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The velocity distribution function for a polymer chain

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Abstract. The Gibbs distribution for a polymer molecule contains implicitly the correlation functions for velocity and position of the constituent monomers. The purely spatial part, ignoring potentials, gives the random flight distribution; in this paper the velocity correlation function is calculated, exploiting the markovian structure of the problem in phase space. It is shown that the problem can be reduced to an eigenfunction problem and hence solved. The form of the correlation function is quite accurately given by

$$(v_{n_1} - v_{n_2})^2 = (2kT/m)\{1 - \exp(-c|n_1 - n_2|)\}$$

where v_{n_1} , v_{n_2} are the velocities of the n_1 th and n_2 th monomers and $c \cong 1$.

1. Introduction

This paper concerns several points of interest which arise when calculating the distribution function of a polymer which can be represented without loss of generality, by a chain of rigid rods. In order to investigate the dynamics of a polymer molecule a model was constructed (Edwards and Goodyear 1972, hereafter called I). The model is shown in figure 1. The Gibbs distribution for this problem in the absence of potentials is discussed in I. In the case of the discrete rods shown in figure 1 the distribution function is

$$f_{eq} = \prod_n \delta\{(\mathbf{r}_n - \mathbf{r}_{n-1}) \cdot (\mathbf{v}_n - \mathbf{v}_{n-1})\} \prod_n \delta\{(\mathbf{r}_n - \mathbf{r}_{n-1})^2 - l^2\} \delta\left(E - \frac{1}{2}m \sum_n \mathbf{v}_n^2\right) \tag{1.1a}$$

passing into the continuous limit gives

$$f_{eq} = \prod_s \delta(\mathbf{r}'(s) \cdot \mathbf{v}'(s)) \prod_s \delta(\mathbf{r}'^2(s) - l) \delta\left(E - \frac{m}{2} \int \mathbf{v}^2(s) \frac{ds}{l}\right). \tag{1.1b}$$

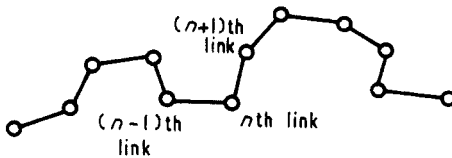


Figure 1.

It was shown that this distribution function is the solution of a Fokker-Planck equation

$$\left\{ \frac{\partial}{\partial t} + \int v(\omega) \frac{\partial}{\partial r(\omega)} d\omega - \frac{2kT}{ml} \int \omega^2 r(\omega) \frac{\partial}{\partial v(\omega)} d\omega - \int \frac{\partial}{\partial v(\omega)} D(\omega) \left(\frac{\partial}{\partial v(-\omega)} + \frac{3mv(\omega)}{4kT} \right) \right\} f = 0 \quad (1.2)$$

this equation being derived from a stochastic Liouville equation

$$\left(\frac{\partial}{\partial t} + \int v(s) \frac{\partial}{\partial r(s)} ds - \int \frac{F(s)}{m} \frac{\partial}{\partial v(s)} ds \right) f([r(s)], [v(s)], t) = 0$$

$$(r'(s) \cdot v'(s)) f([r(s)], [v(s)], t) = 0. \quad (1.3)$$

F represents the force experienced by one point on the chain due to interactions with its surroundings. It is to be noted that this force has a systematic as well as a random component, and it is the random part which gives rise to the diffusion.

This paper concerns three main observations, one of which was noted in I. The points are as follows:

(i) The total energy of the chain drops from $\frac{3}{2}NkT$ to $\frac{2}{2}NkT$. This is caused by the constraint $\delta(r'(s) \cdot v'(s))$ acting on each link.

(ii) The velocity correlation function is not strictly a δ function on the length of the chain. It would seem to go like $1 - \exp(-cq)$.

(iii) The effect of the constraint $\delta(r'(s) \cdot v'(s))$ does not destroy the independence of the r and v distribution.

2. Integral equation for the chain

We shall give a short summary of the facts as presented in I. The kinetic energy of the chain is

$$E = \frac{1}{2} \sum_n m \dot{r}_n^2 \quad (2.1)$$

and the Lagrangian of the chain (including the constraint)

$$L = \frac{1}{2} \sum_n m \dot{r}_n^2 + \frac{1}{2} \sum_n p_n \{ (r_n - r_{n-1})^2 - l^2 \}. \quad (2.2)$$

