

## The dynamics of a polymer molecule

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1972 J. Phys. A: Gen. Phys. 5 965

(<http://iopscience.iop.org/0022-3689/5/7/007>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.73

The article was downloaded on 02/06/2010 at 04:38

Please note that [terms and conditions apply](#).

# The dynamics of a polymer molecule

SF EDWARDS and AG GOODYEAR

Theoretical Physics Department, The Schuster Laboratory, University of Manchester,  
Manchester M13 9PL, UK

MS received 17 January 1972

**Abstract.** This paper is the first of a series discussing different aspects of the dynamics of macromolecules. The different kinds of motion to be expected are classified in terms of the relative magnitudes, expressed in time scales, of inertia, viscosity, barrier energies and temperature. In particular, and as a comparison for other cases, the idealized case of a strictly inextensible, but otherwise freely flexible chain, is solved in detail. The nonlinear nature of the constraint is shown to lead to the generation of a Fokker-Planck equation. This Fokker-Planck equation shows that there are wave-like solutions to the motion for long wave fluctuations in the conformation of the chain (second sound) in the absence of viscosity. In the high viscosity limit the equation has Rouse-like solutions which correspond to short wave changes in conformation. In general, the equilibrium function is modified so that if the chain is considered as a series of connected mass points, the energy is  $kT$  per point, not  $\frac{3}{2}kT$ , a result which though intuitively obvious, is difficult to establish. This idealized model can be related to several realistic cases but a reinterpretation of the constants is involved.

## 1. Introduction

Since polymer molecules occur in so many situations, the special properties of their dynamics are increasingly being studied. Several important and awkward points of principle arise in the study of their dynamics but the different physical regimes that could arise are of very different importance in applications. Thus great attention has been paid to the dynamics of a polymer in a dilute solution, but little to 'cold' polymers, or to a gas of 'hot' polymers. A discussion of the validity of any treatment, however, naturally takes one to the border of its validity, and one gains great insight by studying the behaviour outside the region of immediate importance. These other regions are of importance in themselves, particularly as the range of polymer studies increases. In this paper we shall try to describe the different regimes that can arise, what physical parameters determine the regimes, and how a polymer moves in the different regimes. Many of the physical features of the systems encountered in practice will still be omitted, or treated cursorily, since they need a much more elaborate discussion to do them justice. In particular the complexities of hydrodynamic interaction and of entanglements will be treated in a later paper.

In the model considered, the polymer is a series of monomers with an energy barrier between different configurations, and is immersed in a solvent of a given viscosity. The monomers will be characterized by a length  $l$ . Although several lengths could come into the problem, they will all be of the same magnitude, and will not be distinguished at this stage. The monomer will have a mass,  $m$ , and if its moment of inertia is important

it will be taken to be of the order of  $ml^2$ . The system is characterized in energy by  $kT$ , and by the (lowest) energy barrier encountered,  $Q$  say. Finally there is a viscosity,  $\nu$ , which will appear with the dimensions  $MT^{-1}$ . The three quantities  $kT$ ,  $Q$ ,  $\nu$  can be used to recognize three times  $t_1 = (ml^2/2kT)^{1/2}$ ,  $t_2 = m/\nu$  and  $t_3 = (ml^2/2Q)^{1/2}$ . Six regimes can now be distinguished

(i)  $t_3 > t_1 > t_2$

This is the system commonly studied in which inertia is ignored, and barriers are considered negligible. The initial understanding in this type of model was obtained in the classic papers by Rouse (1953), Beuche (1954) and Zimm (1956). The Rouse model typifies the regime which applies to warm polymer solutions.

(ii)  $t_1 > t_3 > t_2$

This is the case of a cold polymer solution in which the segments hop, under thermal fluctuation, from configuration to configuration, over the barrier and against the viscosity.

(iii)  $t_2 > t_3 > t_1$

This is a case of an isolated hot polymer which has no viscous drag, but freely changes configuration by mounting the barrier. The viscosity and diffusive forces are both supplied by the nonlinearity of the equations of motion which have an inertial origin.

(iv)  $t_3 > t_2 > t_1$

Here is the case of a hot polymer in the vapour phase, and which is freely flexible. It is not really distinguishable from case (iii), since in a hot vapour both  $t_3$  and  $t_2$  can be neglected.

(v)  $t_1 > t_2 > t_3$

This is the cold polymer in solution whose motion comes from occasional changes in configuration across the potential barrier, against the viscosity. In this case we do not ignore inertia as is done in case (iii).

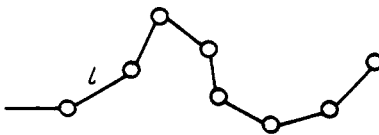
(vi)  $t_2 > t_1 > t_3$

This is the case of an isolated cold chain, and as such is not readily studied. It will apply to cold rubbers and glasses except in as much as neighbouring chains will inhibit the motion.

To start on a detailed study, we shall look in detail at the case of the dynamics of a freely flexible chain. Important points of principle arise in cases (iv) and (iii), and one can easily extend the analysis to case (i).

## 2. The freely hinged chain

The model taken will be that of a set of mass points, separated by a constant distance  $l$ , which are freely hinged



The kinetic energy is  $\frac{1}{2}m\dot{r}_n^2$  and the constraint

$$|r_n - r_{n-1}| = l. \quad (2.1)$$

Thus the Lagrangian is

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

where the  $p_n$  are lagrangian multipliers, the analogue of the pressure of incompressible hydrodynamics. We shall aim to derive Liouville's equation, then the Fokker-Planck equation and finally the diffusion equation of the system. Hence the distribution and correlation functions of the system will be calculated. These will involve probability distributions of the positions and velocities of the  $\mathbf{r}_n$ , hence the additional constraint obtained by differentiating

$$(\mathbf{r}_n - \mathbf{r}_{n-1})^2 = l^2 \quad (2.3)$$

$$(\mathbf{r}_n - \mathbf{r}_{n-1}) \cdot (\dot{\mathbf{r}}_n - \dot{\mathbf{r}}_{n-1}) = 0 \quad (2.4)$$

$$(\dot{\mathbf{r}}_n - \dot{\mathbf{r}}_{n-1})^2 + (\mathbf{r}_n - \mathbf{r}_{n-1}) \cdot (\ddot{\mathbf{r}}_n - \ddot{\mathbf{r}}_{n-1}) = 0. \quad (2.5)$$

