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Density distribution of a confined polymer

R COLLINS and A WRAGG

Department of Mathematics, University of Salford, Salford M5 4WT, UK

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Abstract. Results are presented of numerical calculations of the spatial average density distribution inside a simple cubical box containing a random flight polymer. Various lengths of polymer are considered. Included is a correction to an isotherm calculation in an earlier paper.

1. Introduction

A random-flight polymer molecule confined in a rigid container exerts a pressure on the container wall resulting from the entropic force field produced near the wall. The theoretical interest of this simple system has been pointed out by S F Edwards and collaborators (eg Edwards and Freed 1969 to be referred to as I), who derived the high-density limiting form for the isotherm. More details of the isotherm were given by the authors in a second paper (Collins and Wragg 1969 to be referred to as II). The results of the second paper have been shown to be inconsistent with the exact expression for the entropy of the system given in I. In the present note a revised version of the calculation is given leading to a corrected form for the isotherm. This differs numerically from the previous version but exhibits the same qualitative features. Of some theoretical interest is the actual monomer probability density within the container. This is also calculated in the present note. The results are presented in graphical form, illustrating the systematic change in monomer distribution as the polymer length becomes comparable with the length of the container edge.

The system is idealized by the same simplifying assumptions as in I and II, namely that the polymer molecule is treated as a simple random-flight gaussian trajectory, in which self-interaction terms and topological constraints are neglected.

This type of approach has been used in a number of practical problems in polymer science, including that of the surface tension of a high-polymer solution (see for example Oosawa and Asakura 1954, Asakura and Oosawa 1958).

2. Equation of state

Suppose a polymer chain of total length L to be composed of monomers of length l , where $1 \ll L/l$. The chain is confined in a cubical container of volume $V = b^3$ with rigid walls. In the idealization of the problem dealt with here, molecular self-interactions of the chain are disregarded, as are any topological constraints. An 'allowed configuration' of the chain is any one lying wholly inside the container, and all such configurations are

treated as equally probable. If $\Omega(L, V)$ denotes the total number of such configurations then the entropy S of the chain is given by

$$S = \ln \Omega \quad (2.1)$$

where temperature is to be measured in energy units, so that Boltzmann's constant is unity. To evaluate S , each configuration is treated as a random-walk trajectory of length L in steps of length l . For each allowed configuration there will be two such trajectories (one going each way). Let r_i denote the initial point of an allowed trajectory. Then $G(r_f, r_i|L) d^3r_f$ denotes the probability that any random-flight trajectory of length s which starts at r_i will (i) be an allowed trajectory and (ii) will finish in the element d^3r_f of volume surrounding r_f . Let $\Omega(r_i)$ denote the total number of allowed trajectories starting from r_i . Then

$$\Omega = \frac{1}{2} \int_V d^3r_i \Omega_i. \quad (2.2)$$

Let $N(L)$ denote the total number of (unrestricted) trajectories of length L starting from any given point, and let $W(r_i)$ denote the probability that any random trajectory starting from r_i stays wholly inside the box. Then

$$\frac{\Omega_i}{N} = W(r_i) \propto \int_V d^3r_f G(r_f, r_i|L) \quad (2.3)$$

and

$$\begin{aligned} S &= -\ln 2 + \ln \int_V d^3r_i \frac{\Omega_i}{N} N \\ &= \ln\left(\frac{1}{2}N\right) + \ln \int_V d^3r_i W(r_i) \\ &= \ln(\text{constant}) + \ln \int_V d^3r_i \int_V d^3r_f G(r_f, r_i|L). \end{aligned}$$

