The entropy of a confined polymer: II

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Abstract. The pressure exerted by an idealized 'random-flight' polymer on the walls of a container is calculated for the complete range of polymer lengths. The calculation uses a numerical approach based on the method initiated by Edwards and Freed.

1. Introduction

Edwards and Freed (1969, to be referred to as I) have directed attention to the theoretical importance of the simple problem of the pressure P exerted on the walls of a container of volume V by a single polymer molecule of total length L. The problem is idealized in the sense that the polymer is assumed to consist of monomers each of length l and completely freely hinged. Excluded-volume effects are neglected and L is assumed to be very large in comparison with l, but not necessarily large compared with $V^{1/3}$. For $L/V^{1/3} \ll 1$, P is given approximately by the perfect gas expression T/V, as shown in I, where an expression for P in the asymptotic region $1 \ll L/V^{1/3}$ is also derived. The purpose of the present paper is to investigate the variation of P for intermediate values of $L/V^{1/3}$, and in particular the speed with which the asymptotic regions are approached. The quickest and most convenient method of doing this is by the direct numerical evaluation of the Green function for the appropriate random-walk problem. For this particular purpose we adopt a slightly modified version of the formulation given in I.

2. Formulation of the problem

As pointed out in I, the problem essentially reduces to that of determining, for a Brownian particle starting at r' inside a box of volume V, the probability that, at a later time, the particle will be at r and never have reached the container walls in the interim period. 'Time' here refers to arc length s along a possible configuration of the polymer chain. In the approximation we use here, we are only concerned with polymer molecules which are very much longer than their consituent monomers, i.e. $l \ll L$. Except for a very small fraction of the molecule we may suppose that $l \ll s$ and the Gaussian approximation holds, the polymer configuration following the trajectory of a typical purely diffusive Brownian walk. For a free Brownian motion, it is well known that the motion can be regarded as a superposition of three similar but uncorrelated one-dimensional diffusion processes (e.g. Chandrasekhar 1943). The same is clearly true for a Brownian motion inside an absorbing box, *provided* that the box is rectangular, and the coordinate axes are chosen parallel to the box edges, since then the absorption from, say, the yz faces will not affect the x trajectory (cf. Chandrasekhar 1943, p. 57). The same is not true in general for any other shaped box. The general problem of diffusion in the presence of absorbing barriers has been discussed by a number of authors (e.g. Chandrasekhar 1943, p. 60 *et seq.*).

In treating the three-dimensional box problem in this approximation, we accordingly consider three uncorrelated Brownian trajectories parallel to the x, y and z axes each with 'time' s, where $0 < s < L$. (To deal with the case where $L \sim l$ we would have to use the Fokker–Planck equation instead of the diffusion equation.) In this approximation the three component entropy contributions are clearly additive and (for a cubical box of side L) the same.

Let us consider a one-dimensional interval of length b,

$$b = V^{1/3} \tag{1}$$

and a polymer length

$$L = Ql \qquad (1 \ll Q). \tag{2}$$

Let us consider the random-walk problem where a trajectory consists of steps of length l either in the positive or negative x direction. Let $M_\infty(L)$ be the total possible unrestricted paths of length L starting from a *specific* fixed point (x', say) when

$$S_\infty(L) = \ln M_\infty(L) \tag{3}$$

is the corresponding entropy. (The temperature here is measured in energy units, so that Boltzmann's constant is unity and S is dimensionless.) We take the origin at the centre of the interval b and suppose one end of the polymer is at x' ($-\tfrac{1}{2}b < x' < \tfrac{1}{2}b$). Let $M_b(L, x)$ be the number of the unconstrained (one-dimensional) paths of length L which start at x' and never go outside the interval $(-\tfrac{1}{2}b, \tfrac{1}{2}b)$. Then the corresponding entropy $S_b(L, x)$ is given by

$$\begin{aligned} S_b(L, x') &= \ln M_b(L, x') \\ &= \ln\{M_\infty(L) W_b(L, x')\} \\ &= S_\infty(L) + \ln W_b(L, x') \end{aligned} \tag{4}$$

where $W_b(L, x)$ is the probability that a path of length L, starting at x, stays inside $(-\tfrac{1}{2}b, \tfrac{1}{2}b)$. If $G_b(x|x', L)\, dx$ is the probability that such a path finishes between x and $x + dx$, then