One can also difference equation (2.3) to get

$$(\mathbf{r}_n - \mathbf{r}_{n-1})^2 = (\mathbf{r}_{n-1} - \mathbf{r}_{n-2})^2 \quad (2.6)$$

$$(\mathbf{r}_n - 2\mathbf{r}_{n-1} + \mathbf{r}_{n-2}) \{ (\mathbf{r}_n - \mathbf{r}_{n-1}) + (\mathbf{r}_{n-1} - \mathbf{r}_{n-2}) \} = 0 \quad (2.7)$$

and similarly

$$\begin{aligned} & (\mathbf{r}_n - 3\mathbf{r}_{n-1} + 3\mathbf{r}_{n-2} - \mathbf{r}_{n-3})(\mathbf{r}_{n-1} - \mathbf{r}_{n-2}) \\ & - (\mathbf{r}_n - 2\mathbf{r}_{n-1} + \mathbf{r}_{n-2})(\mathbf{r}_n - \mathbf{r}_{n-1}) \\ & - (\mathbf{r}_{n-1} - 2\mathbf{r}_{n-2} + \mathbf{r}_{n-3})(\mathbf{r}_{n-2} - \mathbf{r}_{n-3}) = 0. \end{aligned} \quad (2.8)$$

Now consider the equation of motion from the Lagrangian

$$m\ddot{\mathbf{r}}_n = p_n(\mathbf{r}_n - \mathbf{r}_{n-1}) - p_{n+1}(\mathbf{r}_{n+1} - \mathbf{r}_n). \quad (2.9)$$

If this equation is differenced and a scalar product with  $(\mathbf{r}_n - \mathbf{r}_{n-1})$  taken, one has

$$\begin{aligned} m(\ddot{\mathbf{r}}_n - \ddot{\mathbf{r}}_{n-1}) \cdot (\mathbf{r}_n - \mathbf{r}_{n-1}) &= p_n(\mathbf{r}_n - \mathbf{r}_{n-1}) \cdot (\mathbf{r}_n - \mathbf{r}_{n-1}) - p_{n-1}(\mathbf{r}_{n-1} - \mathbf{r}_{n-2}) \cdot (\mathbf{r}_n - \mathbf{r}_{n-1}) \\ &\quad - p_{n+1}(\mathbf{r}_{n+1} - \mathbf{r}_n) \cdot (\mathbf{r}_n - \mathbf{r}_{n-1}) \\ m(\ddot{\mathbf{r}}_n - \ddot{\mathbf{r}}_{n-1}) \cdot (\mathbf{r}_n - \mathbf{r}_{n-1}) &= -m(\dot{\mathbf{r}}_n - \dot{\mathbf{r}}_{n-1})^2 \\ &= 2p_n(\mathbf{r}_n - \mathbf{r}_{n-1})^2 - p_{n-1}(\mathbf{r}_n - \mathbf{r}_{n-1})(\mathbf{r}_{n-1} - \mathbf{r}_{n-2}) \\ &\quad + p_{n+1}(\mathbf{r}_n - \mathbf{r}_{n-1})(\mathbf{r}_n - \mathbf{r}_{n+1}). \end{aligned} \quad (2.10)$$

These equations take on a simpler form if  $\mathbf{r}_n$  is considered as a continuous function  $\mathbf{r}(s)$ , when, using a prime to denote differentiation with respect to  $s$ , and a dot with respect to  $t$

$$\begin{aligned} \mathbf{r}'^2(s) &= 1 \quad (\text{ie } s \text{ is in units of the length } l) \\ \mathbf{r}'' \cdot \mathbf{r}' &= 0 \\ \mathbf{r}''' \cdot \mathbf{r}' + \mathbf{r}'^2 &= 0 \end{aligned} \quad (2.11)$$

and

$$\begin{aligned} \mathbf{r}' \cdot \dot{\mathbf{r}}' &= 0 \\ \dot{\mathbf{r}}'^2 + \mathbf{r}' \cdot \ddot{\mathbf{r}}' &= 0. \end{aligned}$$

The equation of motion is

$$m\ddot{r} = -p'r' - pr'' \tag{2.12}$$

and is simplified by differentiating

$$m\dot{r}' = -p''r' - 2p'r'' - pr''' \tag{2.13}$$

which can be taken in a product with  $r'$  to give

$$-m\dot{r}'^2 = pr''^2 - p'' \tag{2.14}$$

or

$$\left(\frac{\partial^2}{\partial s^2} - r''^2\right)p = mv'^2. \tag{2.15}$$

In terms of the discrete variables this becomes

$$\begin{aligned} (p_{n+1} - 2p_n + p_{n-1}) - (r_n - r_{n-1})\{(r_{n+1} - 2r_n + r_{n-1}) \\ - (r_n - 2r_{n-1} + r_{n-2})\}p_n = m(\dot{r}_n - \dot{r}_{n-1})^2. \end{aligned} \tag{2.16}$$

This equation (2.15) can be solved with the aid of the boundary condition that  $p = 0$  at both ends of the chain, or the cyclic condition. One can proceed with

$$p = p([r], [v], s).$$

The explicit structure being discussed more fully below. The equations of motion are now expressed in terms of  $r$  and  $v$

$$\begin{aligned} m\dot{v} &= -(pr')' \\ v &= \dot{r} \\ r' \cdot v' &= 0 \end{aligned} \tag{2.17}$$

and so can be deployed into the Liouville form. Let  $f([r], [v], t)$  be the probability that  $r(s, t) = r(s)$  and  $v(s, t) = v(s)$  at the time  $t$ . Then

$$\begin{aligned} \frac{\partial f}{\partial t} + \int ds \frac{\partial}{\partial r(s)} v(s) f - \int ds \frac{\partial}{\partial v(s)} (pr'(s))' f = 0 \\ (r'(s) \cdot v'(s)) f = 0. \end{aligned} \tag{2.18}$$

The first equation being a standard form, whilst the second is a convenient form of (2.4), a Fermi supplementary condition. One may equally write these equations in terms of

$$\begin{aligned} \rho &= r'(s) \quad (\text{ie } \rho_n = (r_n - r_{n-1})) \\ u &= v'(s) \end{aligned} \tag{2.19}$$

$$\begin{aligned} \frac{\partial f}{\partial t} + \int \frac{\partial}{\partial \rho} u f ds - \int \frac{\partial}{\partial u} (p\rho)' f ds = 0 \\ (\rho \cdot u) f = 0. \end{aligned} \tag{2.20}$$

