ll R_3(N)$ the effective dimensionality of the system changes from three to two. The critical behaviour of a magnetic system with a finite width was studied by Fisher *et al.* [8, 9] using scaling arguments. Recently Daoud and de Gennes [10] have applied similar arguments to the polymer chain in a slab : the chain of N monomers is viewed as made up of n blobs or subchains of size D each containing

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(N/n) monomers. Each blob is considered to be three dimensional with $D \sim a(N/n)^{3/5}$ where a is the distance between monomers, while the chain as a whole behaves asymptotically, i.e. when there are many blobs, as if it were two dimensional. This leads to a scaling relation, for the end-to-end distance of the chain in the slab,

$$R(N, D) \sim Dn^{3/4} \sim DN^{3/4} \left(\frac{a}{D}\right)^{5/4} \qquad (1.1)$$

where we have used the Flory expression [11] $R_2(N) \sim aN^{3/4}$, $(R_3(N) \sim aN^{3/5})$ for the asymptotic size of an unconfined two (three) dimensional chain of N monomers. Formula (1.1) is a limiting case of the scaling relation $R^2(N, D) = R_3^2(N)\, f(D/R_3)$, c.f. eq. (3.3). A similar result has been obtained recently by Kosmas and Freed [12] by an alternative scaling approach.

The main results of our computation are : the first numerical confirmation of which we are aware of the Flory formula for $R_2(N)$ for a continuum chain, and good agreement with (1.1) for $D/R_3(N) \lesssim 0.45$ and $D \gtrsim a$. We also discuss, in an appendix, the behaviour of $R^{(0)}(N, D)$ in a chain without excluded volume when there is no change in the critical exponents : $R_d^{(0)}(N) \sim N^{0.5}$ for all dimensionalities.

2. **The Monte-Carlo model.** — The model chain is made up of $N + 1$ beads located at positions $\{ \mathbf{r}_i \}$, $i = 0, ..., N$ separated by links of fixed length and direction. Any two beads in the chain interact *via* a short range repulsive potential which represents the excluded volume interactions between different parts of a polymer chain in a good solvent. This model is similar to the beads-on-a-string model which has been widely used in the theories of polymer statistics [13, 14]. The short range interaction we use is a truncated Lennard-Jones potential of the form :

$$v(r_{ij}) = \begin{cases} 4\varepsilon \left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6} + \frac{1}{4}\right], & r_{ij} < r_m \\ 0, & r_{ij} > r_m \end{cases} \qquad (2.1)$$

where $r_m = 2^{1/6}\sigma$, $r_{ij} = |\mathbf{r}_j - \mathbf{r}_i|$.

The confinement is represented by infinite step potentials at $z = 0$ and $z = D$. The total interaction energy for a chain configuration X is thus given by :

$$U(X) = \begin{cases} \sum_{i>j} v(r_{ij}), & 0 \leqslant z_i \leqslant D, \; i = 0, ..., N \\ \infty, & \text{otherwise.} \end{cases} \qquad (2.2)$$

An ensemble of configurations distributed according to the canonical distribution

$$P(X) \propto e^{-\beta U(X)} \qquad (2.3)$$

was generated by a reptation Monte-Carlo (MC) dynamics, as follows. A configuration $X' = \{ \mathbf{r}'_i \}$ is generated from the configuration X by the following transformation

$$\begin{aligned} \mathbf{r}'_i &= \mathbf{r}_{i+1}, \quad \text{for} \quad i = 0, ..., N-1 \\ \mathbf{r}'_N &= \mathbf{r}_N + \mathbf{s}, \quad |\mathbf{s}| = a, \end{aligned} \qquad (2.4)$$

and the direction of s is chosen at random from a uniform distribution. With equal probability, this transformation is carried backwards, i.e., with $\mathbf{r}'_i = \mathbf{r}_{i-1}$ and $\mathbf{r}'_1$ in a random direction at a distance a from $\mathbf{r}_1$.

