

A General Solution to the Necklace Model Problem in the Rheology of Macromolecules

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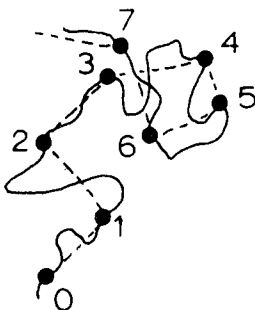
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SUMMARY

A very general solution is given of a problem which plays a vital role in certain molecular theories on the deformation of macromolecules. In these theories use is made of the necklace model, in which the macromolecule in solution is supposed to be built up of submolecules or segments. The total hydrodynamic resistance of the monomers in a segment is assumed to be concentrated in the end points of the segments: the beads. By applying a macroscopic field of flow to the solution, forces are exerted on the beads which are compensated by entropy-elastic forces in the segment. The configuration of the beads is described by a distribution function which must satisfy an equation of continuity. This equation is now solved by means of Fourier transformation for any time-dependent field of flow for which the velocities are linear functions of the coordinates. The solution appears to be a Gaussian distribution whose second moments have to satisfy a system of linear first-order time-dependent differential equations. Once the distribution function is known, all kinds of macroscopically measurable quantities of the solution can in principle be calculated.

1. The Necklace Model

In the necklace model of a linear macromolecule in solution, developed on the basis of Kuhn's [1] work, the molecule is assumed to be split up into submolecules (segments or links). These segments constitute the connections between "beads" in which the hydrodynamic resistance of the monomers of a segment is supposed to be concentrated. Part of the chain model used is represented in the figure below:



The length of a segment is determined by the configuration of the monomers within this segment. This length is taken to be a stochastic variable. In principle, the number of monomers comprised in one segment can still be chosen freely; it is assumed that this number is in any case such that the segments can rotate freely with respect to one another. (The beads do not accept moments).

Also the position of the centre of gravity of the beads is assumed to be a stochastic variable. It is further assumed that as long as no external forces act on the solution, the three following conditions are met:

- (1) the length of a segment can be described by a Gaussian distribution function;
- (2) the length of the various segments and the position of the centre of gravity are stochastically independent;
- (3) the centres of gravity of the macromolecules are homogeneously distributed over the solution.

Let us assume that the above conditions can be met by dividing the macromolecule into n segments, which constitute the links between $n + 1$ beads. The configuration of the macromolecule can then be described as follows.

A system of cartesian coordinates is introduced, in which $r_0, r_1, r_2, \dots, r_n$ are the position vectors of the beads. Let R be a rectangular matrix of $n + 1$ rows and 3 columns, which contains the vectors r_i^T as rows. The matrix R then completely defines the configuration of the macromolecule.

The configuration can also be defined by giving the dimensionless position of the centre of gravity of the beads and the n dimensionless position differences of the beads as follows.

Let $3b^2$ be the mean square of the segment lengths if no forces are exerted on the solution*. Now define

$$s_0 = \frac{\sum_{i=0}^n r_i}{b} \tag{1.1}$$

$$s_k = \frac{r_k - r_{k-1}}{b} \quad \text{for } k = 1, 2, \dots, n. \tag{1.2}$$

Let S be a rectangular matrix of $n + 1$ rows and 3 columns, which contains the vectors $s_0^T, s_1^T, \dots, s_n^T$ as rows. Also by giving the matrix S , the configuration of the macromolecule is completely determined. Between S and R there is a unique relation, given by

$$S = \frac{1}{b} aR \tag{1.3}$$

in which a is a square $(n + 1) \times (n + 1)$ matrix of the following form :

$$a = \begin{bmatrix} 1 & 1 & 1 & 1 & \dots & 1 & 1 \\ -1 & 1 & 0 & 0 & \dots & 0 & 0 \\ 0 & -1 & 1 & 0 & \dots & 0 & 0 \\ 0 & 0 & -1 & 1 & \dots & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & & \vdots & \vdots \\ 0 & 0 & 0 & 0 & \dots & -1 & 1 \end{bmatrix} \tag{1.4}$$

The elements of this matrix are called a_{ik} with i and $k = 0, 1, 2, \dots, n$. The possible configurations of macromolecules are described by a distribution function of the stochastic variables R or S . This distribution function is called ψ . If no external forces are exerted on the solution, the conditions of Gaussian distribution, independence and homogeneity of centres of gravity, formulated above, are applicable. The special distribution function satisfying these conditions is called ϕ . In the absence of external forces we can therefore put $\psi = \phi$.