These equations have the equilibrium solution

$$\prod_s \delta(r' \cdot v') \prod_s \phi_s(r'^2(s)) \psi \left( \int v^2(s) ds \right) \tag{2.21}$$

where  $\phi_s$  is any function and need not be anywhere continuous, that is for every  $n$  one may have a different function of  $(\mathbf{r}_n - \mathbf{r}_{n-1})^2$ . This is proved by noticing that since Liouville's equation is linear each term can be taken in turn. The term  $\prod \delta(\mathbf{r}' \cdot \mathbf{v}')$  satisfies the supplementary condition. The second term  $\prod_s \phi(\mathbf{p}^2(s))$  satisfies the equation since

$$\prod \delta(\mathbf{r}' \cdot \mathbf{v}') \frac{\partial \phi}{\partial t} = - \prod \delta(\mathbf{r}' \cdot \mathbf{v}') (\mathbf{u} \cdot \mathbf{p}) \phi' \equiv 0 \quad (2.22)$$

and the last term satisfies the equation because

$$\int \frac{\partial}{\partial \mathbf{v}} \psi \left( \int \mathbf{v}^2 ds \right) \prod_s \delta(\mathbf{r}' \cdot \mathbf{v}') (p \mathbf{r}') ds = \int \prod_s \delta(\mathbf{r}' \cdot \mathbf{v}') p \mathbf{r}' \cdot \mathbf{v}' \frac{\partial \psi}{\partial \mathbf{v}} ds \equiv 0. \quad (2.23)$$

The physical solution is

$$f_e = \prod_s \delta(\mathbf{r}' \cdot \mathbf{v}') \prod_s \delta(\mathbf{r}'^2 - 1) \delta \left( E - \frac{1}{2} m \int \frac{\mathbf{v}^2(s)}{l} ds \right). \quad (2.24)$$

Note the fact that each  $\mathbf{r}'^2 = 1$  has to be put in as a boundary condition on (2.24), and similarly the total energy. The result is trivial, but at this point it is worth evaluating the total energy of the chain. One can see that each mass has lost one degree of freedom, so that instead of  $E = \frac{3}{2} NkT$  one can expect  $E = NkT$ . This is indeed the case, for the entropy

$$\begin{aligned} e^{S/k} &= \int \prod_s d\mathbf{r}_n d\mathbf{v}_n \delta(\mathbf{r}' \cdot \mathbf{v}') \delta(\mathbf{r}'^2 - 1) \delta \left( E - \frac{1}{2} m \sum \mathbf{v}_n^2 \right) \\ &= E^N \times \text{constant} \end{aligned} \quad (2.25)$$

since

$$\begin{aligned} \int \delta(\mathbf{r}'^2 - 1) \delta(\mathbf{r}' \cdot \mathbf{v}') \prod_s d\mathbf{r} &= \int \delta(\mathbf{p}^2 - 1) \delta(\mathbf{p} \cdot \mathbf{v}') \prod_s \delta \mathbf{p} \\ &= \frac{1}{|\mathbf{v}'|} \end{aligned} \quad (2.26)$$

so the dimension of the integral  $\prod_s d^3 \mathbf{v} / |\mathbf{v}'|$  is  $\mathbf{v}^{2N}$ . Thus

$$\begin{aligned} S &= Nk \ln E + \text{constant} \\ E &= NkT \end{aligned}$$

since

$$T = \frac{\partial E}{\partial S}. \quad (2.27)$$

The discussion here has used the microcanonical ensemble. For further progress one must make the transition to the canonical ensemble. For a term like  $\delta(E - \frac{1}{2} m \sum \mathbf{v}_n^2)$  the transition is to  $\exp(-\frac{1}{2} m \sum \mathbf{v}_n^2 / kT)$  and similarly one might think of putting

$$\prod_s \delta(\mathbf{r}'^2 - 1) \rightarrow \exp \left( -\frac{3}{2l} \sum \mathbf{r}'^2 \right) \quad (2.28)$$

but clearly this cannot be valid, for the right hand side is a *precise* constraint on  $(\mathbf{r}_n - \mathbf{r}_{n-1})^2$ , and not a very gentle constraint as is  $\delta(E - \frac{1}{2} m \sum \mathbf{v}_n^2)$  on any one of the  $\mathbf{v}_n$ . The

correct transition to the canonical system comes in the use of Fourier components. Introduce

$$r_n = \sum_u \exp(-2\pi i n u / L) r_u \tag{2.29}$$

$$u = 0, \pm 1, \pm 2 \dots$$

where for convenience the cyclic closed chain will be considered so that

$$\exp(-2\pi i u N l / L) = 1.$$

Thus if  $2\pi u / L = \omega$  and  $n l = s$  for  $0 < |\omega| < \pi / l$ ,  $\omega$  lies in the first cell of reciprocal space.

$$r_u = \frac{1}{2\pi} \sum_n \exp(2\pi i n u / L) r_n \tag{2.30}$$

which in the continuum limit goes over to

$$r(\omega) = \int_{-\infty}^{\infty} e^{-i\omega s} r(s) ds \tag{2.31}$$

$$r(s) = \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i\omega s} r(\omega) d\omega.$$

Now if we consider

$$\begin{aligned} \chi &= \int \delta(r(\omega) - \Sigma) \delta(r^*(\omega) - \Sigma^*) \prod_s \delta(r'^2 - 1) \prod_s \delta r \\ &\quad \times \left( \int \prod_s \delta(r'^2 - 1) \prod_s dr \right)^{-1} \end{aligned} \tag{2.32}$$

one finds

$$\chi = \exp\left(-\frac{3}{2l} \int \omega^2 r(\omega) r^*(\omega) [d\omega]\right) \tag{2.33}$$

or a canonical ensemble of

$$\exp\left(-\frac{3}{2l} \int \omega^2 |r(\omega)|^2 d\omega\right) \tag{2.34}$$

that is

$$P([r]) = \mathcal{N} \exp\left(-\frac{3}{2l} \int r'^2(s) ds\right) \tag{2.35}$$

where  $\mathcal{N}$  is a constant normalization. It now must be understood that this distribution may only be used for the evaluation of quantities which depend on  $\omega$  in the first cell of reciprocal space, that is functions which are defined over large distances correspond to 'small  $\omega$ '. It is well known that functional distributions like (2.35) are equivalent to the diffusion equation. If

$$G(r_1 r_2; s_1 s_2) = \int_{r(s_1)=r_1}^{r(s_2)=r_2} \exp\left(-\frac{3}{2l} \int_0^l r'^2(s) ds\right) \delta r(s) \tag{2.36}$$

$$\frac{\partial G}{\partial s} - \frac{l}{6} \nabla^2 G = \delta(r_2 - r_1) \tag{2.37}$$

where now  $\int (\delta r)$  means integrate over all paths such that  $r(s_2) = r_2$  and  $r(s_1) = r_1$  (all  $[r_n]$  having these end points).

