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The role of rigidity constraints in the rheology of dilute polymer solutions

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This paper investigates a class of bead–rod and bead–spring models which have been proposed to describe the dynamics of an isolated macromolecule in a flowing solution. Hassager (1974*a*) has pointed out a surprising result in regard to these models: the statistical conformation of a molecule (and hence its influence on the flow) apparently depends upon whether a very stiff-springed model structure or a rigid one is used. This paradox is examined and resolved. It is shown that a unique answer is obtained by regarding the system as the classical limit of a quantum-mechanical one. The extent of the quantum influence can be characterized by a dimensionless group Q. For a 'hot' or 'large' system (for which $Q \rightarrow 0$) the classical (stiff spring) results are recovered. The effects of the parameter Q on the size of the molecules and the rheology of the solution are calculated in detail for a simple model, and the gross features are identified for a more realistic Rouse chain model, each in both weak and strong flows.

A final section considers weak, rapidly varying flows. It is shown that, within the context of classical (non-quantum) physics, for sufficiently rapid changes any model structure will tend to move with the applied flow, and therefore exert no stresses on the fluid. This explains the theoretical observation of Fixman & Evans (1976) that, in regard to the particle stress, the limits of rigidity and infinitely high frequency do not commute.

1. Introduction

Polymer solutions, and polymeric materials generally, frequently display complex, non-Newtonian flow behaviour. In the case of polymer melts, an understanding of the rheology has direct industrial application; for dilute solutions the flow properties can be used to infer the gross features of the structure of the dissolved molecule, and are also of interest in their own right in that the solution affords an example of a non-Newtonian material whose constitutive equation can be *predicted* from a knowledge of the constituent parts of the solution, at least in so far as such molecular information is available. A linear polymer molecule may be envisioned as a long chain of say 10^4 rigid repeating units (monomers) each of length about 3 Å hinged to their neighbours at the backbone carbon atoms at their ends. The hinges, while providing some constraining potentials to resist relative rotational motions, permit considerable flexibility in the structure, which therefore changes in response to both random Brownian motions and coherent forces exerted by the solvent molecules. Since these solvent molecules are very much smaller than the polymer, the solvent may be regarded as a

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continuum, but with an appropriate allowance for the thermal fluctuations. (The fact that the solvent molecules are comparable in size with the *monomers* means that the solvent–solute interactions involved in these thermal motions are complex. Their detailed calculation remains an open question.) With this simplification, the problem of determining the constitutive relation for the solution regarded as a continuum follows in essentially the same way as for suspensions of rigid particles (see e.g. Batchelor 1970), but with the additional theoretical difficulty of finding a suitable, tractable model of the molecule that will incorporate its important physical features.

The simplest macromolecular model, the *dumb-bell* model, was introduced by Kuhn in 1934. The solvent–molecule interaction is imagined to be concentrated in two point friction centres (called 'beads'), joined by a Hookean spring connector (assumed to exert no hydrodynamic force, and of zero natural length). The elasticity of the connector (the 'entropic spring') is chosen to model the random thermodynamic motions of the backbone carbon atoms of the real chain which endeavour to keep the chain in its most probable, spherically symmetric configuration.

This model was later improved by Rouse (1953) and Zimm (1956) who incorporated more of the known structure by means of a chain of $(N+1)$ beads joined by N Hookean springs. This structure has become known as the *Rouse–Zimm chain.* In Rouse's version the beads are hydrodynamically independent (this simplification permits an analytic solution) while, in Zimm's treatment, Oseen interactions are included. In either case, however, the linearity of the springs means that when the model is placed in a sufficiently strong flow, the solvent forces on it will dominate the restoring force and so the extension will grow without bound. This defect can be remedied by replacing the springs with rods (a 'bead–rod' model). This idea seems first to have been suggested by Kramers (1944), in a paper which attracted little attention, and more recently has been exploited by Hassager (1974*a*) in discussing rheological properties.

Polymer models are used to estimate the average dimensions of macromolecules for the interpretation of both light-scattering experiments and also sedimentation data. The standard results for equilibrium properties are given by Flory (1969), who again uses a bead–rod model, though as we note below his results differ from those of Kramers.

More recently, all manner of combinations of beads, springs and rods have been used in ever more sophisticated models (see the review article of Bird *et al.* 1977). In addition a difficulty has arisen. Hassager (1974*a*) has pointed out that, in models where Brownian effects are present, there is apparently a quantitative difference between structural features involving rigid constraints (rods) and the limiting process in which flexible constraints (springs of non-zero equilibrium length) are frozen. This discrepancy manifests itself in calculations both of the average size of the macromolecules, and of their rheological influence. In § 2 we demonstrate this difference explicitly. It is of some theoretical importance, since conceptually there is no difference between the two cases, at any rate from a classical mechanical point of view, and the absence of agreement casts doubt on both sets of results.

In § 3 we demonstrate that the problem has arisen from a failure to recognize the importance of quantum mechanics when limits of rigidity are to be taken. The same difficulty arises in calculating the specific heats of polyatomic molecules at low temperatures. The expectation that 'stiff' and 'rigid' are equivalent may *not* be valid in statistical mechanics, and quantum physics are required to resolve the problem.

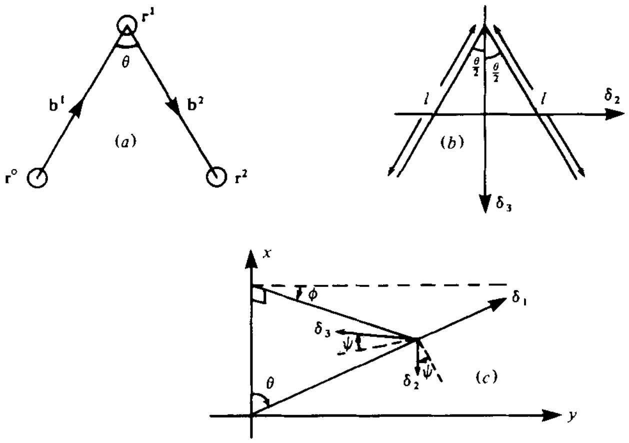

FIGURE 1. (*a*) Definition sketch for the trumb-bell. (*b*) Vectors defining the plane of the trumb-bell. (*c*) Euler angles defined by the orientation of the trumb-bell.

The rheological and geometrical influence of the quantum terms are evaluated for a Rouse chain in equilibrium (§ 4) and flow, both weak and strong (§ 5). In order to produce a tractable solution we shall make the Rouse approximation of ignoring hydrodynamic interactions between the beads of any one macromolecule. Further the assumption of diluteness means that inter-molecular interactions are to be ignored; neither of these features is central to the physics of the paradox under discussion, and each would unnecessarily obscure the issue.

A further difficulty for models with rigid components has been pointed out by Fixman & Evans (1976), who consider stresses induced by weak but very high frequency flows. They show that the limits of freezing degrees of freedom and of infinitely high frequency do not commute. In § 6 we demonstrate that this phenomenon is, in fact, entirely distinct from the quantum-mechanical one previously described, and advance a classical physical explanation for the difference between the two limiting processes.

A summary of the principal conclusions of the paper is given in § 7.

2. Summary of previous work

We start by giving an example of the type of difficulty which arises. The simplest is afforded by a Rouse chain with $N = 2$ (Hassager 1974*a*), i.e. with just two springs of non-zero equilibrium length and three beads as shown in figure 1. We will call such a particle a *trumb-bell*. The same term will be used when the springs are replaced by rods. As usual, the springs are supposed freely hinged at $\mathbf{r}^1$ so that no potential hinders the free rotation of $\mathbf{b}^2$ relative to $\mathbf{b}^1$. We now consider a suspension of such model particles in a viscous fluid, with no imposed flow. Then the effect of Brownian agitations will be to cause the system to settle down to thermodynamic equilibrium. The question arises as to the distribution $p(\theta)$ of the included angle θ for this equilibrium state.

Now we may plainly factor out an irrelevant motion associated with the system centre of mass, and also an overall rotation of the plane of the trumb-bell. With these

Author(s)	Type of model particle	Method of handling constraint	Trumb-bell result†	Strength of flow considered in detail	Notes
Kramers 1944	Bead–rod chain	Generalized co-ordinates	(2.3)	Linear	Derived from phase space
Kirkwood & Riseman 1948	Bead–rod chain	Generalized co-ordinates	(2.3)	Linear	Derived from configuration space
Rouse 1953; Zimm 1956	Bead, linear-spring chain	No constraints	(2.2)	Linear	
Lodge & Wu 1971	Bead, linear-spring chain	No constraints	(2.2)	Arbitrary	
Prager 1958, Giesekus 1956	Dumb-bell	Generalized co-ordinates	§	Arbitrary	
Several	Rigid body§	Generalized co-ordinates	§	Arbitrary	
Bird *et al.* 1969‡	Bead, nonlinear spring	Springs frozen	(2.2)	Steady linear	Consistent results for the zero shear viscosity but not the first normal stress difference
Hassager 1974*a*‡	Bead–rod chain	Generalized co-ordinates	(2.3)	Steady quadratic	
Hassager 1974*b*‡	Bead–rod chain	Generalized co-ordinates	(2.3)	Unsteady linear	
Hinch 1976	Inextensible thread	Generalized co-ordinates	(2.2)	Arbitrary	Infinity of degrees of freedom
Curtiss *et al.* 1974‡	Arbitrary bead rod spring system	Generalized co-ordinates	(2.3)	Arbitrary	Full phase space derivation, including $\boldsymbol{\sigma}$
Edwards & Freed 1974, Freed & Edwards 1974	Arbitrary chain	Generalized co-ordinates	(2.2)	Arbitrary	‘Hopping time scale’ analysis for the Brownian motions

Flory 1969	Bead–rod chain	Transformed Cartesian co-ordinates	(2.2)	Mainly linear	Concerned with statistical rather than rheological properties
Fixman & co-workers (1974*a*, *b*, 1975, 1976	Bead–rod chain	Lagrange multipliers, tensions in rods	(2.2)	Linear	‖
Titulaer 1977 Titulaer & Deutch 1975	Bead–spring chain	Springs frozen	(2.2)	Nonlinear oscillatory Linear oscillatory	Agrees with Fixman *et al.* Disagrees with Hassager
Gō & Scheraga 1969, 1976	Arbitrary system	Quantum mechanics	(4.14)	None	Not concerned with rheology
Gottlieb & Bird 1976‡	Trumb-bell	Lagrange multipliers, tensions in rods	(2.3)	None	Numerical simulation of Brownian agitations
Present work	Bead–rod chain	Quantum/classical mechanics	(4.14)/(2.2)	Arbitrary	

† Not all the papers quoted give a result for the trumb-bell. For the sake of ready comparison, however, we have given the equation which would be obtained for the equilibrium configuration distribution of a trumb-bell using the same method.

