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1969 J. Phys. A: Gen. Phys. 2 145

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The entropy of a confined polymer: I

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MS. received 7th November 1968

Abstract. A study is made of the entropy of a random-flight polymer confined in a box of volume V . It is shown that when the natural radius of the polymer approaches the linear size of the box, the entropy ceases to have the normal form of a thermodynamic function and the pressure is not a function of the density but takes the form

$$PV = \frac{\pi^2}{3} \left(\frac{Ll}{R^2} \right) \kappa T$$

where L is the polymer length, l the step length and R equals V , and the density of the system even though strictly in equilibrium is not uniform. It is shown how the introduction of constraints due to forces, cross linkages and very long-lived quasi-invariants restores the equation of state to a thermodynamic form $P = P(\rho)$ where $\rho = L/Vl$.

1. Introduction

A polymer consisting of N units, each of length l and (for the sake of simplicity) assumed to be freely hinged, represents a system whose properties are intermediate between a system with a full $3N$ degrees of freedom and a system of just 3. In particular, consider a polymer in a box of volume V . If the polymer is very much smaller than the box it will behave as a single molecule with internal degrees of freedom. Thus its free energy will depend upon volume just as in the usual gas case

$$\frac{F}{\kappa T} = \ln V + \text{terms independent of } V. \quad (1.1)$$

Since the molecule has a random-flight structure its mean linear dimension will be given by the Einstein value $(Nl^2)^{1/2}$, so the condition for equation (1.1) is

$$(Nl^2)^{3/2} \ll V. \quad (1.2)$$

This will normally be satisfied in, say, a polymer solution by an enormous factor. But now suppose the polymer reaches a size $(Nl^2)^{3/2} \sim V$. This of course cannot happen for a macroscopic box and a single molecule, but is of interest because a large molecule can be boxed in, in a semi-permanent environment in a solid or dense liquid, and also, in either a dense system or a cross-linked system, it would appear physically that the fact that the system is not made of a single polymer should not matter too much. Thus, if a giant molecule fills a box densely, and then a number n of cuts are made in it, so that $N \gg n \gg 1$, it would appear that physically, since $N \gg n$, there should not be a dramatic change in the free energy. A third reason for looking at the box-filling molecule is on purely theoretical grounds. One normally discusses systems in which the free energy is extensive, i.e. $F \propto Vf(\rho)$, ρ being the density. It turns out that this is not the case here and since this property of F is considered fundamental it is of interest to see what has happened.

A numerical assessment of the results is given in the following paper by Collins and Wragg (1969).

2. The single very long chain

Let us then consider a single very long chain confined to a box in thermal equilibrium.

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The entropy is purely due to configurations and

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

where Ω is the total number of configurations. Since the whole problem will depend on long-range behaviour it will be accurate (to order $1/N$) to consider the probability distribution of the links in the approximation in which it satisfies a diffusion equation. The number of configurations of a chain which starts at \mathbf{r}' and ends at \mathbf{r} is given by

$$G(\mathbf{r}, \mathbf{r}'; L) = \mathcal{N} \int_{\mathbf{R}(0)=\mathbf{r}'}^{\mathbf{R}(L)=\mathbf{r}} \exp\left(-\frac{3}{2l} \int \mathbf{R}^2 ds\right) \delta_{\text{box}} \mathbf{R} \quad (2.2)$$

where the integration is taken over all paths (\mathbf{R}/s) commencing at \mathbf{r}' , ending at \mathbf{r} , and lying within the box ($L = Nl$). The normalization \mathcal{N} represents the number of configurations of a completely unconfined chain, since this is a constant and permits the use of the Wiener integral. In terms of unconfined integration

$$G = \mathcal{N} \int_{\mathbf{R}(0)=\mathbf{r}'}^{\mathbf{R}(L)=\mathbf{r}} \exp\left(-\frac{3}{2l} \int \dot{\mathbf{R}}^2 ds\right) \prod_s \Theta(\mathbf{R}) \delta \mathbf{R} \quad (2.3)$$

where

$$\begin{aligned} \Theta &= 1 && \mathbf{R} \text{ in } V \\ &= 0 && \text{otherwise.} \end{aligned} \quad (2.4)$$