The constant additive first term may be omitted and we get

$$S = \ln \int_V d^3r_i \int_V d^3r_f G(r_f, r_i|L) \quad (2.4)$$

as in paper I (equations (2.1) and (2.5)). S can be found either by evaluating (2.4) directly or by splitting into two terms, (i) the entropy of selection of the initial point r_i and (ii) the average entropy of allowed trajectories which start at r_i . If $p(r_i) d^3r_i$ is the probability of an allowed trajectory starting in d^3r_i then in this form

$$\begin{aligned} S &= - \int_V d^3r_i p(r_i) \ln p(r_i) + \langle S(r_i) \rangle \\ &= - \int_V d^3r_i p(r_i) \ln p(r_i) + \int_V d^3r_i p(r_i) \ln \int_V d^3r_f G(r_f, r_i|L). \end{aligned} \quad (2.5)$$

In paper II this was evaluated taking all initial points to be equally likely, that is $p(r_i) = \text{constant}$. In fact this is inconsistent with (2.4). Because of the actual symmetry between initial and final ends, we must take

$$p(r_i) = W(r_i). \quad (2.6)$$

Disregarding the multiplicative constant N , we can take

$$\Omega = \int_V d^3r_f d^3r_i G(r_f, r_i|L) \tag{2.7}$$

as in I (equation (2.5)), which gives

$$p(r_i) = W(r_i) = \frac{1}{\Omega} \int_V d^3r_f G(r_f, r_i|L) \tag{2.8}$$

that is, the correct form for the probability function for the initial point r_i is in fact the (renormalized) probability function for the final end-point r_f if a uniform distribution over r_i had been assumed. From (2.8) and (2.5)

$$\begin{aligned} S &= \int_V d^3r_i p(r_i) \ln \left(\frac{1}{p(r_i)} \int_V d^3r_f G(r_f, r_i|L) \right) \\ &= \int_V d^3r_i p(r_i) \ln \Omega \\ &= \ln \Omega \end{aligned}$$

in agreement with (2.1). As in paper I, we have

$$S = \text{constant} + \ln V + 3 \ln \left\{ \frac{16}{\pi^2} \sum_n^{(\text{odd})} \frac{1}{n^2} \exp \left(-\frac{n^2 \pi^2 u}{16} \right) \right\} \tag{2.9}$$

where

$$u = 8lL/3b^2 = 8lL/3V^{2/3}. \tag{2.10}$$

Defining

$$\psi(u) = \frac{16}{\pi^2} \sum_n^{(\text{odd})} \frac{1}{n^2} \exp \left(-\frac{n^2 \pi^2 u}{16} \right) \tag{2.11}$$

then the equation of state is

$$\frac{P}{T} = \frac{\partial S}{\partial V} = \frac{1}{V} + \frac{3}{\psi} \frac{\partial \psi}{\partial V}. \tag{2.12}$$

Since $u \propto V^{-2/3}$ this becomes

$$\frac{PV}{T} - 1 = -2u \frac{d}{du} (\ln \psi). \tag{2.13}$$

For large u , relation (2.11) can be used as it stands, giving

$$\begin{aligned} \frac{PV}{T} - 1 &= \frac{\pi^2 u}{8} \left(1 + e^{(1-3^2)\pi^2 u/16} + e^{(1-5^2)\pi^2 u/16} + \dots \right) \\ &\quad \times \left(1 + \frac{1}{3^2} e^{(1-3^2)\pi^2 u/16} + \frac{1}{5^2} e^{(1-5^2)\pi^2 u/16} + \dots \right)^{-1} \\ &= \frac{1}{8} \pi^2 u \left(1 + \frac{8}{9} e^{-\pi^2 u/2} + \dots \right). \end{aligned} \tag{2.14}$$