‡ A summary of all these papers may be found in the recent book by Bird *et al.* (1977).

§ In these cases, no paradox arises and it is therefore unclear which of (2.2) or (2.3) would appear. The rigid body entry is given for completeness. In principle, rigid bodies (e.g. the systems of § 3) could be treated by regarding them as having infinitely many degrees of freedom of which almost all are constrained. A satisfactory account should handle this as a relatively trivial case.

‖ There is a further discrepancy here. Fixman & Evans (1976) show that, for the intrinsic viscosity, the limits of infinitely high frequency and rigidity do not commute. We discuss this point in § 6.

TABLE 1. Survey of the literature.

simplifications there remain just three degrees of freedom: the lengths of the springs and the included angle. In the case where the springs are frozen into rods, there is just one degree of freedom left, θ. For a system in thermodynamic equilibrium we have (Landau & Lifschitz 1959) that the phase space distribution f is Maxwell–Boltzmann, i.e.

$$f(\mathbf{p},\mathbf{q}) = \text{const.}\exp\left[-\epsilon(\mathbf{p},\mathbf{q})/kT\right],$$

where the $\mathbf{q}$'s are generalized co-ordinates for the system and the $\mathbf{p}$'s are the conjugate momenta. ϵ is the energy associated with the phase point $\mathbf{p}$, $\mathbf{q}$; T is the temperature, and k Boltzmann's constant. Further, since on the time scale of interest it is only the distribution of the $\mathbf{q}$ that need concern us, the *configuration space* probability distribution is given by

$$\rho(\mathbf{q}) = \int f(\mathbf{p},\mathbf{q})\,d\mathbf{p} = \text{const.}\int \exp\left(-\epsilon(\mathbf{p},\mathbf{q})/kT\right)d\mathbf{p}. \tag{2.1}$$

Now it is straightforward to show that in the case of springs *of arbitrary stiffness*, (2.1) gives for the trumb-bell

$$\rho(\theta) = \text{const.}\sin\theta. \tag{2.2}$$

Whereas if the springs are considered rigid, so the momenta conjugate to their lengths never appear, then

$$\rho(\theta) = \text{const.}\left(1-\tfrac{1}{4}\cos^2\theta\right)^{\frac{1}{2}}\sin\theta. \tag{2.3}$$

Equation (2.3) is derived on the assumption that the masses of all the beads are equal; (2.2) is valid independently of such an assumption. Explicit derivations are given in §§ 4.2 and 4.3. We see that the expressions are unequal. Equation (2.3) would appear first to have been derived by Kramers (1944), and effectively the same result is used by Kirkwood and co-workers (1948, 1967). More recently results of the same type have been developed (Hassager 1974*a*, *b*; Curtiss, Bird & Hassager 1974). On the other hand Flory (1969) in his work on polymer configurations has employed (2.2) and its analogues; while Fixman & Kovac (1974*a*, *b*) and Fixman & Evans (1976) have calculated rheological properties on essentially the same basis. A comparative analysis of these approaches is given in table 1.

We shall see in §§ 3 and 4 that (2.2) is valid for the trumb-bell in appropriate limiting circumstances, but that in general a new form (4.14) is required. Equation (2.3) never appears as a natural limit when a full quantum-mechanical analysis is performed for the trumb-bell with quantized vibrations of the springs. It remains possible that (2.3) might arise as the classical limit of a quantum system in which the degrees of freedom corresponding to the rods were absent *ab initio*, but only in so far as such an analysis is itself a consistent application of quantum mechanics to the trumb-bell with rods. This paper takes the view that it is not, because of the uncertainty in the momentum of a rod given its length. The formal correctness of (2.3) is strongly supported by the evidence of the numerical experiment of Gottlieb & Bird (1976), but their use of classical rather than quantum dynamics in the formulation of the numerical equations of course begs the question raised in this paragraph.

3. Order of magnitude analysis

The substance of our explanation of the discrepancy will involve quantum mechanics, so before considering the detailed mathematics of the problem we give some order of magnitude estimates of the physical parameters which appear.

Consider some degree of freedom for the system in the limit as the force which constrains it become infinitely large (i.e. that degree of freedom disappears). It is perhaps conceptually easiest to imagine a 'spring' of non-zero natural length in the limit as it becomes a 'rod'. Then there are two natural dimensionless parameters associated with that degree of freedom: its rigidity; and its smallness on a scale naturally associated with Planck's constant $\hbar$. Thus, if l is a typical length, κ a stiffness (which becomes arbitrarily large), and ϵ a typical vibrational energy, then

$$\alpha = (\epsilon/\kappa l^2)^{\frac{1}{2}} \tag{3.1}$$

measures the dimensionless variation in the length of the spring, and $\alpha \to 0$ for a very stiff spring.

A second dimensionless parameter appears, however, from the consideration of quantum mechanics. Associated with the large (but finite) stiffness there will be a natural frequency of oscillation ν with $\nu \sim (\kappa/ml^2)^{\frac{1}{2}}$, where m is a typical mass. It follows that, if the corresponding quantized energy $\hbar\nu$ is comparable to ϵ, then classical mechanics will be inappropriate. In other words, defining

$$\beta = \hbar\nu/\epsilon, \tag{3.2}$$

quantum mechanics become important when $\beta \gtrsim 1$.

It is clear that α and β are independent parameters characterizing the system and we may therefore identify two limiting parameter regimes which are different, though both are rigid in the sense $\alpha \ll 1$.

(i) $\alpha \ll 1$, $\beta \gtrsim 1$, the *rigid quantized* regime.
(ii) $\alpha \ll 1$, $\beta \ll 1$, the *rigid classical* regime.

It will be shown that the failure to distinguish between (i) and (ii) has been the source of much of the confusion in the literature.

We consider first near-equilibrium states for which (by energy equipartition) ϵ may be replaced by kT. Then if we take a value $\alpha = 10^{-1}$ to define a 'stiff' system, (3.2) gives $\beta = (10\hbar/l)\,(kT/m)^{\frac{1}{2}}$. Substituting typical values does not provide any clear indication as to which of (i) or (ii) to use, for if m and l are taken as those appropriate to a monomer unit then β is large, about 10, and so, hardly surprisingly, quantum physics are important in handling the molecular vibrations (cf. spectral analysis). On the other hand if, in the spirit of modelling, m, l are representative of random coil of say 10^4 bonds, then β is small and (ii) can be used.

There are two circumstances in which our estimate of β may be altered. The first is that where a strong flow is present, then ϵ is no longer typically kT but ζEl^2 where ζ is a friction constant for a bead, and E is a measure of the shear rate. Second, this estimate of the flow strength is itself altered when there are N ($\gg 1$) units in the chain (for the flow, when strong, can extend the chain and so produce very large velocity differences between its ends). These considerations lead us to define the following dimensionless parameters.

(i) A monomer Péclet number $P = \zeta E l^2/2kT$, the ratio of flow forces to thermal vibrations for a single unit. (3.3)

(ii) A polymer Péclet number $\mathscr{P} = NP$ appropriate for extended states. (3.4)

(ii) A quantum number appropriate for near equilibria $Q = \hbar\nu/kT$. (3.5)

(iv) A quantum number appropriate for strong flows $\mathscr{Q} = Q/NP$. (3.6)

4. The equilibrium problem

4.1. *General formulation*

In this section we follow Gō & Scheraga (1969) and construct an apparatus to deal with a general system in equilibrium, and derive the rigid quantized and rigid classical limits. In § 5 the analysis for the rigid quantum limit is generalized to include the non-equilibrium problem, and detailed solutions are given for the test case of a trumbbell.