The diffusion equation describes the long distance behaviour of the chain, but not the short, so that the probability for  $r_n, r_{n+M}$  is

$$\exp\left(-\frac{3}{2l^2} \frac{(r_n - r_{n+M})^2}{M}\right) \quad (M \gg l) \quad (2.38)$$

but for  $M = 1$  it must be  $\delta\{(r_n - r_{n+1})^2 - l^2\}$ , which is poorly represented by

$$\exp\left(-\frac{3}{2l^2} (r_n - r_{n+1})^2\right).$$

Returning to  $\delta(E - \frac{1}{2}m\Sigma v_n^2)$  alone, whose canonical form is

$$\exp\left(-\frac{m}{2kT} \Sigma v_n^2\right)$$

there is obviously no difficulty in using the  $v(\omega)$  to get

$$\exp\left(-\frac{m}{2kT} \int |v(\omega)|^2 d\omega\right)$$

so one must derive the canonical form for the full distribution by taking  $r(\omega), v(\omega)$  and first evaluating

$$\frac{\int \delta(r(\omega) - R)\delta(v(\omega) - v)\Pi_s\delta(r'^2 - 1)\Pi_s\delta(r' \cdot v')\delta(E - \frac{1}{2}m\int v^2 ds)\Pi_s dr dv}{\int \Pi_s\delta(r'^2 - 1)\Pi_s\delta(r' \cdot v')\delta(E - \frac{1}{2}m\int v^2 ds)\Pi_s dr dv} \quad (2.39)$$

and the result is as one would expect

$$\exp\left\{-\left(\frac{3}{2l} \int \omega^2 |r(\omega)|^2 d\omega + \frac{3m}{4kT} \int |v(\omega)|^2 d\omega\right)\right\}.$$

Note that the coefficient of  $|v(\omega)|^2$  is not  $m/2kT$  but  $3m/4kT$  (which gives  $kT$  for the energy not  $\frac{3}{2}kT$ ), and there are no terms in  $r' \cdot v'$ . This is because terms in  $r' \cdot v'$  are of order  $1/L$  compared to the  $r'^2$  and  $v^2$  terms kept. The situation here is similar to the transition

$$\Pi\delta(r'^2 - 1) \rightarrow \exp\left\{-\frac{3}{2l} \int r'^2 ds + O\left(\frac{r'^4}{L}\right)\right\}. \quad (2.40)$$

The higher terms that give the small scale structure do not effect large distances. Similarly  $\Pi\delta(r' \cdot v')$  alters the  $v^2$  coefficient, but does not otherwise appear and its precise structure is what results from  $r(\omega) \cdot v(\omega)$  terms. One must now, starting from the Liouville equation, undertake the same steps which in gas dynamics reduce this to the Boltzmann, or more appropriately in our case, the Fokker-Planck equation, an equation whose equilibrium solution is

$$f_{0e} = \mathcal{N} \exp\left(-\frac{3}{2l} \int_0^L r'^2 ds - \frac{3m}{4kT} \int v^2 ds\right). \quad (2.41)$$



### 3. The Fokker-Planck equation for a polymer chain

If the expressions for the pressure (2.15) are averaged and defined by

$$p_0 = \frac{1}{L} \sum_n p_n([\mathbf{r}], [\mathbf{v}]) f_e \prod_n d\mathbf{r}_n d\mathbf{v}_n$$

or

$$p_0 = \frac{1}{L} \int ds p(s, [\mathbf{r}], [\mathbf{v}]) f_e \delta \mathbf{r} \delta \mathbf{v} \quad (3.1)$$

in the continuous form, one may write

$$(\mathbf{p}\mathbf{r}')' = p_0 \mathbf{r}'' + F \quad (3.2)$$

and rewrite (2.18) as

$$\left( \frac{\partial}{\partial t} + \int \mathbf{v} \frac{\partial}{\partial \mathbf{r}} ds - \int p_0 \mathbf{r}'' \frac{\partial}{\partial \mathbf{v}} ds - \int \frac{\partial}{\partial \mathbf{v}} F([\mathbf{r}], [\mathbf{v}], s) ds \right) f = 0. \quad (3.3)$$

If  $F$  is ignored for the moment

$$\left( \frac{\partial}{\partial t} + \int \mathbf{v} \frac{\partial}{\partial \mathbf{r}} ds - \int p_0 \mathbf{r}'' \frac{\partial}{\partial \mathbf{v}} ds \right) f_{0e} = 0 \quad (3.4)$$

provided that

$$p_0 = \frac{2kT}{ml} \quad (3.5)$$

and so indeed it is from (2.15). The situation is now analogous to that of ordinary brownian motion (Chandrasekhar 1943 see also Wax 1954) in a gas

$$\left( \frac{\partial}{\partial t} + \sum_i \mathbf{v}_i \frac{\partial}{\partial \mathbf{r}_i} + \sum_i \frac{\mathbf{F}_i}{m} \frac{\partial}{\partial \mathbf{v}_i} \right) f = 0 \quad (3.6)$$

is the full equation. The Maxwell-Boltzmann solution is  $\exp(-\frac{1}{2}m \sum_i \mathbf{v}_i^2/kT)$  and satisfies

$$\left( \frac{\partial}{\partial t} + \sum_i \mathbf{v}_i \frac{\partial}{\partial \mathbf{r}_i} \right) \exp\left(-\frac{1}{2}m \sum_i \frac{\mathbf{v}_i^2}{kT}\right) = 0. \quad (3.7)$$

This latter equation however only represents free particles, and the single particle equation derived from (3.6) is the Boltzmann or Fokker-Planck equation according to the circumstances. The analogy here is with the Fokker-Planck equation

$$\left\{ \frac{\partial}{\partial t} + \sum_i \mathbf{v}_i \frac{\partial}{\partial \mathbf{r}_i} - \sum_i \frac{\partial}{\partial \mathbf{v}_i} D \left( \frac{\partial}{\partial \mathbf{v}_i} + \frac{m\mathbf{v}_i}{kT} \right) \right\} f_{F-P} = 0 \quad (3.8)$$

which is equivalent to

$$f_{F-P} = \prod_{i=1}^N f_0(\mathbf{r}_i, \mathbf{v}_i, t) \quad (3.9)$$

here  $f_0(\mathbf{r}_i, \mathbf{v}_i, t)$  represents the single particle distribution function. Hence

$$\left\{ \frac{\partial}{\partial t} + \mathbf{v}_i \frac{\partial}{\partial \mathbf{r}_i} - \frac{\partial}{\partial \mathbf{v}_i} D \left( \frac{\partial}{\partial \mathbf{v}_i} + \frac{m\mathbf{v}_i}{kT} \right) \right\} f_0 = 0. \quad (3.10)$$