In the same spirit that allows a chain of links to be replaced by the Wiener integral, we can replace $\sum \ln \Theta$ by an integral, to give

$$G = \mathcal{N} \int_{\mathbf{R}(0)=\mathbf{r}'}^{\mathbf{R}(L)=\mathbf{r}} \exp\left\{-\frac{3}{2l} \int \dot{\mathbf{R}}^2 ds + \int ds \ln \Theta(\mathbf{R})\right\} \delta \mathbf{R}$$

and

$$\Omega = \int d^3r d^3r' G(\mathbf{r}, \mathbf{r}'; L). \quad (2.5)$$

Let us consider Θ as 'softened' when \mathbf{R} nears the boundaries to make $\ln \Theta$ a less severely behaved function, and take the limit at the end. Now $\ln \Theta$ is a 'potential' and it is well known that G must satisfy

$$\left\{ \frac{\partial}{\partial s} + \frac{l}{6} \nabla^2 + \ln \Theta(\mathbf{R}) \right\} G = \delta(\mathbf{r} - \mathbf{r}') \delta(s - s')$$

(s' here is the origin of s).

(2.6)

Now $\ln \Theta$ simply represents an infinite potential wall and the problem amounts to solving

$$\left(\frac{\partial}{\partial s} + \frac{l}{6} \nabla^2 \right) G = \delta(\mathbf{r} - \mathbf{r}') \delta(s - s') \quad (2.7)$$

where G is to be constructed from eigenfunctions which vanish at and outside the walls of the box. Thus

$$\begin{aligned} G &= \left(\frac{2}{R}\right)^3 \sum_1^\infty \sum_1^\infty \sum_1^\infty \sin\left(\frac{n_1 \pi x}{R}\right) \sin\left(\frac{n_1 \pi x'}{R}\right) \sin\left(\frac{n_2 \pi y}{R}\right) \sin\left(\frac{n_2 \pi y'}{R}\right) \sin\left(\frac{n_3 \pi z}{R}\right) \\ &\quad \times \sin\left(\frac{n_3 \pi z'}{R}\right) \exp\left\{-\frac{l \pi^2}{6 R^2} (n_1^2 + n_2^2 + n_3^2) L\right\} \end{aligned} \quad (2.8)$$

where $R^3 = V$. Thus, relative to a free chain,

$$\Omega = \left(\frac{2}{R}\right)^3 \sum_{\text{odd}} \sum_{\text{odd}} \sum_{\text{odd}} \left(\frac{2R}{\pi n_1}\right)^2 \left(\frac{2R}{\pi n_2}\right)^2 \left(\frac{2R}{\pi n_3}\right)^2 \exp\left\{-\frac{l \pi^2}{6 R^2} (n_1^2 + n_2^2 + n_3^2) L\right\}. \quad (2.9)$$

Two limiting cases are $L \sim 0$, i.e. $L \ll R$ and $L \gtrsim R$. In the first, the sum can be replaced by an integral and

$$\ln V + \text{constants} = \ln \Omega \quad (2.10)$$

in the second, only $n_1 = n_2 = n_3 = 1$ is significant and

$$\ln \Omega = -\frac{l \pi^2}{2 R^2} L - \ln V + \text{constants}. \quad (2.11)$$

Since in the present problem $F = -TS$, one has, for $Ll \ll R^2$,

$$F = -\kappa T \ln V + \text{constants} \quad (2.12)$$

$$PV = \kappa T \quad (2.13)$$

whilst for $Ll \gg R^2$

$$F = \kappa T \left(\frac{Ll}{R^2} \right) \frac{\pi^2}{2} - \kappa T \ln V \quad (2.14)$$

$$PV = \frac{\pi^2}{3} \left(\frac{Ll}{R^2} \right) \kappa T + \kappa T \quad (2.15)$$

the single κT being a negligible addition to the main term. Thus the pressure is like that of a perfect gas of

$$m = \frac{\pi^2}{3} \left(\frac{Ll}{R^3} \right) \text{ molecules}$$

where

$$m^{3/2} \propto \left\{ \frac{\text{natural mean volume of polymer molecule}}{\text{volume of gas}} \right\}. \quad (2.16)$$