4.1.1. *Notation and conventions.* Suppose we have a system characterized by generalized co-ordinates q^i, $i = 1, \ldots, N$. We shall be concerned to 'freeze' the co-ordinates $q^A, A = M+1, \ldots, N$ to values of zero, say, while leaving the q^α, $\alpha = 1, \ldots, M$ unconstrained. We adopt the convention that suffixes $i, j, \ldots$ are to run from 1 to N; $\alpha, \beta, \ldots$ from 1 to M; and $A, B, \ldots$ from $M+1$ to N. Where matrices are partitioned this will be shown by their suffixes, e.g.

$$g_{ij} = \left(\begin{array}{c|c} g_{\alpha\beta} & g_{\alpha A} \\ \hline g_{A\alpha} & g_{AB} \end{array}\right).$$

We suppose that the system has kinetic and potential energies given by

$$T = \tfrac{1}{2} g_{ij}\dot{q}^i\dot{q}^j; \quad V = \tfrac{1}{2} V_{ij} q^i q^j,$$

where g_{ij} and V_{ij} are each functions of the variables q^i. We then regard g_{ij} as the 'metric tensor' for the co-ordinates, and define g^{ij} as its inverse, i.e.

$$g^{ij} g_{jk} = \delta^i_k. \tag{4.1}$$

Note that in general the partitioned form of g^{ij} does *not* consist of the inverses of the partitioned form of g_{ij}: the typical relationships between them are given by

$$g^{\alpha\beta} = (g_{\alpha\beta} - g_{\alpha A}\, g^{-1}_{AB}\, g_{B\beta})^{-1},$$

$$g^{\alpha A} = -(g_{\alpha\gamma} - g_{\alpha C}\, g^{-1}_{CD}\, g_{D\gamma})^{-1} g_{\gamma B}\, g^{-1}_{BA}.$$

Finally, the momenta conjugate to the q's are defined by

$$p_i \equiv g_{ij}\dot{q}^j = \partial T/\partial \dot{q}^i.$$

4.1.2. *Classical thermodynamic equilibrium.* In thermodynamic equilibrium, the phase space distribution for the system is Maxwell–Boltzmann and thus the configuration space distribution is

$$\rho(\mathbf{q}) = \text{const.} \int \exp\left[-(g^{ij} p_i p_j + V_{ij} q^i q^j)/2kT\right] d^N\mathbf{p}. \tag{4.2}$$

On performing the integration this gives

$$\rho(\mathbf{q}) = \text{const.}\, g^{\frac{1}{2}} \exp(-V/kT), \quad \text{where} \quad g = \det g_{ij}.$$

This result was derived by Kramers (1944) and also Kirkwood & Riseman (1948). Note that since $g^{\frac{1}{2}}$ is in general a function of the q's we do not have a simple Maxwellian distribution $\exp(-V/kT)$. In addition we see that the stiffness of the constraining potentials in no way affects the derivation.

If then for V_{ij} we take the particular form†

$$V_{ij} = \left(\begin{array}{c:c} V_{\alpha\beta} & V_{\alpha A} \\ \hdashline V_{A\alpha} & \epsilon^{-2}\delta_{AB} \end{array}\right)$$

with $V_{\alpha\beta}$, $V_{\alpha A}$, $V_{A\alpha}$ all functions of the q^α only, then, in the limit $\epsilon \to 0$,

$$\rho \to \text{const.}\, g^{0\frac{1}{2}} \exp(-\tfrac{1}{2}V_{\alpha\beta}\, q^\alpha q^\beta) \prod_A \delta(q^A) \tag{4.3}$$

with $\delta(\ )$ a Dirac delta-function, and the superscript 0 indicating evaluation with all $q^A = 0$. If however we had taken $\epsilon = 0$ *ab initio*, then the q^A co-ordinates would never have appeared, and we should have obtained

$$\rho = \text{const.}\, g'^{\frac{1}{2}} \exp(-\tfrac{1}{2}V_{\alpha\beta}\, q^\alpha q^\beta/kT) \prod_A \delta(q^A)$$

with

$$g' = \det g_{\alpha\beta}. \tag{4.4}$$

Thus the two cases are the same, and no paradox arises, if and only if $g^0 = g'$ to within a multiplicative constant. It is easy to show that for systems which are rigid (after constraining) $g^0 = g'$ always (see the dumb-bell case in § 4.2) and therefore problems only arise for systems with internal degrees of freedom, and the trumb-bell would seem the simplest such (§ 4.3). It is also easy to show *via* Lagrange's equations that the classical *dynamics* of the constrained system are the same as the limiting form for the unconstrained system, so that it is solely the thermodynamic aspects which are responsible for the difficulty. The problem here is exactly the same as occurs for the specific heat calculation (see Sommerfeld 1956, § 30), and its resolution, as there, is *via* quantum mechanics.

4.1.3. *Quantum thermodynamic equilibrium.* We now suppose that the q^A co-ordinates are quantized, while the q^α remain classical. Then for given p_α, q^α the set of allowable energies is quantized, and can be labelled by a quantum number n characteristic of the state, E_n. Then the Maxwell–Boltzmann distribution gives (Landau & Lifschitz 1959, § 28)

$$f(n; p_\alpha, q^\alpha) = \text{const.} \exp(-E_n(p_\alpha, q^\alpha)/kT), \tag{4.5}$$

and (4.2) is replaced by

$$\rho(q) = \text{const.} \sum_{n=1}^{\infty} \int \exp(-E_n(p_\alpha, q^\alpha)/kT)\, d^M p_\alpha. \tag{4.6}$$

Now, we assume that the energies are decomposable into two contributions, one arising from the quantized degrees of freedom, and one from the classical.

Quantum contribution. Writing

$$g^{ij} = \left(\begin{array}{c:c} \cdots & \cdots \\ \hdashline & g^{QAB} \end{array}\right),$$

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† The more general case in which V_{AB} also depends on the q^α is considered in appendix A.

where as given earlier, $g^{QAB} = (g_{AB} - q_{A\alpha} g^{-1}_{\alpha\beta} g_{\beta B})^{-1}$,

we can write the Hamiltonian for the quantum part as

$$\mathscr{H} = \tfrac{1}{2} g^{QAB} p_A p_B + \tfrac{1}{2} \epsilon^{-2} \delta_{AB} q^A q^B. \tag{4.7}$$

Furthermore, since the vibrations are (by definition) small, we may evaluate g^{QAB} at $q^A = 0$, and at fixed values of the q^α, p_α which therefore appear only as parameters here. (Similarly, there is no reason in principle why we should not make our choice of potential considerably more complex: δ_{AB} is the simplest available which demonstrates the features we are interested in. Appendix A explores this point further.) Now (4.7) is the Hamiltonian for a set of coupled harmonic oscillators, and so the associated energy levels are (e.g. Fay 1965, § 12.5)

$$E = \sum_{A=M+1}^{N} (n_A + \tfrac{1}{2}) \hbar \nu_A, \tag{4.8}$$

where the n_A are integers and the normal mode frequencies ν_A satisfy

$$\det (g^{QAB} - (\nu^2/\epsilon^2) \delta_{AB}) = 0 \tag{4.9}$$

and are, in general, functions of the q^α through g^{QAB}.

Classical contribution. Here we effectively have all the $q^A = 0$, so writing

$$g^{C\alpha\beta} = g^{-1}_{\alpha\beta}|_{q^A=0}, \tag{4.10}$$

the kinetic energy from the classical degrees of freedom is $\frac{1}{2} g^{C\alpha\beta} p_\alpha p_\beta$.

Thus collecting together the two contributions, and substituting in (4.6), we have

$$\begin{aligned} \rho(\mathbf{q}) &= \text{const.} \sum_{n_A=0}^{\infty} \int \exp [- (\tfrac{1}{2} g^{C\alpha\beta} p_\alpha p_\beta + \tfrac{1}{2} V_{\alpha\beta} q^\alpha q^\beta + \sum_A (n_A + \tfrac{1}{2}) \hbar \nu_A)/kT] \, dp_\alpha \\ &= \text{const.} \, g'^{\frac{1}{2}} e^{-V/kT} \frac{\exp [- \frac{1}{2} \hbar \sum_A \nu_A / kT] \prod_A \delta(q^A)}{\prod_A (1 - \exp(-\hbar \nu_A / kT))}, \end{aligned} \tag{4.11}$$

where g' is as defined in (4.4).

On comparing (4.4) and (4.11) we see that the effect of including the quantum energies for the 'frozen' degrees of freedom is to introduce a new factor

$$\exp(-\tfrac{1}{2}\hbar \sum_A \nu_A/kT) / \prod_A (1 - \exp(-\hbar \nu_A / kT))$$

into $\rho(\mathbf{q})$. If the ν_A are independent of the q^α, this is just a constant and therefore irrelevant. If, however, the quantum energies vary with the classical co-ordinates, which is a common feature of systems with internal degrees of freedom, then this factor must be included.

We note too that this resolves the discrepancy that arises from classical thermodynamics in computing $\rho(\mathbf{q})$ by the two routes. For now if we take the limit $\hbar \nu_A / kT \to 0$, so that the quantum states become more energetic and so classical, we find

$$\rho(\mathbf{q}) = \text{const.} \, g'^{\frac{1}{2}} \exp(-V/kT) \prod_A \delta(q^A) / \prod_A \nu_A,$$

and, using (4.9), this gives

$$\rho(\mathbf{q}) = \text{const.} \, g^{0\frac{1}{2}} \exp(-V/kT) \prod_A \delta(q^A),$$

thereby recovering the classical result (4.3). Those treatments that have not included the quantum behaviour of the constrained co-ordinates at all (Kramers 1944; Kirkwood & Riseman 1948; Curtiss *et al.* 1974, Bird *et al.* 1977) have thus failed to account for the variation of the zero point energies of the suppressed degrees of freedom with the retained classical co-ordinates. This is the heart of the problem, and explains the danger of simply ignoring the constrained co-ordinates as if the system were classical: such a simplification may be valid for the mechanics, and yet not for the statistical mechanics of a system.

We now illustrate the analysis by evaluating these limits for two very simple systems, the dumb-bell and trumb-bell.

4.2. *The dumb-bell*

We consider a dumb-bell with beads of equal mass (though the conclusions are wholly unaltered for the unequal mass case). Axes are chosen at the centre of mass, and the state of the system is described by spherical polars so that $(q^1, q^2, q^3) = (\theta, \phi, r)$. Then setting aside the irrelevant centre of mass motion, the kinetic energy is

$$T = \tfrac{1}{4}m(r^2\dot{\theta}^2 + r^2\sin^2\theta\dot{\phi}^2 + \dot{r}^2),$$

which gives
$$g_{ij} = \tfrac{1}{2}m\left(\begin{array}{cc:c} r & 0 & 0 \\ 0 & r\sin\theta & 0 \\ \hdashline 0 & 0 & 1 \end{array}\right) \quad \text{and} \quad g^0 = \tfrac{1}{8}m^3r^2\sin\theta,$$

and thus
$$g_{\alpha\beta} = \tfrac{1}{2}m\begin{pmatrix} r & 0 \\ 0 & r\sin\theta \end{pmatrix} \quad \text{and} \quad g' = \tfrac{1}{4}m^2r^2\sin\theta = \text{const.}\times g^0.$$

In other words, for this system there is no difference in the equilibrium configuration before and after the freezing of the spring. Hence, results (Giesekus 1956; Prager 1957) for the rheology of a rigid dumb-bell suspension are consistent with those for the stiff-spring dumb-bell. The crucial degeneracy associated with the dumb-bell is that after freezing *no internal degree of freedom remains*.