This suggests that one might expect a form like

$$\left\{ \frac{\partial}{\partial t} + \int d\omega \mathbf{v}(\omega) \frac{\partial}{\partial \mathbf{r}(\omega)} - \int p_0 \omega^2 \mathbf{r}(\omega) \frac{\partial}{\partial \mathbf{v}(\omega)} - \int \frac{\partial}{\partial \mathbf{v}(\omega)} D(\omega) \left( \frac{\partial}{\partial \mathbf{v}(-\omega)} + \frac{3m}{4kT} \mathbf{v}(\omega) \right) \right\} f = 0 \quad (3.11)$$

which has a separable solution so is equivalent to

$$\left( \frac{1}{\Delta} \frac{\partial}{\partial t} + \mathbf{v}(\omega) \frac{\partial}{\partial \mathbf{r}(\omega)} - p_0 \omega^2 \mathbf{r}(\omega) \frac{\partial}{\partial \mathbf{v}(\omega)} - \frac{\partial}{\partial \mathbf{v}(\omega)} D(\omega) \left( \frac{\partial}{\partial \mathbf{v}(-\omega)} + \frac{3\mathbf{v}(\omega)}{4kT} \right) \right) f_0 = 0 \quad (3.12)$$

where, to avoid  $d\omega$  appearing unaccompanied by an integral sign, there has been a reversion to Fourier components where  $\Delta = L/2\pi$ . Whereas for a gas  $D$  is  $D(\mathbf{v})$ , it will turn out that for the chain case  $D$  will be  $D(\omega)$  in the limit of a long chain (because for the chain,  $\mathbf{v}(\omega)$  has infinitesimal weight, and because the  $\omega$  space is *not* homogeneous as is the ordinary space of gas molecules). The force  $F$  can be written from (2.15), and the important properties are all contained when it is written as

$$F = \sum_{lp} \omega f^{(lp)}(\omega, \omega_1, \dots, \omega_l; \sigma_1, \sigma_2, \dots, \sigma_p) \mathbf{r}(\omega_1) \mathbf{r}(\omega_2) \dots \mathbf{r}(\omega_l) \times \mathbf{v}(\sigma_1) \dots \mathbf{v}(\sigma_p) \delta \left( \sum_1^l \omega_j + \sum_1^p \sigma_j \right). \quad (3.13)$$

Note that  $l$  is odd and  $p$  is even, and that at  $\omega = 0$ ,  $f^{(lp)}$  will not in general vanish but be finite. The first two terms from (3.13) will be  $l = 3, p = 0$  and  $l = 1, p = 2$ . Now it is well known in brownian motion studies (Chandrasekhar 1943 see also Wax 1954) that if a random force  $\mathcal{F}(t)$  acts on a system whose natural decay rate is  $\gamma$ , then the equation

$$\left( \frac{\partial}{\partial t} + \mathcal{F}(t) \frac{\partial}{\partial \mathbf{v}} \right) f = 0 \quad (3.14)$$

is equivalent to

$$\left( \frac{\partial}{\partial t} - \frac{\partial}{\partial \mathbf{v}} D \frac{\partial}{\partial \mathbf{v}} \right) \bar{f} = 0 \quad (3.15)$$

where  $\bar{f}$  is the average distribution (over  $\mathcal{F}$ ), and

$$D = \int_0^\infty \langle \mathcal{F}(t) \mathcal{F}(0) \rangle e^{-\gamma t} dt \quad (3.16)$$

provided that the decay of  $\langle \mathcal{F}(t) \mathcal{F}(0) \rangle$  is faster than  $e^{-\gamma t}$ . Likewise

$$\left( \frac{\partial}{\partial t} + \mathbf{v} \frac{\partial}{\partial \mathbf{r}} + \mathcal{F}(\mathbf{r}, t) \frac{\partial}{\partial \mathbf{v}} \right) f = 0 \quad (3.17)$$

becomes

$$\left( \frac{\partial}{\partial t} + \mathbf{v} \frac{\partial}{\partial \mathbf{r}} - \frac{\partial}{\partial \mathbf{v}} D(\mathbf{v}) \frac{\partial}{\partial \mathbf{v}} \right) \bar{f} = 0 \tag{3.18}$$

where

$$D = \iint \langle \mathcal{F}(\mathbf{r} + \mathbf{v}t, t) \mathcal{F}(\mathbf{r}', 0) \rangle e^{-\gamma t} d^3(\mathbf{r} - \mathbf{r}') dt \tag{3.19}$$

provided that the correlation of  $\langle \mathcal{F} \mathcal{F} \rangle$  decays faster in space than a distance ( $v \times$  decay time of  $\langle \mathcal{F} \mathcal{F} \rangle$ ). These conditions are clearly satisfied in a normal brownian motion problem. They are not satisfied in a plasma (though usually assumed there) and indeed are extremely difficult to satisfy generally. This is because the long time decay of equations of this type generally depends on the collective collision terms rather than the single particle behaviour (here called the ‘natural decay rate’), so that the condition is that the rate of decay must be shorter than itself.

Since these are ‘order of magnitude of dimensions’ arguments, this statement can only mean the success of the reduction of (3.3) to (3.11) depends on the smallness of the ratio of two quantities of identical structure, that is, on a pure number being small. Thus in the Boltzmann equation one may argue validity by invoking the ratio of the size of a gas molecule to the mean free path. The validity of the Fokker–Planck equation of brownian motion depends on the ratio of the rate of change of the direction of the large particle to the rate of collisions of surrounding small molecules. There is clearly no such ratio available to use in this problem. However a pure number does appear in  $\omega$  and a justification for the transition to a Fokker–Planck equation will appear over certain  $\omega$  regions. If then  $F$  of (3.13) is regarded as a random variable one can expect

$$\mathcal{F} \frac{\partial}{\partial \mathbf{v}} \tag{3.20}$$

to be replaced by

$$\frac{\partial}{\partial \mathbf{v}} \int \langle \mathcal{F}(t) \mathcal{F}(0) \rangle e^{-\gamma t} dt \frac{\partial}{\partial \mathbf{v}}. \tag{3.21}$$

However as in the normal Fokker–Planck equation the dependence of  $\mathcal{F}$  upon  $\mathbf{v}(\omega)$ † will lead to a second term which can either be calculated *ab initio* or recognized from the known equilibrium solution to be

$$\frac{\partial}{\partial \mathbf{v}(\omega)} \int_0^\infty \langle \mathcal{F}(t) \mathcal{F}(0) \rangle e^{-\gamma t} dt \left( \frac{\partial}{\partial \mathbf{v}(-\omega)} + \frac{3m}{4kT} \mathbf{v}(\omega) \right)$$

where

$$D = \int_0^\infty \langle \mathcal{F}(t) \mathcal{F}(0) \rangle e^{-\gamma t} dt$$