On the basis of the foregoing we must have :

$$\phi = \frac{1}{(2\pi)^{3n/2}} \exp\left(-\frac{1}{2} S^T : I_0 S\right). \tag{1.5}$$

The expression $S^T : I_0 S$ indicates : the sum of the inner products of the rows of the matrix S^T and the corresponding columns of the matrix $I_0 S$ (the so-called direct product). The matrix I_0 is defined as a square $(n + 1) \times (n + 1)$ matrix, equal to a unit matrix, with the exception of the diagonal element on the row with subscript 0, which equals 0 instead of 1. This matrix occurs in Eq. (1.5), because the distribution of the centres of gravity has been assumed to be homogeneous, so that ϕ is independent of s_0 and hence, s_0 cannot occur in the exponential expression.

The function ϕ has apparently been normalized over the relevant coordinates :

* This is, if no forces act on the solution, the average value of $(r_i - r_{i-1})^T (r_i - r_{i-1})$; the three components of $r_i - r_{i-1}$ are then supposed all to have an average quadratic length of b^2 . This value can be related to the number of monomers in one segment and to the monomer length.

$$\int \phi dI_0 S = 1 .$$

In 1953/1954 Rouse [2] and Bueche [3] gave the first complete description of the necklace model of a polymer in a solution subject to simple shear flow. This case will once more be treated here, but incorporating extensions of the theory (e.g. hydrodynamic interactions). Moreover the distribution function—and not only its moments—will be calculated for each form of time-dependent flow, provided this flow is a linear function of the coordinates.

2. Forces Acting on the Beads of the Necklace Model

1. Entropy-Elastic Forces

If forces are exerted on the solution the distribution function will change and, hence, $\psi \neq \phi$.

If we use Wall's formulae [4] to calculate the difference in entropy caused by a change in distribution function, and assume that the internal energy of the system remains constant when the configuration changes, we have under isothermal conditions:

$$\mu = kT \left(1 + \ln \frac{\psi}{\phi} \right) \quad (2.1)$$

where μ is the thermodynamic potential.

From this the entropy-elastic force is derived:

$$F^e = - \frac{\partial \mu}{\partial R} = -kT \frac{\partial}{\partial R} \ln \frac{\psi}{\phi} \quad (2.2)$$

where F^e is a matrix of $n+1$ rows and 3 columns; the rows in this matrix are the entropy-elastic forces on the beads of the necklace model.

2. Friction Forces

It is assumed that a solution is subject to forces which result in a macroscopic velocity profile in the solution. This macroscopic velocity at the location of the beads can be represented by an $(n+1) \times 3$ matrix V_0 , comprising the vectors v_{0k}^T ($k=0, 1, 2, \dots, n$) as rows. If this macroscopic velocity were equal to the actual velocity of the solvent at the location of the beads, the forces on the beads resulting from friction might be represented by:

$$F^f = f_0 (V_0 - \dot{R}),$$

where f_0 is the Stokes friction coefficient.

For many cases this expression is too simple; we generalize it therefore to

$$F^f = f_0 B^{-1} (V_0 - \dot{R}). \quad (2.3)$$

In this expression B is a symmetric, not further specified $(n+1) \times (n+1)$ matrix. In the Rouse [2] theory B is a unit matrix; in case hydrodynamic interaction is taken into account [5] B is equal to $I + f_0 T$, where I is a unit matrix and T is the so-called Oseen [6] tensor. Formula (2.3), however, can also take into account: increased friction in certain beads or different friction coefficients for all the beads.

In this treatment the macroscopic field of flow should only meet the condition that the velocities are linear functions of the coordinates

$$v_{0k} = \dot{\Gamma}(t) r_k. \quad (2.4)$$

$\dot{\Gamma}(t)$ is here an essentially time-dependent 3×3 matrix with elements $\dot{\gamma}_{ik}$. We would stress that this formula may serve to describe not only any form of time-dependent shear flow, but also for example linear elongational flow. This expression is therefore much more general than the usual expressions for the macroscopic field of flow. For the present purpose we assume a

divergence-free flow and therefore put

$$\text{trace}(\dot{I}) = 0. \tag{2.5}$$

For V_0 we have:

$$V_0 = R\dot{I}^T. \tag{2.6}$$

3. Equations of Motion

In developing equations of motion, inertia forces are neglected.