4.3. *The trumb-bell*

Again, taking beads of equal mass, and setting aside the motion of the centre of mass, we are left with a system of 6 degrees of freedom. This can be dealt with by using spherical polars for each of the connectors; but, following Hassager (1974*a*), we can simplify these by factoring out an overall rotation of the plane of the trumb-bell so that only 3 co-ordinates are required $(q^1, q^2, q^3) = (\theta, b^1, b^2)$. Then we may write down the kinetic energy for the system, and after some straightforward manipulations can show that

$$g' = m(1 - \tfrac{1}{4}\cos^2\theta)^{\frac{1}{2}}\sin\theta, \tag{4.12}$$

while
$$g^{QAB} = \tfrac{1}{3}m\begin{pmatrix} 2 & \cos\theta \\ \cos\theta & 2 \end{pmatrix}. \tag{4.13}$$

Thus, $\nu_1 = \nu(2-\cos\theta)^{\frac{1}{2}}$, $\nu_2 = \nu(2+\cos\theta)^{\frac{1}{2}}$ where ν is a constant. So defining $Q = \hbar\nu/kT$ as in (3.5), we have finally that

$$\rho(\theta) = \text{const.}\sin\theta(1-\tfrac{1}{4}\cos^2\theta)^{\frac{1}{2}}\frac{\exp\{-Q[(2-\cos\theta)^{\frac{1}{2}}+(2+\cos\theta)^{\frac{1}{2}}]\}}{\{1-\exp[-2Q(2-\cos\theta)^{\frac{1}{2}}]\}\{1-\exp[-2Q(2+\cos\theta)^{\frac{1}{2}}]\}}. \tag{4.14}$$

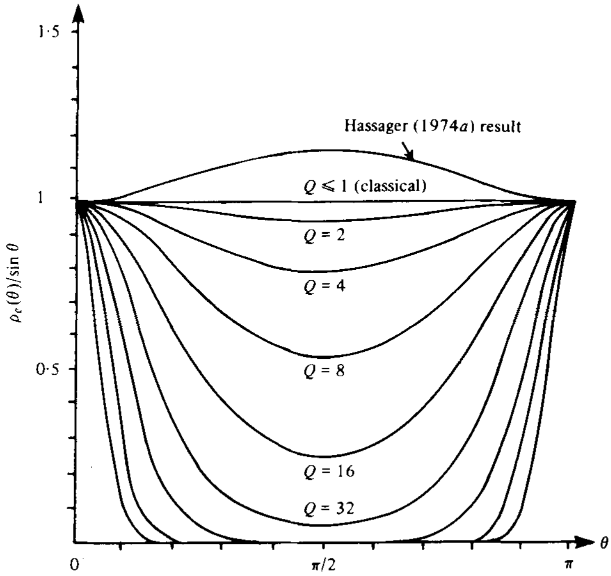

FIGURE 2. Equilibrium distributions $\rho_e(\theta)/\sin\theta$ for the included angle of a trumb-bell normalized to unity at $\theta = 0$.

In the classical rigid limit $Q \to 0$ this gives $\rho \sim$ const. $\sin\theta(1 + O(Q^2))$, while in the high quantum limit $Q \to \infty$,

$$\rho \sim \text{const.} \times \sin\theta(1 - \tfrac{1}{4}\cos^2\theta)^{\frac{1}{2}} \times \exp\{-Q[(2 - \cos\theta)^{\frac{1}{2}} + (2 + \cos\theta)^{\frac{1}{2}}]\}.$$

(This latter result is not wholly consistent however, in that when Q becomes sufficiently large it is no longer valid to regard θ as a classical co-ordinate, and indeed at sufficiently low T (i.e. $Q \to \infty$), the overall rotation of the system is also quantized.) For purposes of comparison, it is convenient to set aside the $\sin\theta$ term which merely arises from the spherical polar angular integration and concentrate on the remaining factor. When the $Q \to \infty$ approximation is sensible, then, it is clear that $\rho/\sin\theta$ is non-zero only near $\theta = 0, \pi$ (i.e. when the trumb-bell is stretched out or folded back on itself), and, for all Q, the effect of including the quantum energies is to enhance the tendency for the system to be in one of these states rather than at some intermediate angle. If the variations in zero-point energies are not included (Hassager 1974*a*) then we obtain instead of (4.14)

$$\rho(\theta) = \text{const.} \sin\theta(1 - \tfrac{1}{4}\cos^2\theta)^{\frac{1}{2}}$$

for which the $\theta = \frac{1}{2}\pi$ state is preferred to $\theta = 0, \pi$. The various distributions are shown graphically in figure 2 (where, for convenience of display, the multiplying constants have been chosen to make $\lim_{\theta \to 0} \rho(\theta)/\sin\theta = 1$ rather than by normalizing ρ so that

$$\int_0^\pi \rho(\theta)\, d\theta = 1).$$

4.4. *The Rouse chain*

The complexity of the result (4.14) for the trumb-bell suggests that analogous results for general N will be exceedingly complex. Fixman (1974) has considered the problem of determining g' and shows that

$$g^{QAB} = \begin{cases} 2, & B = A, \\ \cos\theta_A, & B = A \pm 1, \\ 0 & \text{otherwise}, \end{cases} \tag{4.15}$$

indicating that, for general values of the angles θ_A between the rods, the results will rapidly become too complex to handle.

Further analytic progress is possible in two cases, however: either when the chain is nearly fully extended (by being immersed, say, in a strong stretching flow; see § 5.3), or when $Q \rightarrow 0$ and the conformation is a random walk (Flory 1969). A simple description of the overall size of the molecule is provided by its r.m.s. end-to-end vector $\mathbf{r}$, and for a random walk we have

$$\langle r^2\rangle^{\frac{1}{2}}/Nl \sim N^{-\frac{1}{2}} \quad \text{as} \quad N \rightarrow \infty \quad \text{and} \quad Q \rightarrow 0.$$

For non-zero Q, the effect of the quantum terms is to introduce additional angular potentials at each bead (this is most clearly seen in § 5). As Flory (1969) notes, as regards the conformational statistics of a macromolecule, these potentials are equivalent to changing the *persistence length* of the chain, so that a chain of N units of length l with potentials is equivalent to a chain of N units of length l' without potentials. For $Q \rightarrow \infty$, the strong bias in favour of $\theta = 0, \pi$ will mean that the configuration is approximately that of a one-dimensional random walk; while for $Q \rightarrow 0$, the trumb-bell analysis of §§ 4 and 5 indicates a relation of the form

$$l' = f(Q)\,l \quad \text{with} \quad f(Q) = \begin{cases} 1 + O(10^{-3}Q^4), & Q \rightarrow 0, \\ 1 + O(1/Q), & Q \rightarrow \infty, \end{cases}$$

giving

$$\langle r^2\rangle^{\frac{1}{2}}/Nl \sim N^{-\frac{1}{2}} f(Q).$$

Thus the influence of Q on the equilibrium length of the macromolecule is small, though its aspect ratio will be greater as Q increases.

5. The diffusion problem in the rigid quantized limit

5.1. *General case*

We now suppose that our (general) system is no longer in thermodynamic equilibrium because of the fluid forces on it, and we seek to calculate the effective entropic forces which are attempting to restore it to equilibrium. This may be achieved by a detailed analysis in phase space (see e.g. Curtiss *et al.* 1974), but the time scale for adjustment of momentum is very short, and so the momentum part of phase space can be assumed in equilibrium, and a generalization of the Einstein argument will produce the necessary fluxes.

Hence, given some configuration space probability distribution $\rho(q^\alpha)$, we imagine this as a hypothetical equilibrium for the system with some suitably chosen external potential $V_E(q^\alpha)$. Then ρ must satisfy (4.11), and

$$V_E = -kT \log(\rho/h)$$

where $$h(q^\alpha; \nu_A) \equiv g'^{\frac{1}{2}} \exp[-\tfrac{1}{2}\hbar\Sigma\nu_A/kT] / \prod_A [1-\exp(-\hbar\nu_A/kT)]. \tag{5.1}$$

Now the generalized force on a particle due to the presence of this potential is $-\partial V_E/\partial q^\beta$, and thus if the mobility tensor is $\zeta^{-1\alpha\beta}$ there is an advective particle flux $\mathbf{j}$ given by

$$j^\alpha = -\zeta^{-1\alpha\beta}\rho\,\partial V_E/\partial q^\beta.$$

This must be balanced by a diffusive flux, which is therefore $kT\zeta^{-1\alpha\beta}\rho\,\partial(\log\rho/h)/\partial q^\beta$, and hence we identify the generalized entropic force as $-kT\partial(\log\rho/h)/\partial q^\beta$.