A new configuration X_{new} of a Markov sequence is taken as either X or X' according to the Metropolis criterion [15] :

$$X_{new} = \begin{cases} X' & \text{if} \quad \exp \beta[U(X) - U(X')] > \eta \\ X & \text{otherwise} \end{cases} \qquad (2.5)$$

where η is a random number uniform on (0, 1). The procedure described above obeys the detailed balance condition

$$\begin{aligned} &e^{-\beta U(X')} \times (\text{probability to go from } X' \text{ to } X) \\ &= e^{-\beta U(X)} \times (\text{probability to go from } X \text{ to } X'). \end{aligned} \qquad (2.6)$$

This leads asymptotically to the equilibrium distribution given in eq. (2.3) within any region of the phase space accessible from the starting configuration. In our case this is everywhere.

It is important to note that applying the backwards transformation with probability 1/2 is essential for the validity of the detailed balance condition, eq. (2.6).

This method is an extension of the *slithering snake* idea of Mandel and Wall [16, 17] for generating self avoiding walks on lattices.

The relaxation time of the reptation dynamics described above is of the order of $\sim N^2$ Monte-Carlo steps. Equilibrium averages are obtained by dividing the total sequence of MC steps into 15-20 blocks, each block $> N^2$, and obtaining the final average and the standard deviation by averaging over the block averages, excluding the first couple of blocks during which the system is still in the process of equilibration. It is clear that the relaxation time is the dominant factor determining the computer running time for an experiment. Reptation MC dynamics, while not appropriate for the simulations of real dynamics [18], is a relatively fast procedure for the generation of equilibrium configurations of chains as compared with full molecular dynamics or even with the standard Metropolis method with one bead moved at random in a box.

3. **Results.** — We have studied the squared end-to-end distance and the squared radius of gyration of chains of lengths $N = 5$-80 confined between two infinite walls, as well as purely two dimensional chains. The parameters in $v(r_{ij})$, the bead-bead interaction potential, were chosen as $\beta\varepsilon = 0.1$ and

$\sigma/a = 0.65$ (where a is the link length). An important parameter of the beads on a string model is B/a^3; where

$$B = 4\pi \int (1 - e^{-\beta v(r)}) r^2 \, dr . \qquad (3.1)$$

For a very steep repulsive potential of range σ, $B \sim (4\pi/3)\sigma^3$. With our choice of parameters B/a^3 is of the order of unity. This assures that the large N behaviour for chains with excluded volume, expected for $N > N_c$, will occur even for fairly short chains since $N_c \sim (a^3/B)^2$ in three dimensions and $N_c \sim (a^3/B)$ in two dimensions. The effects on the chain properties of varying B/a^3 will be described elsewhere [19].

3.1 UNCONFINED CHAINS. — For the unconfined 3D case and for the unconfined 2D case we find that both the squared end-to-end distance and the radius of gyration follow a power law for $N \gtrsim 10$. For the squared end-to-end distance

$$R^2 = Aa^2 N^{2\nu} \qquad (3.2)$$

where

$$A = 0.95 \pm 0.05 \quad \text{and} \quad \nu = 1.19 \pm 0.02 \text{ in 3D}$$

$$A = 0.75 \pm 0.05 \quad \text{and} \quad \nu = 1.48 \pm 0.03 \text{ in 2D} .$$

The ratio $S^2/R^2 = 7.1 \pm 0.2$ in 2D and 6.4 ± 0.15 in 3D in agreement with results for lattice walks [21], and is weakly N dependent. The results for the exponents are consistent with Flory's predictions $\nu = 3/(2 + d)$ and with recent ε expansion calculations [22]. The two dimensional result is, we believe, the first one reported for a continuum chain. Within the accuracy of the present results there is no difference between the values of ν for continuum chains and these for self avoiding walks on lattices in both three and two dimensions.