Assuming balance of forces we have:

$$F^e + F^f = 0. \tag{3.1}$$

Eqs. (2.2) and (2.3) can be substituted in (3.1). In doing so we also introduce the afore-mentioned coordinates S according to:

$$S = \frac{1}{b} aR; \frac{\partial}{\partial R} = \frac{1}{b} a^T \frac{\partial}{\partial S}.$$

In addition, we introduce the parameter τ , defined by:

$$\tau = \frac{f_0 b^2}{2kT}.$$

This parameter has the dimension of time, and is therefore to be taken as a characteristic time constant. Eq. (3.1) can now be formulated as follows:

$$-\frac{1}{2\tau} aBa^T \frac{\partial}{\partial S} \ln \frac{\psi}{\phi} + (S\dot{I}^T - \dot{S}) = 0. \tag{3.2}$$

The matrix aBa^T is symmetric; this matrix will henceforth be called A with elements A_{ik} (i and $k=0, 1, 2, \dots n$). If B is a unit matrix, as it is in the Rouse theory [2], this matrix A is about equal to the so-called Rouse matrix, the only difference being that in our treatment one row and one column with subscript 0 are added, for which we have:

$$A_{0k} = A_{i0} = 0 \quad \text{for } i \text{ and } k=1, 2, \dots n; \quad A_{00} = n+1.$$

This difference arises because in the Rouse theory the centre of gravity has not been included.

After substituting the expression for ϕ from Eq. (1.5) one can write:

$$\dot{S} = S\dot{I}^T - \frac{1}{2\tau} A \frac{\partial}{\partial S} \ln \psi - \frac{1}{2\tau} AI_0 S. \tag{3.3}$$

By transformation this system of $3 \times (n+1)$ mutually dependent equations can be split up into mutually independent equations. For this purpose the eigenvalues and the eigenvectors of the matrix AI_0 must first be determined.

The following agreement is now made: a superscript $*$ to a matrix indicates that the matrix is meant, with the exception of the rows and columns containing a subscript 0, e.g. A^* is the square $n \times n$ matrix formed from A by omitting all the elements A_{ik} with i and/or $k=0$.

AI_0 has the following form:

$$AI_0 = \left[\begin{array}{c|c} 0 & A_0^T \\ \hline - & - \\ 0 & \\ \vdots & A^* \\ 0 & \end{array} \right]$$

A_0 is here a vector consisting of the elements $A_{01}, A_{02}, A_{03}, \dots A_{0n}$; where matrix B is a unit matrix, as in the Rouse theory, $A_{00}=0$.

It can be seen at once that one of the eigenvalues of this matrix equals zero ; we call this eigenvalue v_0 . We define a diagonal matrix N , which contains all the eigenvalues $v_0, v_1, v_2, \dots, v_n$ as diagonal elements ; N^* then contains v_1, v_2, \dots, v_n and thus the eigenvalues of A^* .

The eigenvectors of AI_0 satisfy the relation

$$AI_0 Q = QN \tag{3.4}$$

where Q is the matrix consisting of the eigenvectors of AI_0 as columns. It can be proved that Q is composed as follows :

$$Q = \left[\begin{array}{c|c} 1 & A_0^T Q^* N^{*-1} \\ \hline 0 & Q^* \\ \vdots & \\ 0 & \end{array} \right]$$

Q^* is here the matrix of normalized eigenvectors of A^* ; hence $A^* Q^* = Q^* N^*$. Since A^* is symmetric :

$$Q^{*T} = Q^{*-1} .$$

We should stress that although the eigenvectors Q of AI_0 are now not normalized, the determinant of Q is yet equal to 1.

Q^{-1} can be derived from Q and is of the following form :

$$Q^{-1} = \left[\begin{array}{c|c} 1 & -A_0^T Q^* N^{*-1} Q^{*T} \\ \hline 0 & Q^{*T} \\ \vdots & \\ 0 & \end{array} \right]$$

Now we have :

$$Q^{-1} AI_0 Q = N . \tag{3.5}$$

Besides, it is easy to demonstrate that

$$Q^T I_0 Q = I_0 . \tag{3.6}$$

Then we have apparently :

$$N = Q^{-1} AI_0 Q = Q^{-1} A(Q^{-1})^T Q^T I_0 Q = Q^{-1} A(Q^{-1})^T I_0 . \tag{3.7}$$

Obviously, $Q^{-1} A(Q^{-1})^T$ is also a diagonal matrix with all the elements equal to N , except the element on the row with subscript 0, which is not defined by (3.7). We call this diagonal matrix A with elements $\lambda_0, \lambda_1, \dots, \lambda_n$, for which we then apparently have :

$$A^* = N^* . \tag{3.8}$$

For λ_0 we find :

$$\lambda_0 = A_{00} - A_0^T Q^* N^{*-1} Q^{*T} A_0 .$$

We now perform the coordinate transformation

$$P = Q^{-1} S ; \quad \frac{\partial}{\partial S} = (Q^{-1})^T \frac{\partial}{\partial P} .$$