The correcting term is less than 1% for u greater than a limiting value given by

$$u = \frac{2}{\pi^2} \ln \frac{800}{9} \simeq 0.896 \quad (2.15)$$

so that above this value we can write

$$\frac{PV}{T} - 1 \simeq \frac{\pi^2 u}{8} = \frac{\pi^2 L}{3b^2} \quad (0.9 < u) \quad (2.16)$$

as before. For small u the convergence of the series in (2.11) becomes poor, and the Green function G has to be expressed as a set of 'gaussian image' functions as described in II. The net result is

$$\psi(u) = 2 - 4 \left(\frac{u}{\pi} \right)^{1/2} \left\{ \frac{1}{2} E(0) - E \left(\frac{2}{\sqrt{u}} \right) + E \left(\frac{4}{\sqrt{u}} \right) - E \left(\frac{6}{\sqrt{u}} \right) + \dots \right\} \quad (2.17)$$

where

$$E(x) = \sqrt{\pi} \int_x^\infty dy \operatorname{erfc}(y). \quad (2.18)$$

This can be evaluated using the asymptotic expansion (Abramowitz and Stegun 1965, p 300)

$$E(x) \sim \frac{e^{-x^2}}{2x^2} \left(1 - \frac{3!}{(2x)^2} + \frac{5!}{2!(2x)^4} - \frac{7!}{3!(2x)^6} + \dots \right) \quad (2.19)$$

and the result

$$E(0) = \sqrt{\pi} \int_0^\infty dy \operatorname{erfc}(y) = 1 \quad (2.20)$$

to give

$$\begin{aligned} \psi(u) &= 2 - 2 \left(\frac{u}{\pi} \right)^{1/2} \left\{ 1 - E \left(\frac{2}{\sqrt{u}} \right) + \dots \right\} \\ &= 2 - 2 \left(\frac{u}{\pi} \right)^{1/2} + \frac{u^{3/2} e^{-4/u}}{4\sqrt{\pi}} \left(1 - \frac{3u}{8} + \frac{15u^2}{64} - \dots \right). \end{aligned} \quad (2.21)$$

For small u , we may neglect the term in $e^{-4/u}$ and write approximately

$$\psi(u) \simeq 2 \left\{ 1 - \left(\frac{u}{\pi} \right)^{1/2} \right\}$$

giving

$$\frac{PV}{T} - 1 = \frac{2u\psi'(u)}{\psi(u)} \simeq \frac{\sqrt{(u/\pi)}}{1 - \sqrt{(u/\pi)}} \quad (\text{small } u). \quad (2.22)$$

Relations (2.16) and (2.22) give the corrected asymptotic forms for the isotherm for large and small u respectively. In figure 1, the graphs for these two are compared with the correct curve, computed numerically by using the full forms of (2.14) or (2.17). Within the ranges quoted, one or the other of the asymptotic forms is correct to within 1.5%, the worst case occurring just above $u = 0.81$, when the exact curve lies midway between the two asymptotic forms. If figure 1 is compared with figure 2 of paper II, it will be

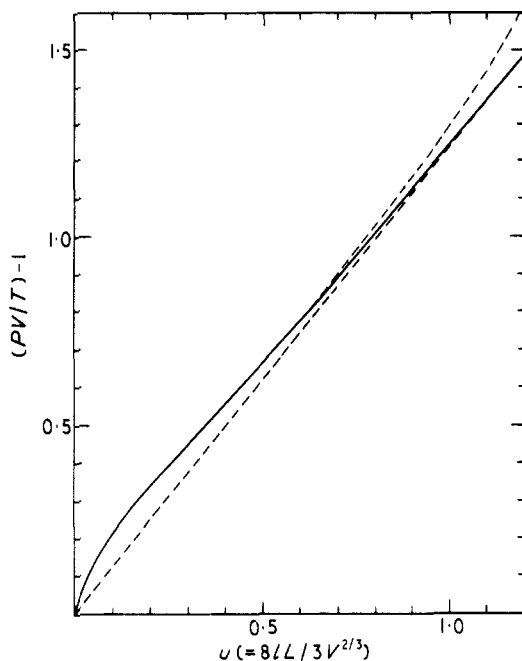


Figure 1. Corrected equation of state for idealized polymer of length L in cubical container of volume V . The broken lines are asymptotic forms.

seen that the corrected curve is qualitatively the same as before, the maximum discrepancy occurring at about $u = 0.3$ where the corrected curve gives a value of $PV/T - 1$ about 20% lower than before.