3.2 CONFINED CHAINS. — For large N, the end-to-end distance $R(N, D)$ (or the radius of gyration) may be expected *a priori* to have the form

$$R^2(N, D) = R_3^2 \, f(D/R_3, D/a) ; \qquad R_3(N) \equiv R(N, \infty) \sim N^{0.6} . \qquad (3.3)$$

The scaling arguments mentioned earlier [10, 11] suggest however that there should be a regime for D somewhat larger than a, in which the dependence on D/a should be very weak. Furthermore, for $R_3 \gg D$, f should behave as a power $f \sim (D/R_3(N))^s$ which when combined with the Flory relations (3.2) leads to

$$N^{3/2} \sim N^{6/5}(D/N^{3/5})^s , \quad R_3(N) \gg D . \qquad (3.4)$$

That is, $s = -1/2$ which leads to $R^2(N, D) \sim D^{-1/2}$, as given in eq. (1.1).

Figure 1 presents the values for R^2 and S^2 for chains of 20-80 beads (with values D/a between about 1 and 10) plotted against D/R_3. In both cases the results for various values of N (and D/a) fall on a single curve within the statistical fluctuations. The error bars are typically about 0.03-0.05 for R^2 and approximately 0.02-0.03 for S^2. The smaller errors for S^2 are reflected in the better fit to a single curve.

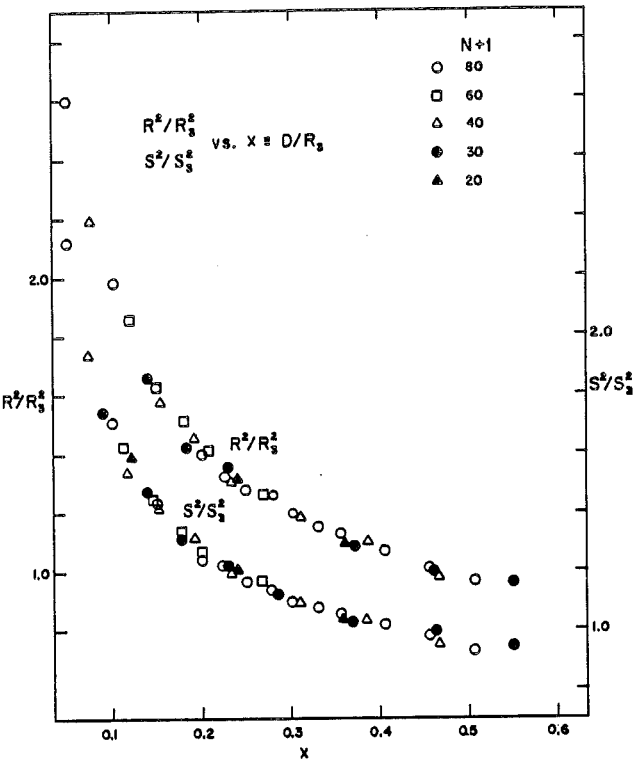

Fig. 1. — R^2/R_3^2 and S^2/S_3^2 *vs.* $x = D/R_3$ for beads on a string chains of $N = 20$-80 confined between two planes separated by a distance D. R_3 and S_3 are the averaged end-to-end distance and radius of gyration of the unconfined chains.

The fact that $f(x, y)$ defined in (3.3) depends only weakly on y for $y \gtrsim 1$ and depends on N and D only through $x = D/R_3(N)$ indicates that the scaling ideas of Daoud and de Gennes [10] are valid for our model in the range of parameter values considered.

To check on the validity of the power law, eq. (1.1), we show in figure 2, a log-log plot of

$$f = R^2(N, D)/R_3^2(N) \text{ vs. } x = D/R_3(N) .$$

There appears to be a good fit (within our statistical errors) to the power law $f(x) = cx^{-s}$, $c = 0.63$, $s = 0.5$ for $x \lesssim 0.25$. The curve then gradually flattens with $f(x) = 1$ at x close to 0.45 (instead of the value 0.94 the power law would give). For $x \gtrsim 0.45$, $f(x)$ is smaller than one, its value when $x \gg 1$, $D \gg R_3(N)$. This is similar to the behaviour of an ideal polymer having no excluded volume when confined in a slab, as discussed in the appendix.