P is again an $(n+1) \times 3$ matrix with vectors $\rho_0^T, \rho_1^T, \dots, \rho_n^T$ as rows. Eq. (3.3) now becomes :

$$\dot{P} = P\dot{P}^T - \frac{1}{2\tau} A \frac{\partial}{\partial P} \ln \psi - \frac{1}{2\tau} NP . \tag{3.9}$$

The matrices A and N are diagonal matrices ; the system of equations has therefore been split

up into $n + 1$ mutually independent equations. The new coordinates P are therefore called normal coordinates [7].

The distribution function $\psi(P, t)$ can now also be written as a product of distribution functions $\psi_k(\rho_k, t)$ ($k=0, 1, \dots, n$).

We then find the following equation :

$$\dot{\rho}_k = \dot{\Gamma} \rho_k - \frac{1}{2\tau} \lambda_k \frac{\partial}{\partial \rho_k} \ln \psi_k - \frac{1}{2\tau} v_k \rho_k. \quad (3.10)$$

The ψ_k should satisfy the normalization conditions

$$\int \psi_k(\rho_k, t) d\rho_k = 1 \quad \text{for } k=0, 1, 2, \dots, n. \quad (3.11)$$

As will appear from what follows, Eq. (3.10) contains a characteristic time constant for each k , except for $k=0$. Therefore we call ρ_0 the coordinates of the translation mode, ψ_0 describing the distribution of the translation mode. Any other $\psi_k(\rho_k, t)$ describes a different normal mode of motion.

4. Equation of Continuity

The change with time of the distribution function ψ_k in a given element $d\rho_k$ is determined by the flux of the ψ_k across the boundaries of the element $d\rho_k$. Hence we have the law of continuity

$$\frac{\partial \psi_k}{\partial t} = - \frac{\partial^T}{\partial \rho_k} (\dot{\rho}_k \psi) \quad \text{for } k=0, 1, \dots, n. \quad (4.1)$$

Substitution of (3.10) on the assumption that the macroscopic field of flow is divergence-free then gives:

$$\frac{\partial \psi_k}{\partial t} = -\rho_k^T \dot{\Gamma}^T \frac{\partial \psi_k}{\partial \rho_k} + \frac{\lambda_k}{2\tau} \frac{\partial^T}{\partial \rho_k} \frac{\partial \psi_k}{\partial \rho_k} + \frac{v_k}{2\tau} \rho_k^T \frac{\partial \psi_k}{\partial \rho_k} + \frac{3v_k}{2\tau} \psi_k \quad (4.2)$$

for $k=0, 1, \dots, n$.

5. Equation of Motion for the Centre of Gravity

From Eq. (4.2) follows the distribution function ψ_0 for the translation mode:

$$\frac{\partial \psi_0}{\partial t} = -\rho_0^T \dot{\Gamma}^T \frac{\partial \psi_0}{\partial \rho_0} + \frac{\lambda_0}{2\tau} \frac{\partial^T}{\partial \rho_0} \frac{\partial \psi_0}{\partial \rho_0}. \quad (5.1)$$

It can at once be seen that a constant normalized over the ρ_0 space is a solution of (5.1), i.e. the distribution of the translation mode is homogeneous.

For the motion of the translation mode one then finds from equation (3.10):

$$\dot{\rho}_0 = \dot{\Gamma} \rho_0. \quad (5.2)$$

The velocity of the centre of gravity is found by transformation of this equation:

$$\dot{s}_0 = \dot{\Gamma} \dot{s}_0 - (\dot{\Gamma} P^{*T} - \dot{P}^{*T}) N^{*-1} Q^{*T} A_0. \quad (5.3)$$

The first term of the right-hand member in (5.3) is exactly the macroscopic velocity in the centre of gravity. The second term incorporates all the velocities of all the normal modes; this term is only zero if $A_0=0$, which is the case if $B=I$, hence in the Rouse theory. Only in that case does the centre of gravity apparently follow the macroscopic field of flow. The second term of the right-hand member can be calculated accurately if the distribution functions of the normal modes are known.