It is now a straightforward matter to set up the diffusion equation for the problem. We follow Kirkwood & Riseman (1948). Probability conservation gives

$$\frac{\partial\rho}{\partial t} + \nabla.\mathbf{j} = 0 \quad \text{i.e.} \quad \frac{\partial\rho}{\partial t} + \frac{1}{g'^{\frac{1}{2}}}\frac{\partial}{\partial q^\alpha}(g'^{\frac{1}{2}}j^\alpha) = 0 \tag{5.2}$$

and $$j^\alpha = \rho\dot{q}^\alpha. \tag{5.3}$$

The 'force' on the system has been derived as $-\partial V/\partial q^\alpha - kT\,\partial(\log\rho/h)/\partial q^\alpha$, where V represents internal and external potentials, and this must be balanced by a hydrodynamic force $\zeta_{\alpha\beta}(u^\beta - \dot{q}^\beta)$, where u^β is the appropriate component of the fluid velocity. Thus

$$\dot{q}^\alpha = u^\alpha - \zeta^{-1\alpha\beta}(\partial V/\partial q^\beta + kT\,\partial(\log\rho/h)/\partial q^\beta, \tag*{(5.4)†}$$

and (5.2), (5.3) and (5.4) can be rearranged to give

$$\frac{\partial\rho}{\partial t} + \frac{1}{g'^{\frac{1}{2}}}\frac{\partial}{\partial q^\alpha} g'^{\frac{1}{2}}\left\{\rho\left(u^\alpha - \zeta^{-1\alpha\beta}\frac{\partial\tilde{V}}{\partial q^\beta}\right) - D^{\alpha\beta}\frac{\partial\rho}{\partial q^\beta}\right\} = 0, \tag{5.5}$$

where the diffusion tensor $$\mathbf{D} = kT\boldsymbol{\zeta}^{-1}, \tag{5.6}$$

and $$\tilde{V} \equiv V - kT\log h.$$

Hence, the diffusion equation is precisely as we would have expected, except that a new term $-kT\log h$ must be added to the potential for the system to take account of the quantum energies of the frozen co-ordinates.

The average particle stress is then given by

$$\bar{\boldsymbol{\sigma}}^p = n\langle\mathbf{s}\rangle \equiv n\int\rho(q^\alpha)\,\mathbf{s}(q^\alpha)\,d^Mq^\alpha, \tag{5.7}$$

where $\mathbf{s}$ is the stresslet exerted by one particle on the fluid, and n is the number density of particles. We now illustrate these general principles by analysing the rheological properties of a suspension of trumb-bells and of Rouse chains.

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† In fact, in (5.4) we have made the simplest possible assumption about the hydrodynamics. In general there can be an additional flux in configuration space arising from components of $\mathbf{u}$ outside that space, e.g. for an extensional flow which is trying to 'pull apart' a rigid (modified) dumb-bell aligned with the principal axis of extension there is no component of $\mathbf{u}$ in the configuration (rotation) space of the system. Nevertheless if the 'beads' of the dumb-bell have the right shape, it may rotate, and thus give a probability flux (see Erpenbeck & Kirkwood in Kirkwood 1967).

5.2. *Rheological properties for the trumb-bell model*

The mathematical details involved in using these quantum models become complex very rapidly. Two cases in which analytic progress can be made are weak flows and potential flows. We examine these in detail.

Weak flows. Earlier workers (e.g. Hassager 1974*a*) have found that the simplest available rheological property, the zero shear viscosity, is independent of their various solutions for the equilibrium probability distribution. We shall reach the same conclusion here. The 'first' case where the quantum influence can be demonstrated and which we can analytically find, then, are the normal-stress-differences (in fact the first, for the second always vanishes for this type of model), and we can again compare with the classical result, and that of Hassager (1974*a*).

We do not present a detailed analysis for the computation of the stress tensor here. It is shown by Hassager (1974*a*) that a more convenient form of (5.7) is

$$\bar{\boldsymbol{\sigma}}^p = \frac{n\zeta l^2}{3}\frac{\delta}{\delta t}\langle \cos^2\tfrac{1}{2}\theta\,\boldsymbol{\delta}_3\boldsymbol{\delta}_3 + 3\sin^2\tfrac{1}{2}\theta\,\boldsymbol{\delta}_2\boldsymbol{\delta}_2\rangle, \tag{5.8}$$

where the unit vectors $\boldsymbol{\delta}_2$, $\boldsymbol{\delta}_3$ define the plane of the trumb-bell as shown in figure 1 (*b*). ζ is the friction coefficient for the beads, l the length of a rod, and $\delta/\delta t$ an Oldroyd derivative given by

$$\frac{\delta}{\delta t}(\;) \equiv \frac{\partial}{\partial t}(\;) - (\nabla \mathbf{u})^T.(\;) - (\;).(\nabla \mathbf{u}).$$

Now correct to quadratic terms $\mathbf{E}\,.\,\mathbf{E}$ and $\delta\mathbf{E}/\delta t$ (assumed of the same order) it may be shown from (5.5) that

$$\rho = \rho_e[1 + \zeta l^2/2kT\mathbf{E}\colon (\cos^2\tfrac{1}{2}\theta\,\boldsymbol{\delta}_3\boldsymbol{\delta}_3 + 3\sin^2\tfrac{1}{2}\theta\,\boldsymbol{\delta}_2\boldsymbol{\delta}_2)], \tag{5.9}$$

where ρ_e is the equilibrium probability distribution given by (4.14). Thus, to find the second-order fluid behaviour, it remains only to substitute (5.9) into the configuration space averages in (5.8). This gives rise to the retarded motion expansion

$$\bar{\boldsymbol{\sigma}}^p = -p\mathbf{I} + 2b_1\,\mathbf{E} - 2b_2\,\delta\mathbf{E}/\delta t + O(P^3), \tag{5.10}$$

where P is the Péclet number given by (3.3), and it may be shown that the dimensionless forms for the constants are given by

$$\begin{aligned} \hat{b}_1 &\equiv b_1/n\zeta l^2 = \tfrac{1}{9}(2 - J_1/J_0), \\ \hat{b}_2 &\equiv kTb_2/n\zeta^2 l^4 = \tfrac{1}{540}(13J_2/J_0 - 16J_1/J_0 + 7) \end{aligned} \tag{5.11}$$

and

$$J_n = \int_0^\pi \cos^n\theta\rho_e(\theta)\,d\theta. \tag{5.12}$$

Now in all the cases considered, ρ_e is even in θ about $\frac{1}{2}\pi$ and hence $J_1 = 0$. This gives rise to the observation above that the zero shear viscosity is given by $\hat{b}_1 = \frac{2}{9}$ in all cases. The various values of $\hat{b}_2$ which have been obtained are shown in table 2, and in graphical form in figure 3. It will be seen that the variation in $\hat{b}_2$ for $Q \leqslant 1$ is very small, $10^{-3}Q^4$, and this indicates that under normal circumstances the quantum effect on the rheological functions will not be very important. It further strengthens the case that the additional mathematical problems posed by handling generalized co-ordinates are

	$\hat{b}_1$	$\hat{b}_2$
Classical case	$\frac{2}{9}$	$\frac{17}{810} = 0{\cdot}0210$
Hassager (1974*a*)		$\frac{1}{1080}\,\frac{80\pi + 3\sqrt{3}}{2\pi + 3\sqrt{3}} = 0{\cdot}0207$
Quantum case $Q \to 0$ (present work)		$\frac{17}{810}\left(1 + \frac{13}{11475}\,Q^4 + O(Q^6)\right)$
Quantum case $Q \to \infty$ (present work)		$\frac{1}{27}(1 + O(e^{-Q}))$

TABLE 2. Zero shear viscometric coefficients for the trumb-bell.

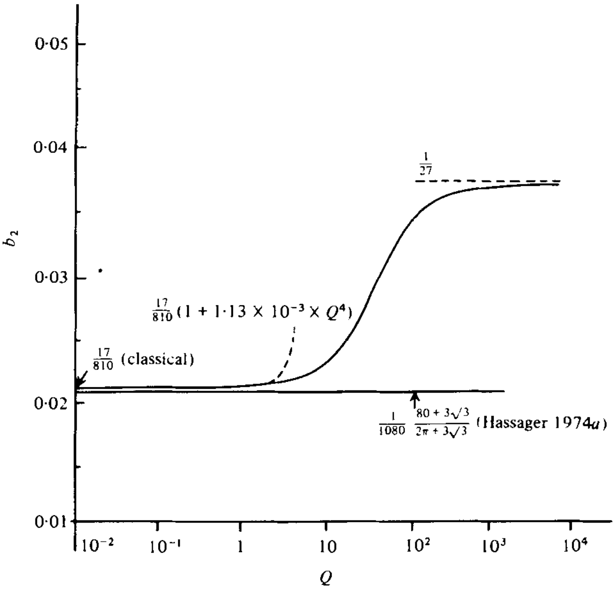

FIGURE 3. Variation of the first normal-stress-difference with Q for a trumb-bell suspension.

not rewarded by attendant improvements in the quality of the answers: quantum effects are undoubtedly part of the physics of the problem, but seem to have little effect on the rheology, at any rate for weak flows.

Strong flows. In order to exploit the known solution of the diffusion equation for potential flows, we consider a steady extensional flow

$$\mathbf{E} = E\begin{pmatrix} 2 & & \\ & -1 & \\ & & -1 \end{pmatrix}.$$

It follows (Hassager 1974*a*) that

$$\rho = \rho_e \exp\Big[\sum_{\text{beads}} \mathbf{r}^i . \mathbf{E} . \mathbf{r}^i / 2D\Big]. \tag{5.13}$$

	$\langle r\rangle/2l$	$\hat{\mu}_e$
Weak flow:		
$P\to 0 \quad Q\to 0$	$\frac{2}{3}\left[1+\frac{124}{1575}P^2+O(Q^4)+O(P^3)\right]$	$\frac{2}{9}\left[1+\frac{34}{81}P\left(1+\frac{13}{11475}Q^4\right)+O(Q^6)+O(P^2)\right]$
$Q\to\infty$	$\frac{1}{2}\left[1+\frac{K}{Q^{\frac{1}{2}}}+O\left(\frac{1}{Q}\right)\right] \times\left[1+\frac{16}{45}P^2\left(1-\frac{2K}{Q^{\frac{1}{2}}}\right)+O(P^3)\right]$ $K=[\pi/(3-\sqrt{3})]^{\frac{1}{2}}$	$\frac{2}{9}\left[1+\frac{20}{27}P+O\left(\frac{1}{Q}\right)+O(P^2)\right]$
Strong flow:		
$\mathscr{P}=2P\to\infty$ $\mathscr{Q}=Q/2P$ arbitrary	$1-\frac{1}{\mathscr{P}}\frac{6}{7+\mathscr{Q}(3-\sqrt{3})}+O\left(\frac{1}{\mathscr{P}^2}\right)$	$\frac{2}{3}\left[1-\frac{1}{4\mathscr{P}}\frac{18+\mathscr{Q}(3-\sqrt{3})}{7+\mathscr{Q}(3-\sqrt{3})}+O\left(\frac{1}{\mathscr{P}^2}\right)\right]$

TABLE 3. Asymptotic results for the trumb-bell in extension.