The ratio of R^2/S^2 for different values of D appears within our statistical errors to be a function of x only. For $x \lesssim 0.2$ the ratio is close to its two dimensional

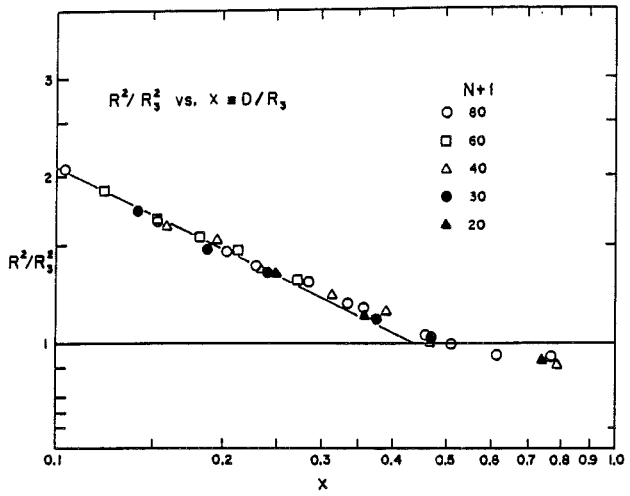

Fig. 2. — Log-log plot of R^2/R_3^2 *vs.* x for $0.1 \leqslant x < 0.6$. The solid line has a slope of 0.5.

value of 7.1 ± 0.2 changing over gradually to the three dimensional value of 6.4 ± 0.1 for $x \gtrsim 0.5$. One would need better statistics to learn still more about the crossover region from this quantity.

The dependence of $R(N, D)$ on N for fixed D is given in figure 3. It is seen there that for any fixed D the asymptotic behaviour for large N is very close to the Flory prediction in two dimensions, $R_2(N) \propto N^{3/4}$.

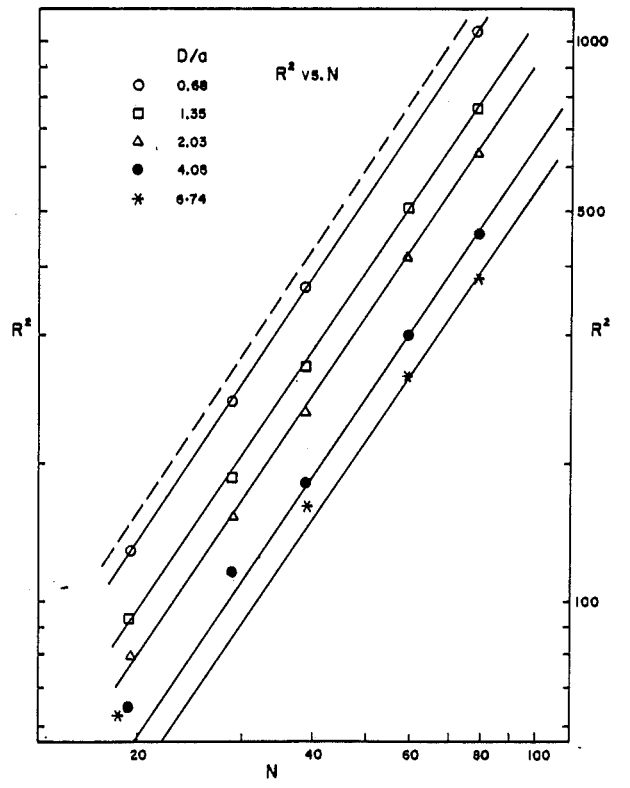

Fig. 3. — Log-log plot of the N dependence of R^2 for various values D of the confinement width. The solid lines are all of slope 1.5 consistent with a two-dimensional power law dependence. The dashed line represents the results for nonconfined two dimensional chains.

