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SHORT COMMUNICATION

ON THE ENTROPY OF SINGLE POLYMER CHAINS

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Abstract—Two expressions for the entropy of isolated polymer chains in general, and Gaussian chains in particular, are examined, and the correct expression indicated. In particular, it is shown that the Wall equation for the entropy change upon perturbation of a Gaussian chain is correct.

INTRODUCTION

The results reported in this Short Communication for the entropy change upon perturbation of a single polymer chain are not unknown to polymer theorists, and correspond to the standard results of rubber elasticity theory [1–3]. However, since this classical theory has been sometimes challenged [4], it may be useful to confirm it using a somewhat different approach, which, at the same time, discusses the Wall equation [1(b)], relevant to this theory but apparently neglected in the literature.

The Wall equation relates the entropy change ΔS of a single (isolated) chain to the end-to-end distribution functions $p^0(r)$ and $p^1(r)$ of that chain is some initial state 0 and final state 1:

$$\Delta S/k = -\int p^1(r)\ln[p^1(r)/p^0(r)]\,\mathrm{d}^3r. \tag{1}$$

If the distribution functions are specified as Gaussian distributions of mean square end-to-end distances $\langle r_0^2\rangle$ and $\langle r_1^2\rangle$, respectively, substitution in equation (1) yields the Flory–Wall equation [1, 3] for the elastic energy difference of the chain between states 0 and 1 [5]:

$$\Delta F_{el}/kT = -\Delta S/k = (3/2)(\alpha^2 - 1) - \ln \alpha^3 \tag{2}$$

where

$$\alpha^2 = \langle r_1^2\rangle/\langle r_0^2\rangle. \tag{3}$$

Equation (2) assumes that the free energy change upon deformation of the chain is exclusively entropic in nature. This assumption will be held throughout this paper, so that energetic contributions between chain segments will not be taken into account.

Let us then now write, using the basic relationship for the entropy,

$$S/k = -\int p(r)\ln p(r)\,\mathrm{d}^3r \tag{4a}$$

so that

$$\Delta S/k = (S^1 - S^0)/k = -\int p^1(r)\ln p^1(r)\,\mathrm{d}^3r + \int p^0(r)\ln p^0(r)\,\mathrm{d}^3r. \tag{4b}$$

Upon substitution of the above two Gaussian distributions in equation (4b), one now finds

$$\Delta S/k = \ln \alpha^3. \tag{5}$$

The contradiction is due to the fact that the end-to-end distance r is not an adequate parameter through which to express the probabilities in equations (4a,b). Rather, one has to take account of all microstates of end-to-end distance r, and replace in equations (4a,b) the simple by double sums.

Let us then write,

$$S/k = -\iint p(r, L)\ln p(r, L)d^{\mathrm{D}}r\,\mathrm{d}L + C. \tag{6}$$

Here L is a parameter which defines continuously all configurations of end-to-end distance r of a chain in D dimensions. $\mathrm{d}L$ is for instance a short-hand for $\mathrm{d}r_1 \ldots \mathrm{d}r_{N+1}$, where r_1 and r_{N+1} are the vectors joining the origin and end of the chain respectively, with the origin of coordinates. C is a constant, originating in the fact that in the continuous case the value of the entropy depends on the choice of the coordinate system [6]. For convenience, we assume that the coordinates have been so chosen as to allow $C = 0$. We further define

$$Z_0 = \iint d^{\mathrm{D}}r\,\mathrm{d}L \tag{7}$$

as being the "phase space" of the chain. For a "free" chain, upon which no forces or constraints are acting, it is warranted to assume that each microstate has the same probability Z_0^{-1}. One then has from equations (6) and (7):

$$S^0/k = -Z_0^{-1}\ln[Z_0^{-1}]\iint d^{\mathrm{D}}r\,\mathrm{d}L = \ln Z_0 \tag{8}$$

as expected. If now some constraint acts on the chain, such as a force at the two ends, the entropy is no longer given by equation (8). Quite generally, one may write for the probability of microstate (r, L):

$$p(r, L)d^{\mathrm{D}}r\,\mathrm{d}L = Z_1^{-1}g(r, L)d^{\mathrm{D}}r\,\mathrm{d}L \tag{9a}$$

where

$$Z_1 = \iint g(r, L)d^{\mathrm{D}}r\,\mathrm{d}L. \tag{9b}$$

Here Z_1 is the partition function of the perturbed chain, and $g(r, L)$ is some weighing factor which needs not be further specified here, except in that all $g(r, L)$ values should not be equal to one.