$$S_b(L, x') = S_\infty(L) + \ln \int_{-b/2}^{b/2} dx\, G_b(x|x', L). \tag{5}$$

To obtain the ensemble value $S_b(L)$ we have to average over starting position x'. As pointed out in I, we are essentially engaged in a counting problem in which we select at random one end of a possible *unrestricted* trajectory and either count it or not according to whether it *subsequently* crosses the container wall. Apart from the fact that we must have $-\tfrac{1}{2}b < x' < \tfrac{1}{2}b$ there is no reason to weight one value of x' more than another, so a uniform distribution over x' is correct. The selection of the initial point gives an entropy contribution $\ln b$, so we have

$$\begin{aligned} S_b(L) &= \ln b + \langle S_b(L, x') \rangle \\ &= \ln b + S_\infty(L) + \frac{1}{b} \int_{-b/2}^{b/2} dx' \ln \int_{-b/2}^{b/2} dx\, G_b(x|x', L) \end{aligned}$$

i.e.

$$S_b(L) = \ln b + S_\infty(L) + \frac{2}{b} \int_{0}^{b/2} dx' \ln \int_{-b/2}^{b/2} dx\, G_b(x|x', L) \tag{6}$$

since the problem is obviously symmetric between positive and negative values of x'. Typical one-dimensional allowable trajectories are shown in figure 1.

The problem is now reduced to that of finding $G_b(x|x', s)$, the Green function for Brownian motion between fixed absorbing boundaries at $\pm\tfrac{1}{2}b$. This is a special case of a more general one discussed by the authors in a previous paper (Collins and Wragg 1968). If we denote by $G_\infty(x|x', L)$ the corresponding unrestricted Green function (as $b \to \infty$), then

$$G_\infty(x|x', L) = \left(\frac{3}{2\pi l L}\right)^{1/2} \exp\left\{-\frac{3}{2lL}(x-x')^2\right\} \tag{7}$$

satisfying the diffusion equation

$$\frac{\partial w}{\partial L} = \frac{l}{6} \frac{\partial^2 w}{\partial x^2} \tag{8}$$

with

$$w(x, L) \to \delta(x - x') \qquad (L \to 0). \tag{9}$$

The function $G_b(x|x', L)$ satisfies (8) and (9) in $-\tfrac{1}{2}b < x < \tfrac{1}{2}b$ with the additional constraint

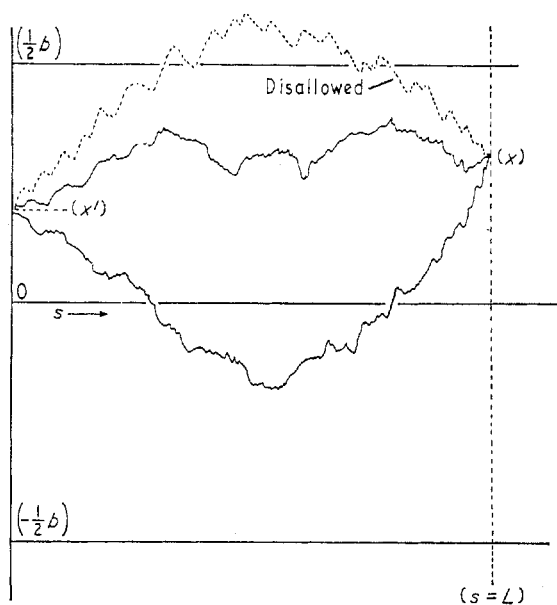$$G_b(x|x', L) = 0 \qquad (x = \pm b). \tag{10}$$

Figure 1. Allowed and disallowed polymer configurations.

For conciseness it is convenient to change to dimensionless variables

$$u = \frac{8l}{3b^2} L \tag{11}$$

$$v = \frac{2}{b} x. \tag{12}$$

We denote by $g(v|v', u)$ the Green function corresponding to $G_b(x|x', L)$. Then (8), (9) and (10) are replaced by

$$\frac{\partial g}{\partial u} = \frac{1}{4} \frac{\partial^2 g}{\partial v^2} \qquad (-1 < v < 1) \tag{13}$$

$$g = 0 \qquad (v = \pm 1, \text{all } u) \tag{14}$$

and (assuming g is properly renormalized)

$$g(v|v', u) \to \delta(v - v') \qquad (u \to 0). \tag{15}$$

The function G_∞ is replaced by

$$g_\infty(v|v', u) = \frac{1}{(\pi u)^{1/2}} \exp\left\{-\frac{(v-v')^2}{u}\right\}. \tag{16}$$