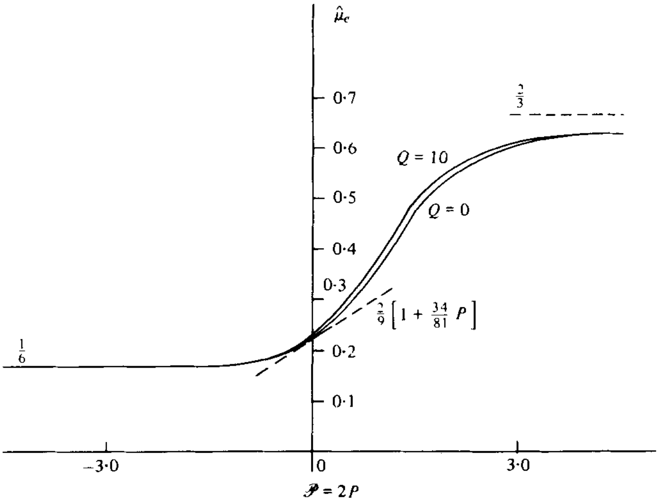

FIGURE 4. Extensional viscosity for a trumb-bell suspension.

This solution corresponds to a balance between advection and diffusion in (5.5). ρ_e is the equilibrium solution given by (4.14). Now, referring to figure 1, this may be written

$$\rho = \rho_e \exp\{l^2\mathbf{E}:[\cos^2\tfrac{1}{2}\theta\,\boldsymbol{\delta}_2\boldsymbol{\delta}_3+3\sin^2\tfrac{1}{2}\theta\,\boldsymbol{\delta}_2\boldsymbol{\delta}_2]/2D\}$$

or, by means of the Euler angle (χ,ϕ,ψ) representation of the $\boldsymbol{\delta}_i$-triad,

$$\rho = \rho_e(\theta)\exp\{\tfrac{1}{6}\mathscr{P}[\cos^2\tfrac{1}{2}\theta(3\sin^2\chi\sin^2\psi-1)+3\sin^2\tfrac{1}{2}\theta(3\cos^2\psi\sin^2\chi-1)]\}, \quad (5.14)$$

where $0\leqslant\psi<2\pi$, $0\leqslant\chi<\pi$, $0\leqslant\theta<\pi$, and the Péclet number $\mathscr{P}$ is as defined in (3.4). The particle stress is given by (5.8), and is most conveniently represented by an extensional viscosity μ_e (defined so as to be equal to the shear viscosity for a Newtonian fluid), thus

$$\hat{\mu}_e = \mu_e/n\zeta l^2 = \bar{\sigma}^p:\mathbf{E}/12n\zeta l^2E^2$$

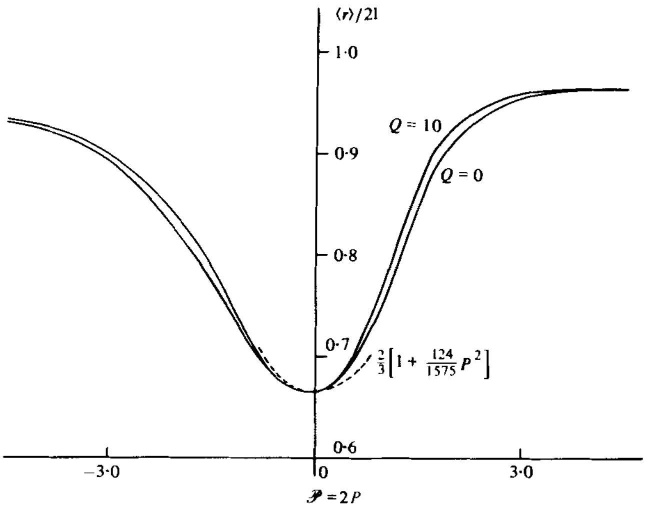

FIGURE 5. End-to-end length for a trumb-bell in an extensional flow.

and with our chosen co-ordinate system this becomes

$$\hat{\mu}_e = \tfrac{1}{18}\langle\cos^2\tfrac{1}{2}\theta[3\sin^2\chi\sin^2\psi+1]+2\sin^2\tfrac{1}{2}\theta[3\sin^2\chi\cos^2\psi+1]\rangle. \qquad (5.15)$$

An appropriate measure of the size of the macromolecule is the end-to-end length given by

$$\langle r\rangle/2l = \langle\sin\tfrac{1}{2}\theta\rangle. \qquad (5.16)$$

These two quantities which may be taken as representative of the rheological influence and geometry of the molecule may now be obtained by substituting the known form of ρ from (5.14) into (5.15) and (5.16) and performing the threefold integrations numerically. Asymptotic results for small P can be obtained from the previous section, and for large $\mathscr{P}$ by simplifying the integrals. These asymptotes are given in table 3. It is again seen from the numerical results (figures 4 and 5) that the effects of non-zero Q are small, and are largest for intermediate flow strengths.

5.3. *Rheological properties for the Rouse chain*

Weak flow. The technical complexities discussed in § 4.4 bedevil a detailed solution for general N. For the classical $Q = 0$ case, a solution for the zero shear viscometric functions is given (Rallison 1977; Hassager 1974*a*) by

$$\hat{b}_1 = \tfrac{1}{36}N^2 f_1(Q); \quad \hat{b}_2 = \frac{1}{72\cdot45}N^4 f_2(Q),$$

where $f_{1,2}(0) = 1$, and, since it is the overall particle radius which determines its hydrodynamic influence, it is anticipated that the behaviour of $f_{1,2}$ will be much the same as that of $f(Q)$ discussed in § 4.4.

Strong flow. We consider finally a Rouse chain immersed in a strong extensional flow at sufficiently high Péclet number $\mathscr{P}$ that the chain is almost fully extended. As noted in § 3, when $\mathscr{P} \gg 1$, the appropriate measure of the importance of quantum mechanics is $\mathscr{Q} = Q/NP$. The geometry of this extended structure is most easily specified by its length measured along the direction of extension, $r_\parallel$, and its mean square displacement perpendicular to that direction at the pth bead, $r_\perp^p$. The rheological influence can be specified by an extensional viscosity as in § 5.2. Thus for $\mathscr{P} \gg 1$ we have

$$\hat{\mu}_e = a_0(N) + \mathscr{P}^{-1} a_1(\mathscr{Q}, N) + O(\mathscr{P}^{-2}), \tag{5.17}$$

$$\langle r_\parallel \rangle / Nl = 1 + \mathscr{P}^{-1} b(\mathscr{Q}, N) + O(\mathscr{P}^{-2}), \tag{5.18}$$

$$\langle r_\perp^p \rangle / l = \mathscr{P}^{-1} c^p(\mathscr{Q}, N) + O(\mathscr{P}^{-2}), \tag{5.19}$$

and our task is to determine the functions a, b and c^p.

As in the trumb-bell case, we have an *exact* solution to the diffusion equation,

$$\rho = \rho_e \exp\Big[\sum_{\text{beads}} \mathbf{r}^i . \mathbf{E} . \mathbf{r}^i / 2D\Big] = \rho_e \exp\left[l^2 \Lambda^{-1ij} \mathbf{b}^i . \mathbf{E} . \mathbf{b}^j / 2D\right] \tag{5.20}$$

where the $(N \times N)$ *structure matrix* Λ (called g^{-1} by Hassager 1974a) is specified by the topology of beads and rods. For a Rouse chain,

$$\Lambda^{ij} = \begin{cases} 2, & i = j, \\ -1, & i = j \pm 1, \\ 0 & \text{otherwise} \end{cases} \quad \text{and} \quad \Lambda^{-1ij} = \begin{cases} i(N+1-j)/(N+1), & i \leqslant j, \\ j(N+1-i)/(N+1), & j \leqslant i. \end{cases}$$

Now the form of expression for ρ may be greatly simplified by exploiting the condition $\mathscr{P} \gg 1$. This is discussed in appendix B. We find on the assumption that $Q \ll NP$ (which is satisfied for typical values of N for a real macromolecule) that (B 6)

$$\rho \sim \text{const.}\,(1 + \mathscr{P}^{-1} \mathscr{M}'_{ij}(x_i x_j + y_i y_j)) \exp\{[\mathscr{Q} \Sigma N_{ij} + L_{ij}][x_i x_j + y_i y_j]\},$$

where the matrices $\mathbf{N}$, $\mathbf{L}$ are defined by (B 5) and (B 2), and x's and y's represent the deviations of the rods from full alignment with the flow direction, multiplied by the large $\mathscr{P}^{\frac{1}{2}}$ factor. L_{ij} here corresponds to the flow in (5.20) while each N_{ij} derives from one of the normal modes in ρ_e. $\mathscr{M}'$ may be determined explicitly, but since it cancels in the final results, we do not give it here. It is convenient to define $R_{ij} = L_{ij} + \mathscr{Q} \Sigma N_{ij}$.