The p_n are Lagrange multipliers used to include the constraint

$$(r_n - r_{n-1})^2 = l^2. \quad (2.3)$$

The Lagrange equations of motion for the p_n were derived, and used to obtain the stochastic Liouville equation (1.3). It was shown how a Fokker-Planck equation could then be derived (1.2). The solution of the equation was shown as

$$f_{eq} = \prod_n \delta(r'(s) \cdot v'(s)) \prod_n \delta(r'^2(s) - 1) \delta \left(E - \frac{m}{2} \int v^2(s) \frac{ds}{l} \right). \quad (2.4)$$

Now we can use this distribution function to calculate the free energy

$$\exp \left(-\frac{F}{kT} \right) = \int \dots \int \exp \left(-\frac{H}{kT} \right) \prod_n \delta(r'(s) \cdot v'(s)) \prod_n \delta(|r_n - r_{n-1}| - l) \prod_n dr_n dv_n \quad (2.5)$$

change variables

$$r_n \rightarrow (r_n - r_{n-1}) = t_n$$

then since the angle between t_n and $(v_n - v_{n-1})$ does not appear other than in $\delta\{(r_n - r_{n-1}) \cdot (v_n - v_{n-1})\}$ one may replace it by its angular integrated average

$$\exp\left(-\frac{F}{kT}\right) = \int \prod_n \frac{\exp(-H/kT)}{|v_n - v_{n-1}|} \delta(t_n - a) \prod_n dt_n dv_n. \tag{2.6}$$

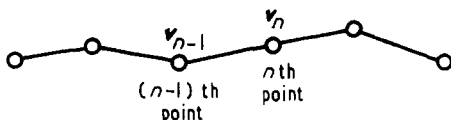
We may simplify this further by integrating out the t_n leaving only an integral equation for the v_n .

$$\exp\left(-\frac{F}{kT}\right) = (2\pi a^2)^n \int \prod_n \frac{\exp(-H/kT)}{|v_n - v_{n-1}|} \prod_n dv_n. \tag{2.7}$$

In future we shall call the constant \mathcal{N} .

The form of this integral equation allows the integration process to be performed in steps. The process is markovian and therefore dependent only on the conditions at the previous link.

Consider the integration at the n th link.



$$C_n \int \prod_n \left\{ \exp\left(-\frac{mv_{n+1}^2}{4kT}\right) \frac{1}{|v_n - v_{n-1}|} \exp\left(-\frac{mv_n^2}{4kT}\right) \right\} \prod_n dv_n = C_n \int \prod_n M(v_{n+1}, v_n) \prod_n dv_n. \tag{2.8}$$

In this expression $M(v_{n+1}, v_n)$ represents a transfer matrix and C_n contains the contributions of the previous n integrations. Hence M is the effect of the $(n + 1)$ th link. After n links we find

$$\phi_n(v_n) = \int M(v_n, v_{n-1})M(v_{n-1}, v_{n-2}) \dots \prod_{m < n} dv_m \tag{2.9}$$

and

$$\phi_{n+1}(v_{n+1}) = \int M(v_{n+1}, v_n)\phi_n(v_n) dv_n. \tag{2.10}$$

It is this integral equation which we shall use to evaluate the total energy. To solve this equation we define functions

$$\phi_{n+1}(v_{n+1}) = A^{-n-1}\psi(v_{n+1}) \tag{2.11}$$

which in turn give

$$\psi(v_{n+1}) = A \int M(v_{n+1}, v_n)\psi(v_n) dv_n. \tag{2.12}$$

By using the identity

$$\nabla_u^2 \frac{1}{|u-v|} = -4\pi \delta(u-v) \tag{2.13}$$

we are able to transform (2.13) into a partial differential equation

$$\nabla^2 \exp\left(\frac{mv^2}{4kT}\right) \psi(v) + 4\pi A \exp\left(-\frac{mv^2}{4kT}\right) \psi(v) = 0 \tag{2.14}$$

and if we write

$$\Psi = \exp\left(\frac{mv^2}{4kT}\right) \psi$$

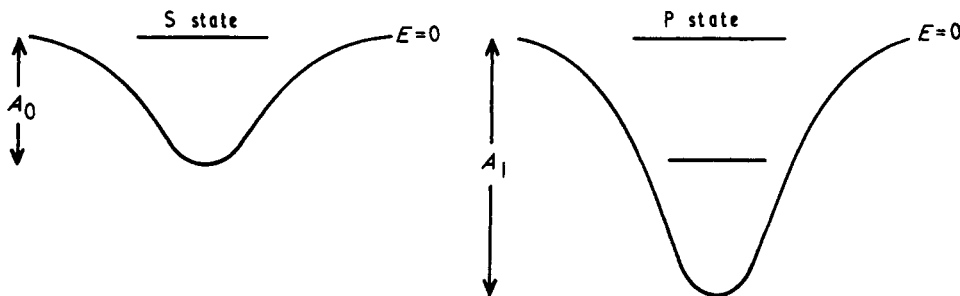
the equation becomes

$$\left\{ \nabla^2 + 4\pi A \exp\left(-\frac{mv^2}{2kT}\right) \right\} \Psi = 0 \tag{2.15}$$