It is interesting that the scaling and power law behaviour is obtained in our simulations even for quite small chains, $N \sim 20$. This is due, we believe, to the fact that $B/a^3 \simeq 1$ in our calculations as discussed at the beginning of this section. There is general belief that, as far as excluded volume effects are concerned, the large N regime is obtained for $N > N_c \sim (a^3/B)^2$ in 3D. This gives some confidence in the application of results obtained from computer simulations of small chains to the prediction of properties of molecules with N about 10^5.

To summarize then, we find that the conformational properties of model polymers confined in a region of finite width follows scaling laws analogous to those which occur in the theory of critical phenomena. This scaling behaviour obtains even for rather short chains. Finally we have further confirmation of the result that in infinite media, the scaling behaviour of the size of continuum models and that of chains restricted to lattices are very similar.

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Appendix. — CONFINED IDEAL CHAINS. — Consider a chain of N links, each of fixed length a, in which there are no correlations between successive links. This is the polymer model described in section 2, having $N + 1$ monomers, when the excluded volume interaction $v(r)$ is set to zero. It can be accomplished by setting $\varepsilon = 0$ or $\sigma = 0$ in (2.1), and is essentially the Rouse chain with fixed link length. Let $\mathbf{r}_j$, $j = 0, 1, \ldots, N$ be the positions of the monomers and $\mathbf{s}_i = \mathbf{r}_i - \mathbf{r}_{i-1}$, $i = 1, \ldots, N$ be the directions of the links.

For the unconfined polymer in d dimensions each $\mathbf{s}_i$ is an independent uniformly distributed vector on a sphere of radius a in d dimensions, $\mathbf{s}_i = (s_i^1, \ldots, s_i^d)$. The expected value of the end-to-end distance squared is then clearly

$$L_d^2(N) = \langle (\mathbf{r}_N - \mathbf{r}_0)^2 \rangle = \sum_{i,j} \langle \mathbf{s}_i . \mathbf{s}_j \rangle = \sum_{i=1}^{N} \langle \mathbf{s}_i^2 \rangle = Na^2 \qquad \text{(A.1)}$$

for any d since $\langle \mathbf{s}_i . \mathbf{s}_j \rangle = 0$ for $i \neq j$. The links are just the steps in a random walk model and $\mathbf{r}_j$ is the position of the walker after j steps. ($L_d(N)$ corresponds to $R_d(N)$ with $\sigma = 0$.)

We now ask what happens to L when this ideal chain is confined to a slab of width D,

$$-\tfrac{1}{2} D \leqslant r_j^{\perp} \leqslant \tfrac{1}{2} D .$$

For fixed $\mathbf{r}_0$, $-\frac{1}{2}D \leqslant r_0^{\perp} \leqslant \frac{1}{2}D$, the joint probability distribution of the s_i is now given by

$$P = C\chi_D(\mathbf{s}_1, \ldots, \mathbf{s}_N) \prod_{i=1}^{N} \rho(\mathrm{d}\mathbf{s}_i)$$

where $\rho(\mathrm{d}\mathbf{s}_i)$ is the uniform distribution on the sphere of radius a, χ_D is the characteristic function of the set $\{-\frac{1}{2}D \leqslant r_j^{\perp} \leqslant \frac{1}{2}D\}$, $j = 1, \ldots, N$ and C is a normalization constant. Let $L^2(N, D, a)$ be the expectation value of $(\mathbf{r}_N - \mathbf{r}_0)^2$ with respect to P where we also average over $r_0^{\perp}$ between $-\frac{1}{2}D$ and $\frac{1}{2}D$,

$$\begin{aligned} L^2(N, D, a) &= \sum_{i,j} \langle \mathbf{s}_i . \mathbf{s}_j \rangle \\ &= Na^2 + \sum_{i \neq j} [\langle s_i^{\perp} s_j^{\perp} \rangle + \langle s_i^{\parallel} . s_j^{\parallel} \rangle] \\ &= Na^2 F\left[\frac{D}{\sqrt{Na}}, \frac{D}{a}\right] \end{aligned} \qquad (A.2)$$