As discussed elsewhere (Collins and Wragg 1968), for small u, $g(v|v', u)$ is most usefully expressed as a sum of image functions formed by successive 'reflections' in the absorbing boundaries with a sign change at each reflection. The first three terms are given by

$$g(v|v', u) = g_\infty(v|v', u) - g_\infty(v|(2 - v'), u) - g_\infty(v|(-2 - v'), u) + \dots . \tag{17}$$

For large u the convergence of the series (17) becomes poor and the most appropriate form for the solution is that given in I, which in these units becomes

$$g(v|v', u) = \sum_{n=1}^{\infty} \exp\left(-\frac{n^2\pi^2 u}{16}\right) \sin\left\{\frac{n\pi}{2}(v'+1)\right\} \sin\left\{\frac{n\pi}{2}(v+1)\right\}. \tag{18}$$

The convergence of the series (17) is satisfactory over the range $0 < u \leqslant 2 \cdot 0$, and that of (18) for $1 \cdot 0 < u$, so that the two forms together enable g to be calculated for all real values of u.

To obtain the entropy S for a three-dimensional cubic box of volume $V = b^3$, we may simply multiply the above entropy by 3, since we assume three uncorrelated one-dimensional random walks. The resulting (three-dimensional) pressure P is given by

$$P = T\frac{\partial S}{\partial V} = \frac{T}{3b^2}\frac{\partial S}{\partial b}$$

$$= \frac{T}{3b^2}\left\{\frac{3}{b} + 3\frac{\partial u}{\partial b}\frac{d}{du}\int_0^1 dv' \ln \int_{-1}^1 dv\, g(v|v',u)\right\}$$

$$= \frac{T}{V} - \frac{16lLT}{3V^{5/3}}\int_0^1 dv'\left\{\frac{\int_{-1}^1 dv\,(\partial/\partial u)g(v|v',u)}{\int_{-1}^1 dv\, g(v|v',u)}\right\}. \tag{19}$$

The partial derivative in (19) was obtained by term-by-term differentiation of the series (17) or (18), and the subsequent integrations carried out numerically. The result is shown in figure 2, where $PV/T - 1$ is plotted against $u = 8lL/3V^{2/3}$.

3. Asymptotic forms

The limiting forms given in I for $1 \ll L/V^{1/3}$ and $L/V^{1/3} \ll 1$ respectively correspond here to $1 \ll u$ and $u \ll 1$, and can be derived from (17) and (18). For large u only the first term in (18) makes a significant contribution, and relation (6) reduces to

i.e.
$$S_b(L) \sim \ln b + S_\infty(L) - \frac{\pi^2 u}{16} + \int_0^1 dv' \ln\left[\frac{4}{\pi}\sin\left\{\frac{\pi}{2}(v'+1)\right\}\right] \tag{20}$$

$$S(L, V) = 3S_b(L)$$

$$\sim \ln V + 3S_\infty(L) - \frac{\pi^2 lL}{2V^{2/3}} + A \tag{21}$$

where

$$A = 3\int_0^1 dv' \ln\left[\frac{4}{\pi}\sin\left\{\frac{\pi}{2}(v'+1)\right\}\right] = 1 \cdot 3549 \tag{22}$$

and is a dimensionless constant computed numerically. The pressure derived from (21) becomes

$$P = T\frac{\partial S}{\partial V} \sim \frac{T}{V} + \frac{\pi^2 lL}{3V^{5/3}} \tag{23}$$

or, since $V^{1/3}/L$ is now small,

$$P \sim \frac{\pi^2 lL}{3V^{5/3}} \qquad (V^{1/3} \ll L) \tag{24}$$

the form given in I.