3. Density distribution inside the container

Consider a particular monomer in the polymer chain. Let s be the chain length from one end to this monomer. Let $\Omega(\mathbf{r}, s | \mathbf{r}_f, \mathbf{r}_i)$ denote the number of allowed configurations in which this monomer lies in the volume element d^3r surrounding the point \mathbf{r} , given that the ends lie at \mathbf{r}_i and \mathbf{r}_f respectively. Then

$$\Omega(\mathbf{r}, s | \mathbf{r}_f, \mathbf{r}_i) \propto G(\mathbf{r}_f, \mathbf{r} | L - s) G(\mathbf{r}, \mathbf{r}_i | s). \quad (3.1)$$

Hence the probability density $p_L(\mathbf{r}, s)$ at point \mathbf{r} for this particular monomer s is given by

$$p_L(\mathbf{r} | s) \propto \int d^3(\mathbf{r}_f, \mathbf{r}_i) G(\mathbf{r}_f, \mathbf{r} | L - s) G(\mathbf{r}, \mathbf{r}_i | s). \quad (3.2)$$

Now from the propagation property of the Green function we have

$$\int d^3r G(\mathbf{r}_f, \mathbf{r} | L - s) G(\mathbf{r}, \mathbf{r}_i | s) = G(\mathbf{r}_f, \mathbf{r}_i | L)$$

and so

$$\int d^3r d^3r_f d^3r_i G(\mathbf{r}_f, \mathbf{r} | L - s) G(\mathbf{r}, \mathbf{r}_i | s) = \Omega(L). \quad (3.3)$$

Hence the normalization constant for $p(\mathbf{r}|s)$ is simply $\Omega(L)$ (for all s) and so (3.2) becomes

$$p_L(\mathbf{r}|s) = \frac{1}{\Omega} \int d^3(\mathbf{r}_f, \mathbf{r}_i) G(\mathbf{r}_f, \mathbf{r}|L-s) G(\mathbf{r}, \mathbf{r}_i|s). \quad (3.4)$$

In particular the probability density $D(\mathbf{r}|0)$ corresponding to a chain end can be obtained by putting $s = 0$ in (3.4) and using

$$G(\mathbf{r}, \mathbf{r}_i|0) = \delta(\mathbf{r} - \mathbf{r}_i) \quad (3.5)$$

to give equation (2.3).

It is more convenient for numerical computation to introduce the dimensionless coordinates (defined in paper II)

$$\mathbf{v} = \frac{2}{b} \mathbf{r} \quad (3.6)$$

and the dimensionless arc length

$$\eta = \frac{8}{3b^2} s \quad (3.7)$$

so that

$$-1 \leq v_1, v_2, v_3 \leq 1 \quad \text{and} \quad 0 \leq \eta \leq u.$$

The Green functions are all separable into three factors, one for each component and the corresponding probability density $\rho_u(\mathbf{v}|\eta)$ is given by

$$\rho_u(\mathbf{v}|\eta) = \rho_u(v_1|\eta) \rho_u(v_2|\eta) \rho_u(v_3|\eta) \quad (3.8)$$

where

$$\rho_u(v|\eta) = \frac{1}{\psi(u)} \int_{-1}^1 dv_f \int_{-1}^1 dv_i g(v_f, v|u-\eta) g(v, v_i|\eta) \quad (3.9)$$

where g is the dimensionless form of Green function defined in paper II. For large η the appropriate form for g is

$$g(v, v'|\eta) = \sum_{n=1}^{\infty} \exp\left(-\frac{n^2 \pi^2 \eta}{16}\right) \sin \frac{n\pi}{2}(v'+1) \sin \frac{n\pi}{2}(v+1) \quad (-1 \leq v, v' \leq 1). \quad (3.10)$$