6. Distribution Function of Normal Modes

From Eq. (4.2) follows the differential equation of the distribution function of the normal modes ($k \neq 0, \lambda_k = \nu_k$).

We define $\tau_k = \tau/\lambda_k$ and henceforth omit the subscript, except in τ_k ; τ_k therefore indicates the normal mode to which the equation relates.

The equation of all the normal modes then is:

$$\tau_k \frac{\partial \psi}{\partial t} = -\tau_k \rho^T \dot{\Gamma}^T \frac{\partial \psi}{\partial \rho} + \frac{1}{2} \frac{\partial^T}{\partial \rho} \frac{\partial \psi}{\partial \rho} + \frac{1}{2} \rho^T \frac{\partial \psi}{\partial \rho} + \frac{3}{2} \psi \tag{6.1}$$

with the normalization condition:

$$\int \psi(\rho, t) d\rho = 1. \tag{6.2}$$

A solution is found after Fourier transformation. An advantage of this transformation is moreover that the Fourier transform of ψ , or the so-called characteristic function, immediately gives the moments of ψ .

We define the Fourier transform $\Psi(u, t)$ of $\psi(\rho, t)$ by:

$$\Psi(u, t) = \int \psi(\rho, t) \exp(iu^T \rho) d\rho. \tag{6.3}$$

Here u is a vector with three components.

Eq. (6.1) and the normalization condition (6.2) are transformed to the following equations:

$$\tau_k \frac{\partial \Psi}{\partial t} = \tau_k u^T \dot{\Gamma} \frac{\partial \Psi}{\partial u} - \frac{1}{2} u^T u \Psi - \frac{1}{2} u^T \frac{\partial \Psi}{\partial u} \tag{6.4}$$

$$\Psi(0, t) = 1 \tag{6.5}$$

The structure of this first-order partial differential equation suggests that a quadratic function may be a solution of the equation. Therefore we apply the method of characteristics and define:

$$g(u, t) = c(t) - \frac{1}{2} u^T M(t) u \tag{6.6}$$

where M is a symmetric 3×3 matrix which—with respect to the notation anticipating the result—is defined as follows:

$$M = \begin{bmatrix} \mu_{200} & \mu_{110} & \mu_{101} \\ \mu_{110} & \mu_{020} & \mu_{011} \\ \mu_{101} & \mu_{011} & \mu_{002} \end{bmatrix}. \tag{6.7}$$

Let us now establish which function of g is a solution of the equation. Substitution in (6.4) and (6.5) gives:

$$\left[-2\tau_k \frac{dc}{dt} + \tau_k u^T \frac{dM}{dt} u + u^T M u - \tau_k u^T (\dot{\Gamma} M + M \dot{\Gamma}^T) u \right] \frac{d\Psi}{dg} = u^T u \Psi \tag{6.8}$$

$$\Psi(c) = 1. \tag{6.9}$$

The equation can be reduced to the very easily solvable equation:

$$\frac{d\Psi}{dg} = \Psi \tag{6.10}$$

if only the following conditions are met:

$$\frac{dc}{dt} = 0 \tag{6.11}$$

$$\tau_k \frac{dM}{dt} + M - \tau_k (\dot{\Gamma} M + M \dot{\Gamma}^T) = I \tag{6.12}$$

where I is a 3×3 unit matrix.

Eqs. (6.9), (6.10) and (6.11) can be met by

$$\Psi = e^{\theta} \text{ with } c(t) = 0. \quad (6.13)$$

Therefore we find as solution of $\Psi(u, t)$

$$\Psi(u, t) = \exp(-\frac{1}{2}u^T M u) \quad (6.14)$$

provided Eq. (6.12) is satisfied.

If the characteristic function is expanded in a Taylor series with respect to u in the neighbourhood of $u=0$, one finds the moments of the distribution function. This implies that the elements of M are precisely the second moments of the distribution function. These second moments are defined as follows:

$$\mu_{200} = \int \xi^2 \psi d\rho = \langle \xi^2 \rangle; \quad \mu_{110} = \int \xi \eta \psi d\rho = \langle \xi \eta \rangle, \text{ etc.}^*$$

Reverse transformation of the characteristic function $\Psi(u, t)$ gives the distribution function itself; this distribution function appears to be a Gaussian function:

$$\psi(\rho, t) = \frac{1}{(2\pi)^{\frac{3}{2}} |M|^{\frac{1}{2}}} \exp(-\frac{1}{2}\rho^T M^{-1} \rho) \quad (6.15)$$

where $|M|$ is the determinant of M .