† It will be noted that the coefficients of the Fokker–Planck equation  $(\partial/\partial \mathbf{v}(\omega))D(\omega)(\partial/\partial \mathbf{v}(-\omega) + \mu(\omega)\mathbf{v}(\omega))$  are no longer constants, but are functions of  $\omega$ . Chandrasekhar (1943) has already noted that this possibility represents a generalization of normal brownian motion, and that the Fokker–Planck equation is still satisfied.

has the form

$$\omega^2 \int \left\langle \sum_{l p' l' p'} f^{(lp)} \{ \mathbf{r}(\omega_1) \dots \mathbf{r}(\omega_l), \mathbf{v}(\omega_1) \dots \mathbf{v}(\omega_p) \}_t \times f^{(l'p')} \{ \mathbf{r}(\omega_1) \dots \mathbf{r}(\omega_{l'}), \mathbf{v}(\omega_1) \dots \mathbf{v}(\omega_{p'}) \}_{t'} \right\rangle e^{-\gamma(\omega)(t-t')} d(t-t'). \quad (3.23)$$

The use made of the equation will not involve the precise evaluation of these expressions. The method of evaluation is shown in the Appendix. The final form of the equation is now

$$\left\{ \frac{1}{\Delta} \frac{\partial}{\partial t} + \mathbf{v}(\omega) \frac{\partial}{\partial \mathbf{r}(\omega)} - p_0 \omega^2 \mathbf{r}(\omega) \frac{\partial}{\partial \mathbf{v}(\omega)} - D(\omega) \frac{\partial}{\partial \mathbf{v}(\omega)} \left( \frac{\partial}{\partial \mathbf{v}(-\omega)} + \frac{3m\mathbf{v}(\omega)}{4kT} \right) \right\} f_0 = 0 \quad (3.24)$$

where

$$D(\omega) = D(0) + \omega^2 D_1 + \dots \quad (3.25)$$

At this point it must be emphasized that this is all for case (iii), where the chain has no external forces and no external viscosity. From the form (3.25), in the case of no external forces or viscosity, one must have  $D(0) = 0$ , and the series commences with an  $\omega^2$  term. The form follows from dimensional analysis, and in the small  $\omega$  region where only the  $\omega^2$  term need be kept is (also including  $p_0$  explicitly at this point, using)

$$D_1 = \left( \frac{kT}{m} \right)^{3/2} d_1 l \quad (d_1 \text{ dimensionless})$$

$$\left[ \frac{1}{\Delta} \frac{\partial}{\partial t} + \mathbf{v}(\omega) \frac{\partial}{\partial \mathbf{r}(\omega)} - \frac{2kT}{ml} \omega^2 \mathbf{r}(\omega) \frac{\partial}{\partial \mathbf{v}(\omega)} - \omega^2 \left( \frac{kT}{m} \right)^{3/2} d_1 l \left\{ \frac{\partial}{\partial \mathbf{v}(\omega)} \left( \frac{\partial}{\partial \mathbf{v}(-\omega)} + \frac{3m\mathbf{v}(\omega)}{4kT} \right) \right\} \right] f = 0. \quad (3.26)$$

This equation is to be contrasted with the situation (i) arising when the chain is immersed in a liquid, becoming subject to random forces and to viscosity. Additional terms

$$\mathcal{F}(t) \frac{\partial}{\partial \mathbf{v}} + \frac{\partial}{\partial \mathbf{v}} \lambda \mathbf{v} \quad (3.27)$$

appear, where  $\mathcal{F}(t)$  is a random force

$$\langle \mathcal{F}(t) \mathcal{F}(0) \rangle = \frac{1}{2} h \delta(t). \quad (3.28)$$

The effect will be to alter  $D(\omega)$  so that now  $D(0)$  is nonzero. In the first approximation  $D(0)$  is just  $h$ , but  $D_1$  will be altered because of the presence of  $D(0)$  and the viscosity. The changes will however not alter the  $3m\mathbf{v}(\omega)/4kT$  form, since the new forces still lead to thermal equilibrium. Thus in the presence of a liquid, the chain behaves as free provided that  $\omega^2 D_1 > D_0$  but there is no simple dependence of  $D_1$  upon  $h, kT$ . Otherwise, the diffusion term can be taken as constant. These cases lead to very different motions.

**4. The motion of the molecule in cases (i) and (iii)**

A property of equations of the type derived is that they are completely specified by the second moments, in particular if the Fourier transforms with respect to time are introduced

$$R(\epsilon, \omega) = \iint R(s, t) \exp(i\omega s + i\epsilon t) ds dt \tag{4.1}$$

$$v(\epsilon, \omega) = i\epsilon R(\epsilon, \omega).$$

$$\langle |R(\epsilon, \omega)|^2 \rangle = \frac{D(\omega)}{\{\epsilon^2 - (2kT/ml)\omega^2\}^2 + (3mD(\omega)/4kT)^2 \epsilon^2} \tag{4.2}$$

and

$$\langle (R(s, t) - R(s', t'))^2 \rangle = \iint \frac{D(\omega) \sin^2(\frac{1}{2}\omega(s - s') + \frac{1}{2}\epsilon(t - t'))}{\{\epsilon^2 - (2kT/ml)\omega^2\}^2 + (3mD(\omega)/4kT)^2 \epsilon^2} d\omega d\epsilon. \tag{4.3}$$

(Note that for  $t = t'$ , this gives  $l|s - s'|$ , as it must.) This expression corresponds to waves of dispersion

$$\epsilon^2 - \frac{2kT}{ml} \omega^2 = 0 \tag{4.4}$$

damped by a dynamical friction  $3mD(\omega)/4kT$ . Consider first the free polymer. In this case  $D \propto \omega^2 D_1$  and the roots of the denominator in (4.3) are

$$\epsilon^2 - \frac{2kT}{ml} \omega^2 \pm i \left( \frac{3m\omega^2 D_1}{4kT} \right) \epsilon = 0 \tag{4.5}$$

$$\epsilon = \frac{1}{2} \left[ (\pm) i \frac{3m\omega^2 D_1}{4kT} \pm \left\{ - \left( \frac{3m\omega^2 D_1}{4kT} \right)^2 + \frac{8kT}{ml} \omega^2 \right\}^{1/2} \right] \tag{4.6}$$

which for small  $\omega$  is dominated by

$$\epsilon = \pm \left( \frac{2kT}{ml} \right)^{1/2} \omega \tag{4.7}$$

and the motion is that of entropy waves ('second sound'). For large  $\omega$ , the friction dominates and the pole comes at

$$\epsilon \simeq i \frac{3mD_1}{4kT} \omega^2 \tag{4.8}$$

the regimes changing over at  $\omega \sim (kT/m)^{3/2}/D_1 = 1/d_1 l$ . This implies that in the former case almost all motions are in fact due to entropy waves.