Using (3.10) in (3.9) gives the result

$$\rho_u(v|\eta) = \frac{1}{\psi(u)} f(v|u-\eta) f(v|\eta) \quad (3.11)$$

$$f(v|\eta) = \frac{4}{\pi} \sum_n^{(\text{odd})} \frac{1}{n} \exp\left(-\frac{n^2 \pi^2 \eta}{16}\right) \sin \frac{n\pi}{2}(v+1). \quad (3.12)$$

The corresponding form for $f(v|\eta)$ when η is small is

$$f(v|\eta) = 1 - \operatorname{erfc} \frac{1-v}{\sqrt{\eta}} - \operatorname{erfc} \frac{1+v}{\sqrt{\eta}} + \operatorname{erfc} \frac{3-v}{\sqrt{\eta}} - \operatorname{erfc} \frac{3+v}{\sqrt{\eta}} + \dots \quad (3.13)$$

This result is obtained from the 'image' series given in II

$$g(v, v') = g_{\infty}(v, v') - g_{\infty}(v, 2-v') - g_{\infty}(v, -2-v') + \dots \quad (3.14)$$

where

$$g_{\infty}(v, v') = \frac{1}{(\pi\eta)^{1/2}} \exp\left(-\frac{(v-v')^2}{\eta}\right). \quad (3.15)$$

Since all the terms in (3.14) have the same η , the explicit η label on the g has been omitted for conciseness. For the mid-point of the polymer chain, $\eta = u/2$ and (3.11) becomes

$$\rho_u(v|\frac{1}{2}u) = \frac{1}{\psi(u)} f^2(v|\frac{1}{2}u). \quad (3.16)$$

Since $\rho_u(v|\eta)$ factorizes in the form given by (3.8) it is sufficient to calculate the one dimensional $\rho_u(v|\eta)$ given by (3.11) and (3.12). This was done numerically by a computer program for various values of polymer length L (different values of u) and for points along the chain given by $\eta/u = 0, \frac{1}{4}, \frac{1}{2}$ corresponding respectively to a monomer at one end, a distance $L/4$ from one end, and at the chain mid-point. The results are shown in figures 2 to 5, and show the progressive change in density distribution across the container from the case $u = 8L/3b^2 = 0.01$ (where the polymer is small compared with the

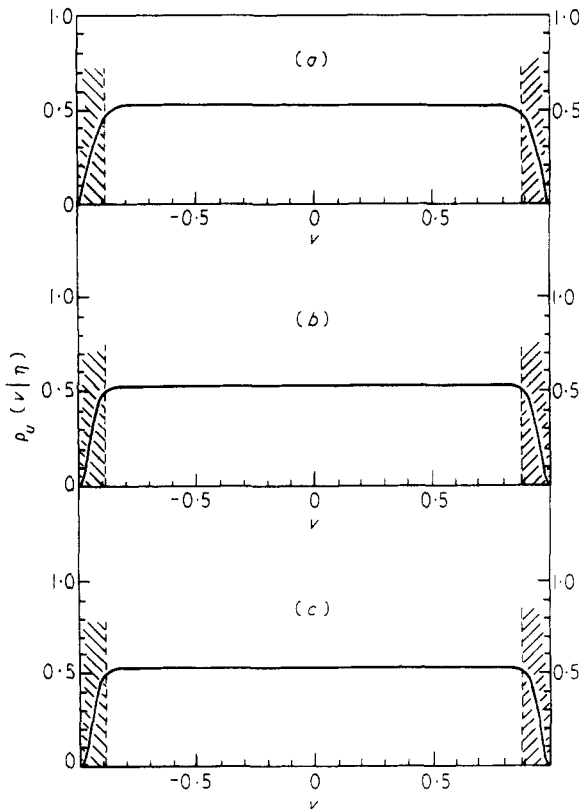


Figure 2. Variation of polymer density $\rho_u(v|\eta)$ across the container for (a) the ends, (b) quarter-points and (c) mid-point of the polymer chain for the case $u = 8L/3b^2 = 0.01$; $d_f = 0.113$.