The distribution of the coordinates of the normal modes is therefore a time-dependent Gaussian distribution whose second moments satisfy a system of linear first-order differential equations. By solving these equations one obtains the moments, with the exception of a constant which must be determined from the initial conditions.

The solution given here applies to any form of time-dependent field of flow, provided it is a linear function of the coordinates and divergence-free.

7. Distribution Function in a Special Case

By way of illustration, the solution will be given for the case of simple shear flow in one direction (e.g. a x -direction) having a time-dependent velocity gradient $\dot{\gamma}$ in a direction normal to it (e.g. a y -direction). Let $\dot{\gamma}_{12} = \dot{\gamma}$ and all other elements of I be equal to zero.

The differential equations (6.12) now become:

$$\tau_k \frac{d\mu_{200}}{dt} + \mu_{200} - 2\tau_k \dot{\gamma} \mu_{110} = 1 \quad (7.1a)$$

$$\tau_k \frac{d\mu_{110}}{dt} + \mu_{110} - \tau_k \dot{\gamma} \mu_{020} = 0 \quad (7.1b)$$

$$\tau_k \frac{d\mu_{101}}{dt} + \mu_{101} = 0 \quad (7.1c)$$

$$\tau_k \frac{d\mu_{020}}{dt} + \mu_{020} = 1 \quad (7.1d)$$

$$\tau_k \frac{d\mu_{011}}{dt} + \mu_{011} = 0 \quad (7.1e)$$

$$\tau_k \frac{d\mu_{002}}{dt} + \mu_{002} = 1. \quad (7.1f)$$

As example we take: $\dot{\gamma} = q + \alpha \omega \cos \omega t$. This is a simple shear flow with constant gradient q with an oscillatory shear of amplitude α superimposed on it.

Eqs. (7.1) now have the solutions:

* ξ, η, ζ are supposed to be the components of the vector ρ .

$$\mu_{002} = \mu_{020} = 1 \quad (7.2a)$$

$$\mu_{101} = \mu_{011} = 0 \quad (7.2b)$$

$$\mu_{110} = \tau_k q + \alpha \frac{\omega \tau_k}{1 + \omega^2 \tau_k^2} [\omega \tau_k \sin \omega t + \cos \omega t] \quad (7.2c)$$

$$\begin{aligned} \mu_{200} = 1 + 2\tau_k^2 q^2 + \alpha \frac{2\omega \tau_k^2 q}{(1 + \omega^2 \tau_k^2)^2} [\omega \tau_k (3 + \omega^2 \tau_k^2) \sin \omega t + 2 \cos \omega t] + \\ + \alpha^2 \frac{\omega^2 \tau_k^2}{1 + \omega^2 \tau_k^2} \left[1 + \frac{3\omega \tau_k}{1 + 4\omega^2 \tau_k^2} \sin 2\omega t + \frac{1 - 2\omega^2 \tau_k^2}{1 + 4\omega^2 \tau_k^2} \cos 2\omega t \right] \end{aligned} \quad (7.2d)$$

Solution (7.2) is not the most general one. The initial conditions have not been incorporated; these initial conditions manifest themselves as coefficients of terms like $\exp(-t/\tau_k)$, $t \exp(-t/\tau_k)$, etc. For a stationary solution such terms are unimportant.

Eq. (7.2) therefore gives the stationary solution for the moments of the distribution function of the normal modes. Substitution in (6.15) then gives the stationary solution for the distribution function of the normal modes. In limiting cases the literature already offers known solutions. For $\alpha=0$ we have the solution of Hermans [8]; for $q=0$ the solution is given by Blatz [9].

7. Conclusion

The distribution function of any normal mode can apparently be calculated for all forms of time-dependent fields of flow, the velocities being linear functions of the coordinates. The form of the distribution function is determined by the field of flow and by the parameters τ_k . The values of these parameters are dependent on all kinds of refinements in the model (which affect τ) and on the eigenvalues of the matrix AI_0 . However, if ψ is known, it is also possible to determine the velocities and thus the motion of the beads, by means of eq. (3.10) and by some reverse transformations [10].

Also the expectation values of all the quantities which are functions of the coordinates, can be calculated. Some simple measures of the average dimensions of the necklace in a flowing solution follow from Eq. (6.12). These second moments are simply related with the optical properties of the solution [5], [8], [10], [11]. Also the stresses arising in the solution can be expressed as expectation values of functions of coordinates [5], [8], [10], [11] and can therefore be calculated as soon as the distribution function is known.

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