which resembles a Schrödinger equation

$$(\nabla^2 + Q(v) - E)\Psi(v) = 0. \tag{2.16}$$

If we vary the strength of the potential A we shall cause the magnitudes of the eigenvalues to vary. As A is varied the eigenvalues in turn pass through zero. Thus there will be a lowest value A_0 which makes the lowest eigenvalue $E = 0$ (s wave), then for a deeper well there will be an A_1 which makes the next highest state (or usually states, because of degeneracy in angle) have eigenvalue zero.



Hence there are a set of states Ψ_α , and A values A_α corresponding to the zero eigenvalue. We can show that these states obey the usual orthogonality conditions. Thus multiplying equation (2.15) by Ψ_β , and the similar equation in E_β by Ψ_α :

$$(A_\alpha - A_\beta) \int \exp\left(-\frac{mv^2}{2kT}\right) \Psi_\alpha \Psi_\beta \, dv = 0 \quad \alpha \neq \beta. \tag{2.17}$$

$$\int \exp\left(-\frac{mv^2}{2kT}\right) \Psi_\alpha \Psi_\beta \, dv = 0$$

$$\int \psi_\alpha \psi_\beta \, dv = 0. \tag{2.18}$$

All the states are real, so one does not need ψ^* , Ψ^* . At this point one can see the general solution, for at any given point v_m , there is a probability distribution

$$\phi_m(v_m) = \sum_{\alpha} \phi_{\alpha} \psi_{\alpha} \quad (2.19)$$

then at a point v_{l+m} one has

$$\phi_{l+m}(v_{l+m}) = \sum_{\alpha} \phi_{\alpha} \psi_{\alpha} A_{\alpha}^{-l} \quad (2.20)$$

if we write $A_{\alpha} = \exp(\epsilon_{\alpha})$

$$\phi_{l+m}(v_{l+m}) = \sum_{\alpha} \phi_{\alpha} \psi_{\alpha} \exp(-\epsilon_{\alpha} l). \quad (2.21)$$

The function M is thus

$$M(v_n, v_{n-1}) = \sum_{\alpha} \psi_{\alpha}(v_n) \psi_{\alpha}(v_{n-1}) \exp(-\epsilon_{\alpha}) \quad (2.22)$$

whereas the normal orthogonality and completeness gives

$$\delta(v_n - v_{n-1}) = \sum_{\alpha} \psi_{\alpha}(v_n) \psi_{\alpha}(v_{n-1}). \quad (2.23)$$

3. The total energy of the chain

Consider for a moment the expression

$$\exp\left(-\frac{F}{kT}\right) = \mathcal{N} \int \prod_n \frac{\exp(-H/kT)}{|v_n - v_{n-1}|} \prod_n dv_n. \quad (3.1)$$

The dimensions of the integral are of order v^{2N} , that is, E^N

$$\exp\left(-\frac{F}{kT}\right) \sim (kT)^N \times \text{constants.}$$

$$F \sim -NkT \ln kT \quad (3.2)$$

and thus we find $U = NkT$ as against the value of $\frac{3}{2}NkT$ for N unconnected points. Clearly the effect of the constraint is to lose $\frac{1}{3}$ of the internal degrees of freedom of the chain.

We shall prove this in a more rigorous form by using the ψ formalism. Whatever the initial distribution the value of ϕ must settle down to be a multiple of ψ_0 since the factor $\exp(-\epsilon_0 p)$ will dominate relative to $\exp(-\epsilon_{\alpha} p)$ as p becomes large.

The mean kinetic energy at any point $\langle \frac{1}{2} m u_p^2 \rangle$ is

$$\frac{\frac{1}{2} m \int u^2 \psi_0^2(u) d^3 u}{\int \psi_0^2(u) d^3 u} = \frac{\frac{1}{2} m \int u^2 \Psi_0^2 \exp(-mu^2/2kT) d^3 u}{\int \Psi_0^2 \exp(-mu^2/2kT) d^3 u}. \quad (3.3)$$

But Ψ_0 satisfies a Rayleigh-Ritz principle (see Landau and Lifshitz 1965).

$$E = \frac{-\int (\nabla \Psi_0)^2 d^3 u - 4\pi A_0 \int \Psi_0^2 \exp(-mu^2/2kT) d^3 u}{\int \Psi_0^2 \exp(-mu^2/2kT) d^3 u}. \quad (3.4)$$

Now the variational principle requires $\delta E = 0$ and the definition of A_0 requires $E = 0$.