Substituting in equation (6), one has

$$S/k = -\iint Z_1^{-1}g(r, L)\ln[Z_1^{-1}g(r, L)]d^{\mathrm{D}}r\,\mathrm{d}L. \tag{10}$$

We can now assume that $g(r, L) = g(r)$, that is the weighting factor depends only on the end-to-end distance r and not on the particular configuration considered. This is a simplifying assumption and excludes consideration of, e.g. Volkenstein's rotational isomers [7]. It is however a convenient simplifying assumption for present purposes. With this assumption, let us define the measure of microstates at r, $Z(r)$, through

$$\iint g(r) d^{\mathrm{D}}r \, \mathrm{d}L = \int Z(r) g^{(r)} d^{\mathrm{D}}r \tag{11a}$$

so that

$$\int_{(\mathrm{at}\ r)} \mathrm{d}L = Z(r), \quad \text{and} \quad \int Z(r)\,\mathrm{d}r = Z_0. \tag{11b,c}$$

One has, from equations (9) and (11):

$$\begin{aligned} S/k &= -\iint p(r, L) \ln p(r, L) d^{\mathrm{D}}r \, \mathrm{d}L \\ &= -\iint Z_1^{-1} g(r) \ln[Z_1^{-1} g(r)] d^{\mathrm{D}}r \, \mathrm{d}L \\ &= -Z_1^{-1} \int Z(r) g(r) \ln[Z_1^{-1} g(r)] \, \mathrm{d}^{\mathrm{D}}r. \end{aligned} \tag{12}$$

Assuming that the imposition of constraints does not affect the number of microstates $Z(r)$ at r, the probability of an end-to-end distance r is then given by

$$p(r) d^{\mathrm{D}}r = Z_1^{-1} Z(r) g(r)\,\mathrm{d}^{\mathrm{D}}r. \tag{13}$$

Substituting the latter expression in equation (12), one finally finds

$$S/k = -\int p(r) \ln[Z(r)^{-1} p(r)]\,\mathrm{d}^{\mathrm{D}}r. \tag{14}$$

It is thus seen that the entropy difference $\Delta S = S_1 - S^0$ between two states 0 and 1 of the chain is not given by equation (4b) but by

$$\begin{aligned} \Delta S/k = & -\int p^1(r) \ln[Z(r)^{-1} p^1(r)]\,\mathrm{d}^{\mathrm{D}}r \\ & + \int p^0(r) \ln[Z(r)^{-1} p^0(r)]\,\mathrm{d}^{\mathrm{D}}r = \\ & - \int p^1(r) \ln[p^1(r)/p^0(r)]\,\mathrm{d}^{\mathrm{D}}r \\ & + \int \{p^0(r) - p^1(r)\} \ln[Z(r)^{-1} p^0(r)]\,\mathrm{d}^{\mathrm{D}}r. \end{aligned} \tag{15}$$

In the particular case where $p^0(r)$ is associated with the probability of an unperturbed Gaussian chain,

$$p^0(r)\,\mathrm{d}^{\mathrm{D}}r = Z_0^{-1} Z(r)\,\mathrm{d}^{\mathrm{D}}r \tag{16}$$

the Wall equation, equation (1) follows, since then, making use of the two conditions $\int p^0(r)\,\mathrm{d}^{\mathrm{D}}r = \int p^1(r)\,\mathrm{d}^{\mathrm{D}}r = 1$, the second integral in the right-hand side of equation (15) vanishes.

Let us point out that in the discreet case simple numerical examples (e.g. short random flight chains on the plane square lattice) will show equation (14) for the entropy to be correct and equation (4a) to be incorrect. Thus, there is no doubt that the correct expression for the entropy change between two states 0 and 1 of a chain is equation (15) and not equation (4b). Equation 1 is a particular case of equation (15).

Equation (14) for the entropy, appears also in other fields of science and especially in information theory [8]. Equation (1) for the entropy change, should be designated in polymer science as the Wall equation, since, to the author's knowledge, he was the first to obtain it in this field [1(b)]. It has been more recently rederived as a particular case of the free energy change of a single polymer chain in solution, when the free energy of interaction between distinct neighbours along the chain is zero [9].

The assumptions made here to derive the Wall equation, firstly that $g(r, L) \equiv g(r)$, and secondly that the initial distribution is Gaussian and unperturbed, so that all microstates are of equal probability, define also the limits of applicability of this equation.

To summarize, if the authors in Ref. [4] arrived at the conclusion that the entropy of deformation of a Gaussian chain is zero, this conclusion originates in the fact that they used the incorrect, in this case, equation (4b), for the entropy change, instead of the correct equation (15). From the latter also follows the correct, within the limits of its applicability, Wall equation.

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