With our solution for ρ it is now a straightforward but tedious matter to evaluate the quantities of interest. We relegate the mathematical details to appendix C. The problem is there reduced to the inversion of the $N \times N$ matrix R_{ij}. For small N this may be achieved analytically (for $N = 2$ the results agree with those given in table 3 for the trumb-bell), but for moderate N a numerical solution is required. For large N, asymptotic estimates are possible. It is easily seen from (B 2) that, as $N \to \infty$,

$$\mathscr{P}\mathbf{L} \sim P \operatorname{diag}(N, \ldots, r(N+1-r), \ldots, N)$$

and thus the flow induces effects which increase as NP for the ends of the chain (this is the magnitude of the flow velocity at the fullest extent of the chain and hence the tension in the end segments), and as N^2P for points in the middle (the tension in the central segments). In addition, as $N \to \infty$, ΣN_{ij} takes the (tridiagonal) form

$$\Sigma N_{ij} \sim \begin{pmatrix} 1 & -\frac{1}{2} & & & & & 0 \\ -\frac{1}{2} & \ddots & \ddots & & & & \\ & \ddots & \frac{1}{2\pi}\log N & \frac{1}{2\pi}\log N & \frac{1}{2\pi}\log N & & \\ & & & & \ddots & \ddots & -\frac{1}{2} \\ 0 & & & & & -\frac{1}{2} & 1 \end{pmatrix}$$

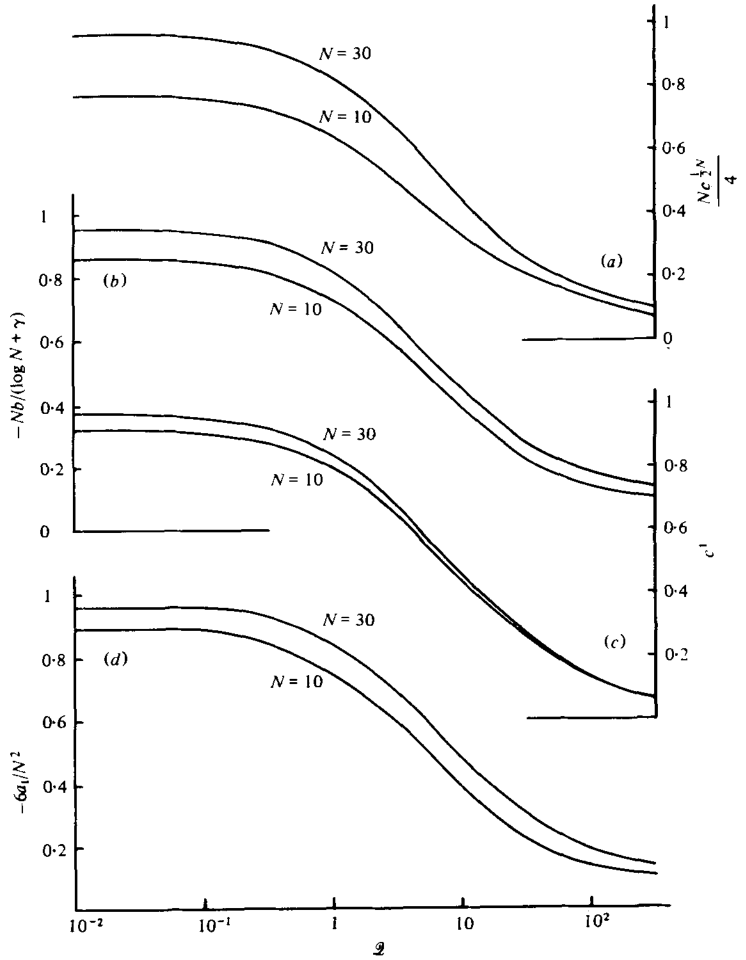

FIGURE 6. Geometrical and rheological properties for an almost fully extended chain. Numerical results for $N = 10$, 30, deviation from full extension. (*a*) Mean square displacement at the centre. (*b*) Mean square displacement at an end. (*c*) Length measured along principal axis of extension. (*d*) Extensional viscosity.

$a_0(N)$	$a_1(\mathscr{Q}, N)$	$b(\mathscr{Q}, N)$	$c^1(\mathscr{Q}, N)$	$c^{\frac{1}{2}N}(\mathscr{Q}, N)$
$\frac{1}{36}N^3$	$-\frac{6a_0}{N^2}(1-\alpha_1\mathscr{Q})$	$-\frac{1}{N}(\log N+\gamma)(1-\alpha_2 Q)$	$(1-\alpha_3\mathscr{Q})$	$\frac{4}{N}\left(1-\alpha_4\mathscr{Q}\frac{\log N}{N}\right)$

TABLE 4. Asymptotic results for an almost fully extended chain $\mathscr{P} \to \infty$, $N \to \infty$. The α_i are all order one constants, $\gamma = 0{\cdot}577$ Euler's constant.

Determination of $\mathbf{R}^{-1}$ in this asymptotic limit now shows that the quantum terms will become significant for displacements of the end segments at $\mathscr{Q} = O(1)$, and for middle segments when $\mathscr{Q} = O(N/\log N)$. The contribution of the particle to the stress is dominated by the longest mode of deformation, and hence again $\mathscr{Q}$ order unity measures the importance of quantum effects in the rheology.

Numerical results for $N = 10, 30$ are plotted in figure 6. Asymptotic results for $N \to \infty$ are given in table 4. At $\mathscr{Q} = 0$, the numerical results for $N = 30$ are within 4 % of the result given by the asymptotic formula. The shapes of the curves for the end-to-end length and the extensional viscosity are very similar, supporting the conclusion that the overall distortion describes the dominant energy-dissipating mode. Physically plausible values for $\mathscr{Q}$ all lie in the plateau region with $\mathscr{Q} < 1$, again showing that quantum effects are small.

6. High frequency behaviour

In the paper so far we have been concerned with either steady states, or with weak flows whose time variations were assumed comparably slow (second-order-fluid expansion). We turn briefly in this section to the physics of unsteady motions for weak flows (linear viscoelasticity), and in particular the limit of infinitely high frequency (ω). The principal motivation for the discussion here is the work of Fixman & Evans (1976) who, in considering a Rouse chain with fixed bond lengths and with angular constraints which can be frozen, demonstrate that the limits of infinitely high stiffness and $\omega \to \infty$ may not commute. It may be thought that the quantum-mechanical analysis presented in the earlier part of this paper would bring together these two limiting procedures, but, in fact, this is *not* the case. We shall show that a fundamentally different, *classical*, phenomenon is responsible, and by using an elastic dumb-bell model (for which we showed in § 4.2 that no quantum-mechanical paradoxes arose) will demonstrate that the two effects are distinct.

6.1. *Elastic dumb-bell model*

As in § 4.2 we consider a Hookean elastic dumb-bell of non-zero equilibrium length l immersed in a weak flow $\mathbf{E}\, e^{i\omega t}$ with $P \ll 1$. The connector force is $\kappa(r-l)$ when r is the length. There are two non-dimensional parameters characterizing the time evolution of the structure: the non-dimensional stiffness $\lambda^2 = \kappa l^2/kT$; and the non-dimensional frequency $\Omega = \zeta l^2 \omega/kT$. The rheological influence of the particles in the suspension is most conveniently given for weak flows by a non-dimensional complex viscosity $\hat{\mu}(\Omega, \lambda^2)$: the ratio of the stress to twice the rate of strain. We shall be concerned to derive the value of $\hat{\mu}$ in the two double limits $\Omega \to \infty$, $\lambda \to \infty$; $\lambda \to \infty$, $\Omega \to \infty$.

Governing equation. If $\mathbf{r}$ is the end-to-end vector for the dumb-bell, then we have as in (5.4) for the equation of motion of the dumb-bell

$$\zeta(\mathbf{E} . \mathbf{r} - \dot{\mathbf{r}}) = \kappa(r-l)\, \mathbf{r}/r + kT \nabla \log \rho, \tag{6.1}$$

together with a conservation equation for the probability,

$$\partial\rho/\partial t + \nabla . \rho\dot{\mathbf{r}} = 0, \tag{6.2}$$

and finally for the particle stress, we have

$$\bar{\boldsymbol{\sigma}}^p = -n\zeta\langle(\mathbf{E} . \mathbf{r} - \dot{\mathbf{r}})\, \mathbf{r}\rangle = -\frac{n\zeta}{2}\frac{\delta}{\delta t}\langle \mathbf{r}\mathbf{r}\rangle. \tag{6.3}$$

The equilibrium solution for ρ is then (in non-dimensional form)

$$\rho_e = \text{const.} \exp\left(-\tfrac{1}{2}\lambda^2(r-1)^2\right) \tag{6.4}$$

and hence, for weak flows for which the perturbation to ρ must be linear in **E**,

$$\rho = \rho_e(1+\mathbf{r}\,.\,\mathbf{E}\,.\,\mathbf{r}g(r;\Omega,\lambda)/r^2+O(P^2)),$$

giving from (6.3) that

$$\hat{\mu} = \frac{1}{12}\left[\int_0^\infty \rho_e r^4\,dr - \frac{i\Omega}{5}\int_0^\infty \rho_e g(r) r^4\,dr\right]\Big/\int_0^\infty \rho_e r^2\,dr.$$

From (6.2) the function g satisfies

$$g'' + 2/r g' - 6/r^2 g - \lambda^2(r-1)g' - i\Omega g = -\lambda^2 r(r-1) \qquad (6.5)$$

with boundary conditions

$$g = O(r^2) \quad \text{as} \quad r\to 0, \quad g = o(\exp(\tfrac{1}{2}\lambda^2(r-1)^2)) \quad \text{as} \quad r\to\infty.$$