This result seems at first sight very reasonable. The molecule moves around the box as a unit, until the box is of the order of its free size, and the pressure thereupon increases as the box gets smaller. However, it must be noticed that the probability distribution of the ends and indeed of any intermediate points tends to a $\sin^2(\pi x/R) \sin^2(\pi y/R) \sin^2(\pi z/R)$ distribution as L becomes very large and is not the uniform distribution which one usually expects. This, however, is to be expected once one bases the calculation on summing all possible states with equal weight. Since any chain reaching the boundary will have a finite probability of crossing it, the only way to forbid crossing is that the density reach zero at the walls. We notice the difference between this case and the trajectory of a random-flight particle. As time goes by a random flight will fill the box with uniform density because whenever the flight reaches the wall it is reflected. This problem has a G made of the cosines rather than sines. The thermodynamic problem can only be considered as an ensemble of random flights by deleting all those flights which reach the wall. A consequence of the non-uniformity is that the free energy does not satisfy the condition $F = Vf(\rho)$, i.e.

$$F = Vf \left(\frac{Ll^2}{V} \right). \quad (2.17)$$

This situation is perfectly satisfactory for a single molecule trapped in some interstitial position, but it is clear that a normal polymerized material does not have uniform density and its free energy will not satisfy (2.17). As remarked in the introduction there seems a paradox here, since for very long strands of material, or cross-linked material in which the cross links are permitted to move or alternatively to be created so slowly that they leave the system in a condition of thermal equilibrium, it should not matter greatly if the system is treated as one vast molecule. This is considered further in the next section.

3. Real systems

To discuss the behaviour of a macroscopic polymerized system, the mode of approach given by Edwards (1967) will be followed. Suppose one did have a very long polymer which

would on average be highly entangled with itself. Let us suppose that this polymer were made by fusing the ends of a large number of sub-polymers which were each small compared with the box and so took up uniform density. Then the presence of all the entanglements would preclude the system from taking up the non-uniform density of (2.8) except on an enormously long time scale, and we can stop it altogether by closing the molecule into one very long highly entangled loop. Suppose there is some specification C describing the (permanent) entanglements so that if Ω_C is the number of configurations permitted under C and p_C the probability of C occurring

$$S = \kappa \sum_C p_C \ln \Omega_C - \kappa \sum_C p_C \ln p_C \quad (3.1)$$

where the second term in S is the 'entropy of formation of the ensemble' and is of constant value in any subsequent history, so can be disregarded. Thus

$$F = -\kappa T \sum_C p_C \ln \Omega_C + \text{constant}. \quad (3.2)$$

Now suppose the volume changes. The probability p_C is laid down initially and does not change, so that

$$\frac{\partial F}{\partial V} = -\kappa T \sum_C p_C \left(\frac{1}{\Omega_C} \frac{\partial \Omega_C}{\partial V} \right). \quad (3.3)$$

If the system had all states equally weighted (as in normal statistical mechanics when the constraints were 'frozen' by closing the polymer or by some degree of cross linking, then

$$p_C = \frac{\Omega_C}{\sum_{C'} \Omega_{C'}} \quad (3.4)$$

so that for infinitesimal changes of volume

$$\frac{\partial F}{\partial V} = -\kappa T \sum_C \frac{1}{\sum_{C'} \Omega_{C'}} \frac{\partial \Omega_C}{\partial V} \quad (3.5)$$

$$= -\kappa T \frac{1}{\sum_{C'} \Omega_{C'}} \frac{\partial}{\partial V} \sum_C \Omega_C. \quad (3.6)$$

Now

$$\sum_{C'} \Omega_{C'} = \Omega \quad (3.7)$$

the total number of configurations, hence

$$\frac{\partial F}{\partial V} = -\kappa T \frac{\partial \ln \Omega}{\partial V}. \quad (3.8)$$

Thus for the purpose of calculating the pressure for an infinitesimal deformation from creation, one may use

$$S = \kappa \ln \Omega \quad (3.9)$$

where Ω is the total number of states permitted under the conditions in which the system was created. This will not be true for an arbitrarily created system in which (3.4) is not strictly satisfied.

At this point consider a fragment of the chain. Let us suppose that the motion of a piece of this chain will be influenced by its immediate surroundings but not by far distant parts of the system. Suppose at any one time its configuration is $\mathcal{R}(s)$. Then subsequently its surroundings will confine $\mathbf{R}(s)$ to be near $\mathcal{R}(s)$. Suppose this confinement is rather weak and assume it is due to a series of segments labelled j . Then the number of states of $\mathbf{R}(s)$ will be

$$\exp \left\{ -\frac{3}{2l} \int \dot{\mathbf{R}}^2(s) ds \right\} \prod_j \prod_s C_j \{ \mathbf{R}(s) - \mathcal{R}(s) \}. \quad (3.10)$$