Redefine A_0 as a_0/T and $E = \epsilon/T$. By varying with respect to T we can prove that

$$-\frac{\delta \epsilon}{T^2} = 0 = 0 + a_0 \delta T \left(\frac{1}{T^2} \int \Psi_0^2 \exp\left(-\frac{m\mathbf{u}^2}{2kT}\right) d^3\mathbf{u} - \frac{1}{kT^3} \int \frac{m\mathbf{u}^2}{2} \Psi_0^2 \exp\left(-\frac{m\mathbf{u}^2}{2kT}\right) d^3\mathbf{u} \right). \quad (3.5)$$

This implies

$$\begin{aligned} \frac{1}{kT} \int \frac{m\mathbf{u}^2}{2} \Psi_0^2 \exp\left(-\frac{m\mathbf{u}^2}{2kT}\right) d^3\mathbf{u} &= \int \Psi_0^2 \exp\left(-\frac{m\mathbf{u}^2}{2kT}\right) d^3\mathbf{u} \\ \frac{\int \frac{1}{2}m\mathbf{u}^2 \psi_0^2 d^3\mathbf{u}}{\int \psi_0^2 d^3\mathbf{u}} &= kT. \end{aligned} \quad (3.6)$$

4. Velocity correlation along the chain

We can calculate the velocity correlation between two points on the chain using the ψ formalism. The power of this method lies in the fact that it avoids the difficult integrals caused by the constraint

$$\prod_s \delta(\mathbf{r}'(s) \cdot \mathbf{v}(s)).$$

The total distribution function for the chain can be represented by integrating the M over the whole length of the chain

$$\langle \mathbf{v}_n \mathbf{v}_m \rangle = \frac{\int \dots \int M \dots M \mathbf{v}_n M \dots M \mathbf{v}_m M \dots M \Pi_n d\mathbf{v}_n}{\int \dots \int M \dots M 1 M \dots M 1 M \dots M \Pi_n d\mathbf{v}_n}. \quad (4.1)$$

We shall use the ψ representation of M

$$M(\mathbf{v}_n \mathbf{v}_{n-1}) = \sum_{\alpha} \psi_{\alpha}(\mathbf{v}_n) \psi_{\alpha}(\mathbf{v}_{n-1}) \exp(-\epsilon_{\alpha}). \quad (4.2)$$

Now integrate up to the $(n-1)$ th link and down to the $(m+2)$ th link.

$$\begin{aligned} \langle \mathbf{v}_n \mathbf{v}_m \rangle &= \frac{\int \dots \int \exp\{(\infty+n)\epsilon_0\} \psi_0(\mathbf{v}_m) \mathbf{v}_m M \dots M \mathbf{v}_m \psi_0(\mathbf{v}_m) \exp\{-(\infty+m)\epsilon_0\} \Pi_k d\mathbf{v}_k}{\int \dots \int M \dots M 1 M \dots M 1 M \dots M \Pi_k d\mathbf{v}_k} \\ &= \sum_{\alpha} \int \int \psi_0(\mathbf{v}_m) \mathbf{v}_m \psi_{\alpha}(\mathbf{v}_n) \psi_{\alpha}(\mathbf{v}_m) \psi_0(\mathbf{v}_m) \exp\{(\epsilon_0 - \epsilon_{\alpha})|n-m|\}. \end{aligned} \quad (4.3)$$

Or using a quantum mechanical notation

$$\langle \mathbf{v}_n \mathbf{v}_m \rangle = \sum_{\alpha} |v_{0\alpha}|^2 \exp\{(\epsilon_0 - \epsilon_{\alpha})|n-m|\} \quad \epsilon_{\alpha} > \epsilon_0. \quad (4.4)$$

Now if we find $n = m$ one has

$$\sum_{\alpha} |v_{0\alpha}|^2 = |v^2|_{00} = kT \quad (4.5)$$

which gives the total energy of the chain.

By saying $n = m$ we are implying no velocity correlation between links of the polymer. If, however, there is a correlation then we can more easily observe the distribution by Fourier transforming with respect to length.