For small u the only appreciable contribution to g in the form of the series (17) comes from the first three terms given. Using (16) in (17) and evaluating the integrals over v, there results eventually

$$\int_{-1}^1 dv\, g(v|v',u) \simeq 1 - \mathrm{erfc}\left(\frac{1-v'}{\sqrt{u}}\right) - \mathrm{erfc}\left(\frac{1+v'}{\sqrt{u}}\right)$$

$$+ \tfrac{1}{2}\mathrm{erfc}\left(\frac{3-v'}{\sqrt{u}}\right) - \tfrac{1}{2}\mathrm{erfc}\left(\frac{3+v'}{\sqrt{u}}\right). \tag{25}$$

For $u \ll 1$, and $0 \leqslant v < 1$, all the terms on the right-hand side of (25) are very small except the first two. Hence we can write

$$\int_0^1 dv' \ln \int_{-1}^1 dv\, g(v|v', u) \simeq \int_0^1 dv' \ln \mathrm{erf}\left(\frac{1-v'}{\sqrt{u}}\right)$$

$$= -\sqrt{u} \int_0^{1/\sqrt{u}} d\lambda \ln \mathrm{erf}\,\lambda. \tag{26}$$

The integrand is very small for large values of the argument, so for small u we may approximate (26) by

$$\int_0^1 dv' \ln \int_{-1}^1 dv\, g(v|v', u) \simeq C\sqrt{u} \tag{27}$$

where

$$C = -\int_0^\infty d\lambda \ln \mathrm{erf}\,\lambda = 1\cdot0344 \tag{28}$$

and

$$S_b \simeq \ln b + S_\infty(L) - C\sqrt{u}$$

$$= \tfrac{1}{3}\ln V + S_\infty(L) - C\left(\frac{8lL}{3V^{2/3}}\right)^{1/2}. \tag{29}$$

If we add the contributions from the other two Cartesian axes and differentiate with respect to V the resulting pressure is given by

$$P = T\frac{\partial S}{\partial V}$$

$$\simeq \frac{T}{V} + C\left(\frac{8lL}{3}\right)^{1/2}\frac{T}{V^{4/3}} \qquad (L \ll V^{1/3}). \tag{30}$$

If we write

$$f(u) = -\int_0^1 dv' \left\{\frac{\int_{-1}^1 dv (\partial g/\partial u)(v|v', u)}{\int_{-1}^1 dv\, g(v|v', u)}\right\} \tag{31}$$

then (19) becomes, for a fluid of N non-interacting polymers,

$$\frac{PV}{NT} - 1 = 2uf(u) \tag{32}$$

while the asymptotic forms (30) and (23) become

$$\frac{PV}{NT} - 1 \simeq C\sqrt{u} \qquad (u \ll 1) \tag{33}$$

$$\frac{PV}{NT} - 1 \sim \frac{\pi^2 u}{8} \qquad (1 \ll u) \tag{34}$$

where, expressed in terms of V, (11) becomes

$$u = \frac{8lL}{3V^{2/3}}. \tag{35}$$

The exact form (32) was computed numerically and is compared with the asymptotic forms (33) and (34) in figure 2 for a single polymer ($N = 1$).

It can be seen that the forms (33) and (34) give excellent agreement with (32) for $0 < u < 0\cdot8$ and $0\cdot8 < u$ respectively (to within 10% in the worst case). Hence the two

asymptotic forms effectively cover the whole range, with a relatively well-defined break-point of $u \simeq 0.65$, i.e.

$$L \simeq 0.24 \frac{V^{2/3}}{l} \qquad (36)$$

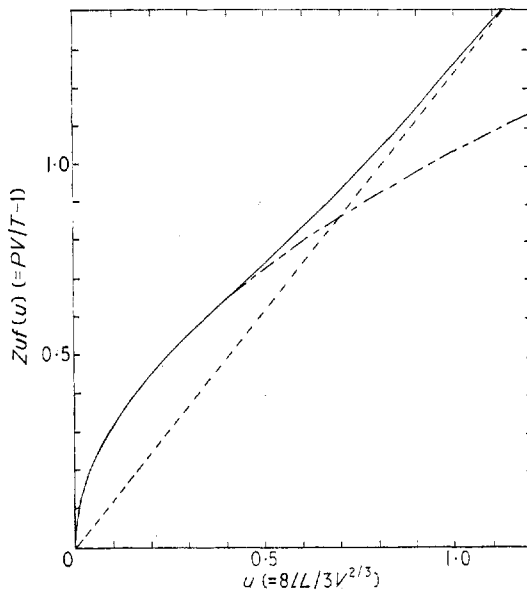when the polymer first 'hits' the box (in an r.m.s. sense).

Figure 2. Equation of state for an idealized single polymer in a cubical container. Full curve, exact form; broken curve, asymptotic form for small container of volume V; chain curve, asymptotic curve for large container of volume V.

Acknowledgments

References

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EDWARDS, S. F., and FREED, K., 1969, J. Phys. A (Gen. Phys.), [2], 145–50.