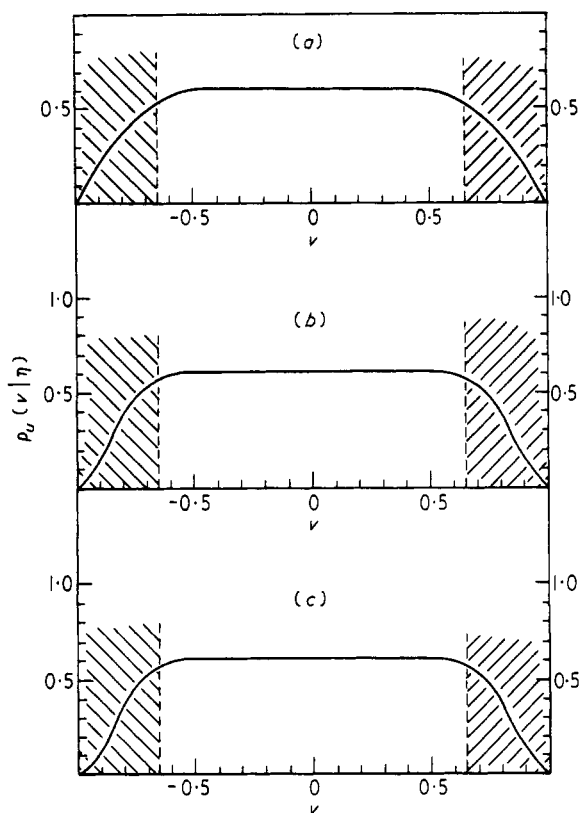


Figure 3. Variation of $\rho_u(v|\eta)$ for the case $u = 0.1$; $d_f = 0.357$.

box) to $u = 0.8$ where the polymer is already effectively in the long-polymer limit. In this limit, the entropic field of force extends over the entire container and we have

$$\text{Long polymer limit} \begin{cases} \rho_u(v|0) = \frac{\pi}{4} \cos \frac{\pi v}{2} \\ \rho_u(v|\frac{1}{2}u) = \cos^2 \frac{\pi v}{2}. \end{cases} \quad (3.17)$$

The probability density of a monomer near the middle of the chain close to the container wall is appreciably lower than that of an end monomer. Roughly speaking this could be expressed by saying that it is statistically easier for the chain end to penetrate the edges and corners of the box than the chain middle. This effect is shown by a positive value of $d^2\rho/dv^2$ (upward curvature) near $v = \pm 1$ for $u = \eta/2$, and the effect remains noticeable down to the lowest values of u for which results have been computed, although it is only in the long-polymer limit that $d\rho/dv$ becomes zero at the container boundary for the chain mid-point. To facilitate comparison with the dimensions of the free (unconfined) polymer chain, the parameter d_f is indicated in figures 2 to 5. This is defined by