where $s_i^{\parallel}$ is the component of $\mathbf{s}_i$ parallel to the wall. Clearly by the symmetry $\langle s_i^{\parallel} . s_j^{\parallel} \rangle = 0$ (since for any fixed $\mathbf{s}_1, \ldots, \mathbf{s}_i$ it is possible to rotate the vector $\mathbf{s}_{i+1} + \cdots + \mathbf{s}_N$ around the $\perp$-axis). It is furthermore clear intuitively (and can be verified easily for a variation of the model in which a walker starts from $\mathbf{r}_0$ and moves randomly until he *hits* the wall when the walk is suitably modified) that $\langle s_i^{\perp} s_j^{\perp} \rangle \leqslant 0$ for $i \neq j$. We therefore expect that $0 < F(x, y) < 1$, ($F(x, y)$ is of course defined precisely only for $x/y = 1/\sqrt{N}$, $N = 1, 2, \ldots$). We expect further that as $N \to \infty$, $F(x, y) \to F(0, y) = \varphi(y)$, such that $\varphi(y) \to 1$ as $y \to 0$. The behaviour of $\varphi(y)$ as $y \to \infty$ is less clear but it can be argued (proven for the modified random walk described earlier) that for $a/D \ll 1$ the problem should be similar to the case when

$$\rho(\mathrm{d}\mathbf{s}) = \prod_{\alpha=1}^{d} \nu(\mathrm{d}s_\alpha) \quad \text{with} \quad \int x^2 \nu(\mathrm{d}x) = a^2/d\,,$$

i.e. each component of s is independent. It is clear that in this case $(Na^2)^{-1} L^2(N, D, a) \xrightarrow[N\to\infty]{} (d-1)/d$ for any fixed $D < \infty$.

Finally keeping $1 < y = D/a$, $N \gg 1$ we would expect to be in the scaling limit where $F(x, y)$ should depend only weakly on y as in the excluded volume case. This is confirmed by a plot $F(x, y)$ *vs.* x for different $y > 1$ in figure 4. It is seen that all the points

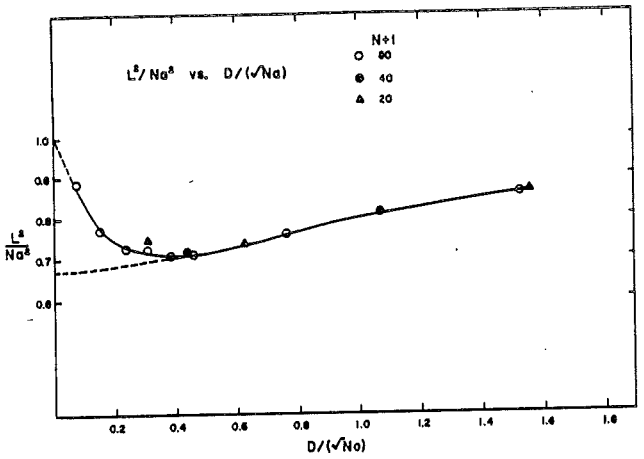

Fig. 4. — The ratio of the squared end-to-end distance of a confined random flight chain to the unconfined chain value for chains of $N = 20$-80 *vs.* the normalized separation between the planes. The extrapolated lines to $L^2/Na = 1$ or $2/3$ for $D/\sqrt{N}a = 0$ correspond to letting $D \to 0$ for fixed N or $N \to \infty$ for fixed $D/\sqrt{N}a$.

fall on a single line within statistical error. It is interesting to note there the slow rise $L(N, D, a^2)$ towards its unconfined value $\sqrt{N}a$. Even for $D = 1.6\sqrt{N}a$, L^2/Na^2 is only about 0.9. This would seem to explain the decrease in $R(N, D)/R_3(N)$ below unity in the excluded volume case (Fig. 1).

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