Let $|n - m| = s$

$$|v(\omega)|^2 = \int_{\alpha} |v_{0\alpha}|^2 \exp\{(\epsilon_0 - \epsilon_{\alpha})|n - m| + i\omega s\} ds = \sum_{\alpha} \frac{|v_{0\alpha}|^2 (\epsilon_0 - \epsilon_{\alpha})}{(\epsilon_0 - \epsilon_{\alpha})^2 + \omega^2}. \tag{4.6}$$

Note that integration over the ω variable gives kT as the total energy of the chain.

To examine this distribution we need to find values for ϵ_0 and ϵ_{α} . In order to do this we must solve a nonstandard Schrödinger equation (2.15). The eigenvalues of square-box and harmonic-well potentials are given in standard texts (eg Landau and Lifshitz 1965).

For low values of potentials, the eigenvalues of the potentials are not too dependent on the exact shape of the potential. For this reason we can solve our equation by expanding the exponential and treating the equation as an harmonic oscillator equation

$$\left\{ \frac{1}{2} \nabla^2 - 2\pi A_{\alpha} - \frac{1}{2} \left(\frac{2\pi m A_{\alpha}}{kT} \right) u^2 \right\} \Psi_{\alpha} = 0. \tag{4.7}$$

The solution occurs when

$$2\pi A_{\alpha} = (n_1 + n_2 + n_3 + \frac{3}{2}) \left(\frac{2\pi m A_{\alpha}}{kT} \right)^{1/2} \tag{4.8}$$

where n_1, n_2, n_3 are integers. This implies

$$A_{\alpha} = \frac{m}{2\pi kT} (n_1 + n_2 + n_3 + \frac{3}{2})^2. \tag{4.9}$$

We shall assume that we only need the first two eigenvalues ψ_0 and $\psi_1 = v\psi_0$; hence only the $\alpha = 1$ term survives. The ratio of the two values

$$\frac{A_1}{A_0} = \frac{(\frac{5}{2})^2}{(\frac{3}{2})^2} = (\frac{5}{3})^2 \tag{4.10}$$

and

$$|v_{01}|^2 = |v_{00}|^2 = kT.$$

Therefore

$$\langle v_m v_n \rangle = kT \exp\{-\ln(25/9)|m - n|\}$$

and

$$\langle (v_m - v_n)^2 \rangle = 2kT[1 - \exp\{-\ln(25/9)|m - n|\}]. \tag{4.11}$$

Although actual results depend on the exact solution of equation (2.15), these approximate results give a clear indication of what happens. It is interesting to note $\ln(25/9) \sim 1$ so that the correlation of velocities of points q steps apart goes like $1 - \exp(-q)$ and this function dies quickly and dimensionlessly. We are able to redefine the step length of the chain in order to reduce the correlation between the redefined 'links'.

5. The interdependence of the spatial and velocity correlations

It remains to be shown that the constraint $\Pi_n \delta(r'(s) \cdot v'(s))$ does not destroy the independence of the spatial and velocity correlations. One can easily generalize the

kernel M to

$$\mathcal{M}((\mathbf{r}_n - \mathbf{r}_{n-1}), \mathbf{v}_{n+1}, \mathbf{v}_n). \tag{5.1}$$

We shall effect the solution by Fourier transform on the r variable

$$\mathcal{M}(\mathbf{k}, \mathbf{v}_{n+1}, \mathbf{v}_n).$$

This kernel can be separated as

$$a(\mathbf{k})M(\mathbf{v}_{n+1}, \mathbf{v}_n)$$

and the generalization of equation (2.12)

$$\psi_\alpha(\mathbf{v}) = \int A_\alpha^{-1}(\mathbf{k})a(\mathbf{k})M(\mathbf{v}'\mathbf{v})\psi_\alpha(\mathbf{v}') d\mathbf{v}' \tag{5.2}$$

which implies

$$A_\alpha(\mathbf{k}) = \frac{1}{a(\mathbf{k})}A_\alpha. \tag{5.3}$$

Hence it is that the probability of finding $\mathbf{r}_n = \mathbf{R}$ and $\mathbf{r}_m = \mathbf{R}'$ separates from the v dependence completely, and yields $a^{n-m}(\mathbf{k})$. Back Fourier transformation of this distribution gives the spatial distribution independently of the velocity distribution.

6. Conclusions

This paper grew out of several mathematical points concerning a model of a polymer molecule as suggested in I. The formalism used to solve these problems is especially suggestive to the solution of other problems of macromolecules.

It is hoped that this paper illustrates some interesting new results about statistical mechanics of systems with constraints as opposed to the statistical mechanics of points.

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References

- Edwards S F and Goodyear A G 1972 *J. Phys. A: Gen. Phys.* **5** 965-80
 Landau L D and Lifshitz E M 1965 *Quantum Mechanics* (London: Pergamon)