For the polymer immersed in the liquid the situation is quite different, for at small  $\omega$  the inertia term can be ignored leaving

$$\epsilon \simeq il^2 v \omega^2. \tag{4.9}$$

This is the case originally considered by Rouse and forms the basis of most of the subsequent literature. For large  $\omega$  the inertial term reappears and the entropy waves

begin to dominate, but now the condition is that

$$\frac{2kT\omega^2}{ml} > \frac{3mD_0}{4kT} \quad \text{or} \quad \omega^2 \gtrsim \left(\frac{m}{kT}\right)^2 D_0. \quad (4.10)$$

If the viscosity of the liquid dominates the friction  $3mD_0/4kT = \lambda$  so that the change over comes at

$$\omega \cong \lambda \left(\frac{m}{kT}\right)^{1/2} \quad (4.11)$$

as one would expect. This condition excludes almost all motion in normal polymer solutions, and the decaying modes dominate. The value of  $\langle (R(s, t) - R(s', t'))^2 \rangle$  is in general a complicated function, but for  $t = t'$  it must be  $l|s - s'|$ . For the case where  $s = s'$ , it also simplifies in the two principal cases. For the free polymer, put

$$\begin{aligned} \langle (R(s, t) - R(s', t'))^2 \rangle &= D_1 \int \frac{\omega^2 \sin^2\{\frac{1}{2}\epsilon(t-t')\} d\omega d\epsilon}{\{\epsilon^2 - (2kT/ml)\omega^2\}^2 + (3mD_1^2/4kT)\omega^4 \epsilon^2} \quad (4.12) \\ &\cong D_1 \int \frac{\sin^2 \frac{1}{2}\omega(2kT/ml)^{1/2}(t-t')}{\omega^2} d\omega \\ &\cong D_1 l \left(\frac{2kT}{ml}\right)^{1/2} |t-t'|. \end{aligned}$$

This is because  $s$  and  $t$  are on the same footing. But for the polymer in solution one obtains

$$\begin{aligned} \langle (R(s, t) - R(s', t'))^2 \rangle &= \int \frac{\lambda \sin^2\{\frac{1}{2}\epsilon(t-t')\} d\omega d\epsilon}{\omega^4 + \lambda^2 \epsilon^2} \\ &\cong (|t-t'|)^{1/2}. \end{aligned}$$

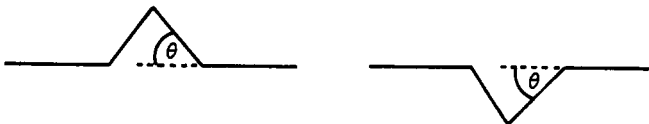
Likewise it follows that the incoherent quasielastic scattering functions from the free case have the conventional form

$$S(\omega, \epsilon) \sim \frac{1}{(D\omega^2)^2 + \epsilon^2} \quad (4.15)$$

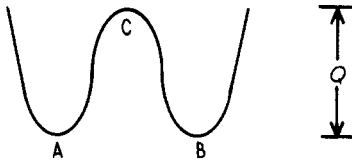
whereas for the polymer in solution the scattering functions have the Fresnel integral structure as discussed by de Gennes (1967).

### 5. The motion of the molecule with potential barriers

The remaining cases are those in which the motion, first studied by Verdier and Stockmayer (1962), is dominated by the potential barrier between configurations. These are cases (ii) and (iii) in which the motion of the chain is caused either by the effects of a surrounding solution which causes the barrier to be surmounted, or by the internal thermal motion of the chain. The situation is described symbolically by saying that the configurations



have a potential energy in  $\theta$  which has two minima



and the motion of the polymer is analogous to the transition under brownian motion between the two wells. In a real case of course a much more complicated motion takes place (Flory 1969, Birstein and Ptitsyn 1966). The motion in  $\theta$  will be governed either by fluctuating forces in the surrounding medium, and the viscosity of that medium (ii), or by the vibrations of the chain as a whole (iii).

Brinkman (1956) has extended Kramers (1940) basic ideas to the more realistic case of two way flow across a potential barrier. Since there are no major alterations to the form of the rate, we shall use, for the sake of simplicity, the Kramers formulation which gives the rate in the quasiequilibrium case, as

$$P \simeq \left( \frac{\omega_A \omega_c}{2\pi\beta} \right) \exp \left( -\frac{mQ}{kT} \right) \tag{5.1}$$

where  $\omega_A$  is defined as the frequency of oscillation of the particle in the region A of the potential field

$$B \simeq \frac{1}{2} \omega_A^2 \theta^2 \tag{5.2}$$

and  $\omega_c$  is the frequency in the region C. The variable  $\beta$  is related to the dynamical friction, and its magnitude gives some estimate of the time to set up a Boltzmann distribution.

Case (ii) is readily translated into these terms, for if one ignores the inertia of the segments and considers the motion as the solution of a diffusion equation of the type

$$\left\{ \frac{\partial}{\partial t} - \frac{\partial}{\partial \theta} \left( \frac{h}{4\nu^2} \frac{\partial}{\partial \theta} + \frac{1}{\nu} \frac{\partial W}{\partial \theta} \right) \right\} P(\theta, t) = 0 \tag{5.3}$$

where  $W(\theta)$  is the potential energy which hinders rotation about the backbone,  $\nu$  an effective viscosity, and  $h$  the effect of the random field of collisions. Since the equilibrium distribution must be  $\exp(-W/kT)$  one has  $h/\nu = kT$ . From this structure one can obtain the Kramers rate. One then has

$$R_n(\Delta t) = R_n(0) + \sum_n (\Delta R_n) \Theta_n(t - t_k) \tag{5.4}$$

where  $\Delta R_n$  is as before in the simple model ( $R_{n+1} - 2R_n + R_{n-1}$ ) and  $\Theta_n$  represents jump functions at times  $t_k$ . Assuming that  $\Delta t$  contains many jump times, but can still be taken over to a differential, as usual in brownian theory, an average can be extracted to give

$$\dot{R}_n = K(R_{n+1} - 2R_n + R_{n-1}) + F \tag{5.5}$$

where  $K$ , the Kramers rate is the average of  $(\sum_n \Theta_n / \Delta t)$  and  $F$  the difference between  $\sum(\Delta R_n) \Theta_n(t - t_k)$  and its average. Treating this latter as a random function in time, one