Now one may write $\prod_j \prod_s C_j$ as

$$\exp \sum_j \sum_s \ln C_j \quad (3.11)$$

and it seems possible that C will be analytic and can be expanded in terms of $\{\mathbf{R}(s) - \mathcal{R}(s)\}^2$ and that only the first term need be kept. The coefficient, since all the j segments will behave equally and (under weak conditions) independently, will be proportional to the density, so one has

$$\exp\{-\rho C \int ds \{\mathbf{R}(s) - \mathcal{R}(s)\}^2\} \quad (3.12)$$

where C is a constant and $\rho = N/V = L/Vl$. There is no harm in considering the number of configurations available to $\mathbf{R}(s)$ and $\mathcal{R}(s)$ though this counts the free chains twice, for these only add constants of the type taken out by \mathcal{N} in § 2. The chains may now be taken as free since the effect of the box is in effect wholly contained in the constraint. (A more elaborate argument is given by Edwards (1967).) Then one may look at $G(\mathbf{r}, \mathbf{r}'; \mathbf{z}, \mathbf{z}'; L)$ which satisfies the differential equation

$$\left\{ \frac{\partial}{\partial s} + \frac{l}{6} \nabla^2 + C\rho(\mathbf{r} - \mathbf{z})^2 \right\} G = \delta(\mathbf{r} - \mathbf{r}')\delta(L - L'). \quad (3.13)$$

One may change variables to $\mathbf{r} + \mathbf{z}$ and $\mathbf{r} - \mathbf{z}$, and discard the former, leaving

$$G = \mathcal{N} \sum_{n=0}^{\infty} \text{He}_n(\mathbf{r} - \mathbf{z}) \text{He}_n(\mathbf{r}' - \mathbf{z}') \exp(-\omega_n L) \quad (3.14)$$

where He_n is the n th Hermite polynomial and

$$\omega_n = l^{1/2} \left(\frac{2C}{3} \right)^{1/2} \rho^{1/2} (n + \frac{1}{2}). \quad (3.15)$$

Therefore, in the limit of large L , the $n = 0$ term dominates and

$$S = -\kappa \left(\frac{C}{6} \right)^{1/2} L(\rho l)^{1/2} + \kappa \ln V \quad (3.16)$$

and

$$PV = \kappa T \frac{1}{2} \left(\frac{C}{6} \right)^{1/3} L(\rho l)^{1/2} + \kappa T \quad (3.17)$$

$$= N\kappa T \left\{ \frac{1}{2} \left(\frac{C}{6} \right)^{1/2} l^{3/2} \rho^{1/2} \right\} + \kappa T. \quad (3.18)$$

This law now does satisfy the usual thermodynamic structure. It is of course based on the approximation (3.12), but it is clear that if more elaborate calculations were performed that any kind of argument like that preceding (3.12) will always lead to a thermodynamic formula since it supposes that the thermodynamic situation exists. For example, it could be held that under dense conditions that the 'potential well' between \mathbf{R} and \mathcal{R} must have a range such that the mean separation of $\mathbf{R} - \mathcal{R} = \mathbf{q}$, say, will be such that $q^2 L \sim V$. That argument would lead to

$$PV \propto N\kappa T(l^3 \rho) \quad (3.19)$$

again in the correct form.

It should perhaps be also remarked that the forces present between non-adjacent links will tend to counteract the non-uniform distribution of § 2, even when the conditions of § 2 are fully obeyed.

4. Conclusion

This paradox between the results of § 2 and § 3 depends on time scales. Given an enormously long polymer, if one waits long enough it will settle down to the distribution of § 2. But this, because of knots and entanglements, will take an unimaginably long time and in practice, if at some initial time the polymer has a uniform mean density, it will keep this effectively for ever. In this state a single very long molecule is a reasonable model for an entangled system of shorter molecules, or a cross-linked system which is in effect a single multiply branched molecule. But for physically reasonably sized molecules, the work of § 2 is significant if they find themselves in a (microscopic) volume which inhibits them from the free configurations, provided they are sufficiently small in size so that they can take up all configurations in a sufficiently small time, and of course set it in an environment which is stable over this period of time. Thus, though the work of § 2 is mainly of theoretical interest, it may have applications in certain special conditions.

Acknowledgments

The authors would like to thank R. Collins and M. A. Oliver for several helpful and illuminating discussions of this work.

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