$$d_f = \frac{2}{b} \bar{X}_f \quad (3.18)$$

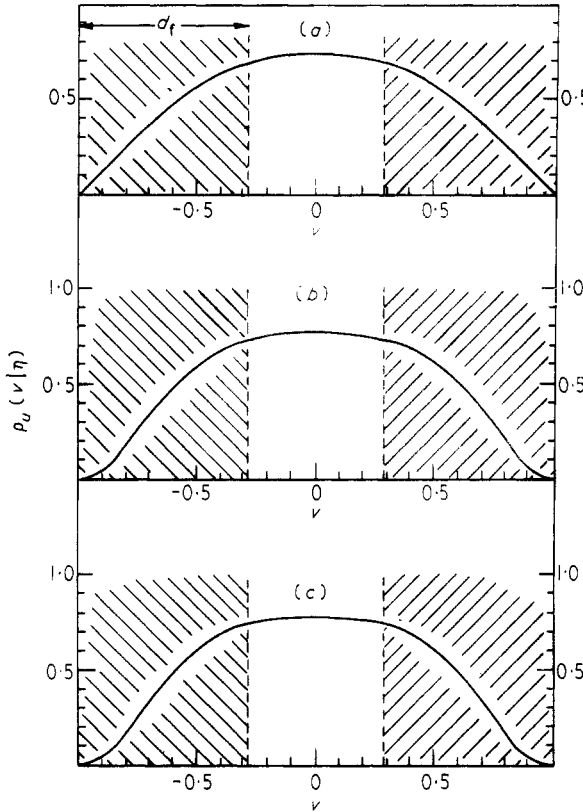


Figure 4. Variation of $\rho_u(v|\eta)$ for the case $u = 0.4$; $d_f = 0.715$.

where \bar{X}_f is the mean maximal projection of the free chain in any given direction. This has a value given by Volkenstein (1963, p 182—his b is our l , and his Zb is our L) of $\bar{X}_f = 0.92\sqrt{(Ll)}$, that is

$$d_f = \frac{1.84}{b}\sqrt{(Ll)} = 1.13\sqrt{u} \tag{3.19}$$

so that d_f increases from a value of 0.113 at $u = 0.01$ to 1.01 at $u = 0.8$. It can be seen that d_f (and hence \bar{X}_f) gives a good measure of the effective ‘range’ of the entropic force field between the polymer and wall, indicated schematically by the shaded region at each end of the interval. At $u = 0.8$ the two regions just overlap in the middle, and it is at about this value (see figure 1) that the curve for $PV/T-1$ changes over from the ‘short-polymer’ form given by (2.22) to the ‘long-polymer’ form given by (2.16). It is accordingly reasonable to describe this change to take place at about the point where the free polymer projected diameter is half as wide as the box.

4. Discussion

Both the density calculations and the revised equation of state are consistent with the description of the statistical behaviour of the system as falling into two fairly clearly defined types which can be described as ‘short-polymer’ and ‘long-polymer’ respectively.

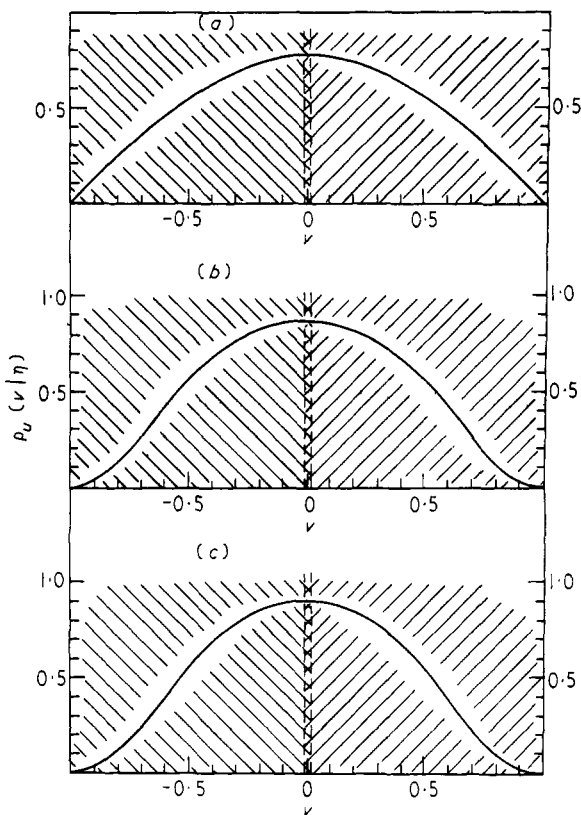


Figure 5. Variation of $\rho_u(v|\eta)$ for the case $u = 0.8$; $d_r = 1.011$.

The transition between the two takes place quite smoothly over a small range of polymer lengths when the entropic force field between polymer and container wall just extends over the whole container volume. In qualitative terms this takes place, as far as it can be said to take place at any one point, when the statistical average free 'diameter' of the polymer is half the length of one edge of the cube.

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