returns to

$$\left\{ \frac{\partial}{\partial t} - \sum_{\omega} \frac{\partial}{\partial \mathbf{r}_{\omega}} \frac{h}{4} \left( \frac{\partial}{\partial \mathbf{r}_{-\omega}} + \omega^2 \mathbf{r}_{\omega} \frac{4K}{h} \right) \right\} P = 0 \quad (5.6)$$

so that  $K = kT/h$ . As before  $\omega^2$  appears in the small limit; in general there is an  $a(\omega^2)$  which for our simple configuration is  $\sin^2 \omega l$ , but will be more complicated for real situations. So this case returns inevitably to the Rouse form with the Kramers rate replacing the inverse of viscosity. Considerable work has been done on the transition from a 'hopping' model of a polymer to the Rouse model. In particular Verdier and Stockmayer (1962) and Orwoll and Stockmayer (1969) have showed that such a reduction is possible. Recent work by Iwata and Kurata (1969) extends the proof.

For case (v), the Fokker-Planck equation for  $\theta$ ,  $\dot{\theta} = \dot{\phi}$  can be derived, and will take the form

$$\left\{ \frac{\partial}{\partial t} + \phi \frac{\partial}{\partial \theta} - \frac{\partial W}{\partial \theta} \frac{\partial}{\partial \phi} - \frac{\partial}{\partial \phi} D \left( \frac{\partial}{\partial \phi} + I \frac{\phi}{kT} \right) \right\} P = 0 \quad (5.7)$$

where  $I$  is the moment of inertia (for simplicity everything is written in two dimensions),  $D$  is a diffusion constant. This form can be derived as before, and can then be used to obtain the analogue of (3.23). In this case, however, the Kramers rate involves dynamical friction rather than external viscosity, and the random fluctuations come from the thermal excitation of the chain rather than molecular bombardment. The calculation then proceeds as before. A physically realistic case will involve both mechanisms at once unless some rather peculiar circumstances arise, such as say a light atom rigid chain in the presence of a solvent of very heavy atoms which would lead to a pure case (ii).

## 6. Conclusion

The present work is still rather idealized and several problems are posed which it is hoped to return to. These include:

- (i) How can *details* of the micromotion be adapted to the macromotion?
  - (ii) How can the entanglements of the molecules be introduced into the dynamics of a single long chain?
  - (iii) How can the entanglements of the molecules be introduced into the dynamics of polymerized material?
  - (v) How can hydrodynamic interactions be introduced into the above categories?
- The problems (i) and (iv) have received considerable study in the context of the Rouse model, but (ii) and (iii) have not been studied extensively, so we hope to return to this topic in later papers.

## Acknowledgments

We have enjoyed the help of Professor Stockmayer during his extended stay in Manchester, and would also like to thank Professor Allen and Dr Higgins for helpful discussions particularly about the experimental situation.

One of us (AGG) would like to thank the UKAEA for financial support during the period that this work was carried out.



## Appendix

Given a polynormal force as in equation (3.13), there is a general method of expansion available, which was invented by one of the authors to study the problem of turbulence. There one has a quadratic equation of the type

$$\left( \frac{\partial}{\partial t} + \sum_k \frac{\partial}{\partial u_k} (M_{kji} u_j u_i + \nu k^2 u_k) \right) F = 0$$

or in many body problems where the interaction is quartic one finds

$$\left\{ \frac{\partial}{\partial t} + \sum_k \frac{\partial}{\partial \psi_k} \left( \frac{\hbar^2}{2m} k^2 \psi_k + \sum V_{kjlm} \psi_j \psi_l \psi_m \right) \right\} F' = 0$$

(Edwards 1964, Edwards and Sherrington 1967). For an equation of the type

$$\left\{ \frac{\partial}{\partial t} + \sum_k \frac{\partial}{\partial x_k} \left( \alpha_k x_k + \sum \beta_{kk_1 k_2 \dots} x_{k_1} x_{k_2} \dots \right) \right\} F = 0$$

the result to a first approximation is given by

$$\left\{ \frac{\partial}{\partial t} - \sum_k \frac{\partial}{\partial x_k} \left( \gamma_k x_k + \epsilon_k \frac{\partial}{\partial x_k} \right) \right\} \langle F \rangle = 0$$

then if  $q_k = \epsilon_k / \gamma_k$  is the equilibrium distribution

$$\gamma_k q_k = \alpha_k q_k + \frac{\sum |\beta_{kk_1 \dots}|^2 q_{k_1} q_{k_2} \dots}{\gamma_k + \gamma_{k_1} + \dots} - \frac{\sum \beta_{k_1 k_1 \dots} \beta_{kk_1 k_2 \dots} q_{k_1} q_{k_2} \dots}{\gamma_k + \gamma_{k_1} + \dots}$$

where the sum sign includes all permutation of the indices. This is simply a Peierls-Boltzmann equation in the sense that if  $\langle |x_k|^2 \rangle$  is time dependent due to slow external effects

$$\frac{\partial q_k}{\partial t} + \alpha_k q_k + \int \Lambda_{kk_1 \dots k_m} q_{k_1} \dots (q_m - q_k) = \text{external effects.}$$

The generalized rules for  $\alpha$  complex, or nondiagonal systems, and for higher orders are contained in the references quoted.

## References

- Beuche F 1954 *J. chem. Phys.* **22** 603-9  
 Birshtein T M and Ptitsyn O B 1966 *Conformation of Macromolecules* (New York: Interscience)  
 Brinkman H C 1956 *Physica* **22** 29-34  
 Chandrasekhar S 1943 *Rev. mod. Phys.* **15** 1-89  
 Edwards S F 1964 *J. Fluid Mech.* **18** 239-73  
 Edwards S F and Sherrington D 1967 *Proc. Phys. Soc.* **90** 3-22  
 Flory P J 1969 *Statistical Mechanics of Chain Molecules* (New York: Interscience)  
 de Gennes P-G 1967 *Physics* **3** 37-45  
 Iwata M and Kurata K 1969 *J. chem. Phys.* **50** 4008-13  
 Kramers H 1940 *Physica* **7** 284-304  
 Orwoll R A and Stockmayer W H 1969 *Adv. chem. Phys.* **15** 305-23  
 Rouse P E 1953 *J. chem. Phys.* **21** 1272-80  
 Verdier P H and Stockmayer W H 1962 *J. chem. Phys.* **36** 227-35  
 Wax N 1954 *Selected Papers on Noise and Stochastic Processes* (New York: Dover)  
 Zimm B H 1956 *J. chem. Phys.* **24** 269-78