Now, for large values of λ, it is easy to see that only the behaviour of g near $r = 1$ affects $\hat{\mu}$, in particular,

$$\hat{\mu} \sim \frac{1}{12}\left\{1-\frac{i\Omega}{5}\left[g(1)+\frac{1}{2\lambda^2}[6g'(1)+i\Omega g(1)]\right]+O\left(\frac{1}{\lambda^2}\right)\right\}$$

and hence by means of a numerical solution for g (given $\lambda \gg 1$, Ω varying) $\hat{\mu}$ is easily computed. In addition, we may obtain analytic results for $\Omega \ll \lambda^2$, $\Omega \gg \lambda^2$. These are

$$g \sim \begin{cases} \dfrac{1}{2}\left[r^2-\dfrac{i\Omega}{i\Omega+6}\right]+O\left(\dfrac{1}{\lambda^2}\right) & \text{for} \quad \Omega \ll \lambda^2, \\ \lambda^2\left[\dfrac{(r-1)r}{i\Omega}+\dfrac{h(r)}{(i\Omega)^2}+O\left(\dfrac{1}{\Omega^3}\right)\right] & \text{with} \quad h(1) = 4 \quad \text{for} \quad \Omega \gg \lambda^2, \end{cases}$$

and hence

$$\hat{\mu} \sim \begin{cases} \dfrac{1}{12}\,\dfrac{1+i\Omega/15}{1+i\Omega/6} \quad \text{for} \quad \Omega \ll \lambda^2, & (6.6) \\ O\left(\dfrac{\lambda^2}{\Omega}\right) \to 0 \quad \text{for} \quad \Omega \gg \lambda^2. & (6.7) \end{cases}$$

The solution (6.6) for $\Omega \ll \lambda^2$ can be obtained independently, as might be expected, by considering a suspension of rigid *rods* with just two degrees of freedom; this is merely a particular case of the more general conclusion of Titulaer & Deutch (1975) and Titulaer (1977) that, for motions *at finite frequency*, the results for an initially rigid system (with Lagrange multipliers to handle the constraints) are the same as those for a springy system in the limit of rigidity. Both (6.6) and (6.7) may also be checked by means of a numerical solution of (6.5). In figure 7 we show values of $\hat{\mu}_r$, $\hat{\mu}_i$ (the real and imaginary parts of $\hat{\mu}$) obtained for $\lambda^2 = 50$, compared with the rigid rod value (6.6). It is seen that for small Ω the deviation is indeed small, but that, for larger Ω, μ_r decays more rapidly and falls below the asymptotic value $\frac{1}{30}$ given by (6.6). The value of μ_i is slightly higher than that for a rigid rod, but both decay to zero as Ω increases.

We see that even when $\Omega \gg 1$, (6.6), corresponding to freezing into rods first gives rise to the non-zero value $\frac{1}{30}$ unequal to (6.7). We have thus reached the same conclusion as Fixman & Evans (1976): the stress generated by the dumb-bells apparently depends on the order in which the limits $\lambda\to\infty$, $\Omega\to\infty$ are taken.

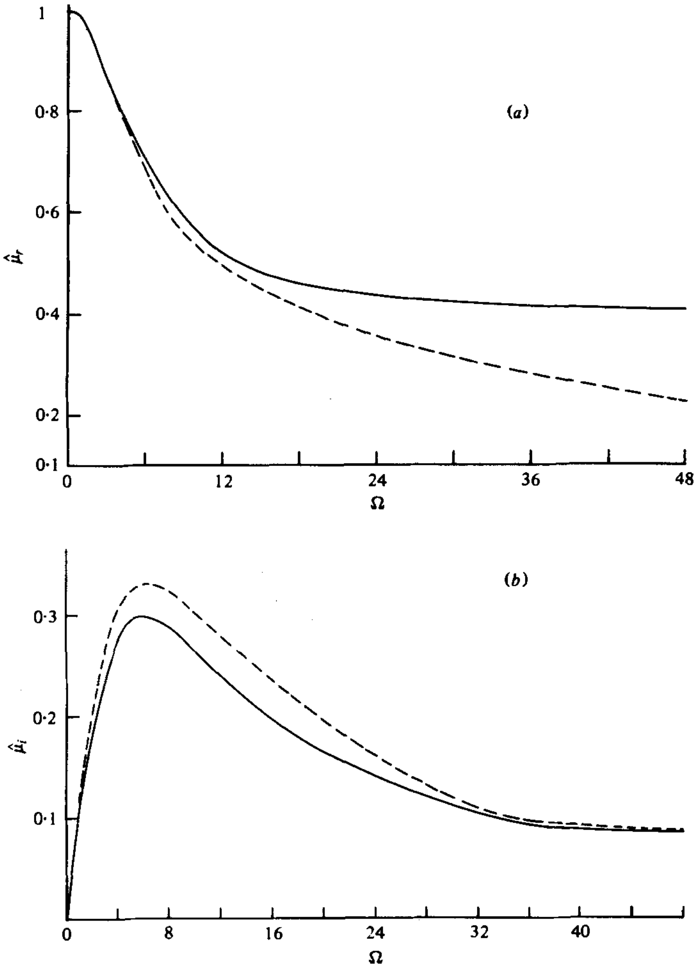

FIGURE 7. Real and imaginary parts of the complex viscosity for a dumb-bell. $\lambda^2 = 50$.

Physical explanation. The discrepancy between the two approaches can be seen most easily by means of (6.1) and (6.3). At high frequency the Brownian term is unimportant and, in an order of magnitude sense,

$$\zeta(Er-\dot{r}) \approx \kappa(r-l), \quad \sigma \propto r(Er-\dot{r}).$$

Now when the springs are frozen into rods first, $\dot{r} = 0, r = l$, and $\sigma \propto El^2$. If, on the other hand, κ is large but finite, then at frequencies ω sufficiently large compared with κ/ζ,

$$r-l \approx El/(i\omega+\kappa/\zeta)$$

and so
$$\sigma \propto El^2 \frac{\kappa/\zeta}{i\omega+\kappa/\zeta} \rightarrow 0 \quad \text{as} \quad \omega \rightarrow \infty.$$

In other words, as $\omega \rightarrow \infty$ the magnitude of variations in length tends to zero as the rigid rod analysis (correctly) assumes, nevertheless the terms $\dot{r}$ and Er remain comparable (and are equal in the limit). Hence, the dumb-bell moves minutely but with the fluid at leading order and therefore generates no stresses.

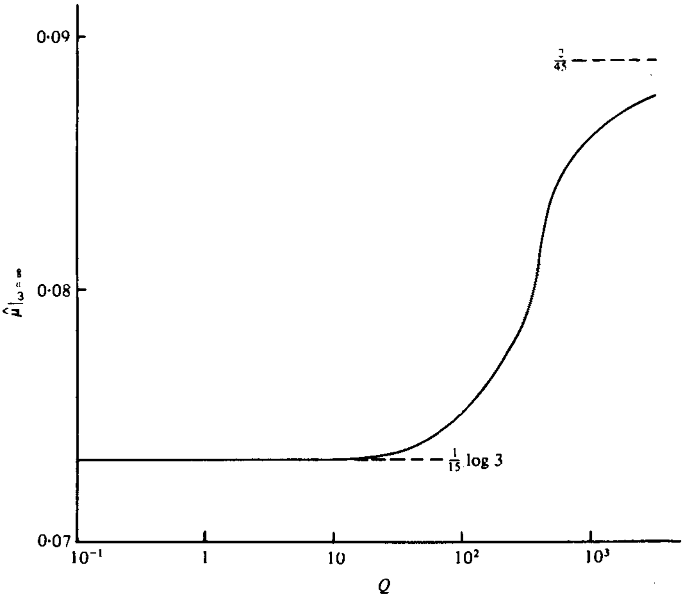

FIGURE 8. Variation of high frequency limiting viscosity with Q for a trumb-bell.

6.2. *Relevance to more complex systems*

We have noted that *provided Ω/λ is not too large*, the high frequency behaviour is correctly given by freezing the dumb-bell first. It follows that in systems with a number of 'stiff' degrees of freedom *based on this criterion* (which is, of course, independent of the quantum-mechanical one), the correct high frequency behaviour will be predicted by freezing those variables while the remainder are left flexible. In fact an example is the analysis of Fixman & Evans (1976) for a Rouse–Zimm chain. There the rod lengths are fixed at the outset and it is only the angular degrees of freedom which are called into question. In consequence, neither of the results for $\hat{\mu}$ is zero as in the simple calculation of § 6.1, but the two results differ.

6.3. *Influence of quantum effects at high frequency*

The discussion above has concerned entirely classical physics. It indicates that at frequencies low compared with the (quantum) frequencies of oscillation of the rods in a bead–rod chain, there will be a non-zero complex viscosity. Further, the value of this viscosity will depend upon the strength Q of quantum effects since, as noted in § 5.1, these introduce effective additional angular potentials. By way of illustration we give the result for a trumb-bell.

As shown by Fixman & Kovac (1974*a*) with appropriate change of notation,

$$\hat{\mu} \sim \tfrac{2}{15}\langle 1/(4-\cos^2\theta)\rangle \quad \text{as} \quad \omega \to \infty,$$

and the average may be taken at thermodynamic equilibrium. (This result is easily derived on noting that to sufficient accuracy the probability distribution is unchanged from its equilibrium value; that the diffusion stress vanishes as $\omega \to \infty$; and that the remaining hydrodynamic stress is due to the tensions in the inextensible rods.) The appropriate equilibrium distribution is given by (4.14) and $\hat{\mu}(Q)$ is then easily obtained numerically. The asymptotic result ($Q \rightarrow 0$) $\hat{\mu} \sim \frac{1}{16} \log 3$ agrees with Fixman & Kovac (1974*a*). In figure 8 the variation of this high frequency limiting viscosity with Q is plotted. The variation is small, and only manifests itself for large ($\geqslant 10$) values.

7. Conclusions

We gather here the principal results and conclusions of the paper.

1. The classical statistical mechanics of a system may predict quantitatively different results when certain components of that system are permitted to become rigid constraints rather than spring-like connectors (§ 2).

2. A proper treatment of such a system requires quantum mechanics, and the importance of the quantum nature of the physics may be estimated by a dimensionless group Q (§ 3).

3. The inclusion of quantum effects makes the limit of rigidity consistent in the sense that when $Q \rightarrow 0$ the classical results with stiff but flexible connectors are recovered (§ 4).

4. For a linear hydrodynamic macromolecular model, the quantum terms may effectively be replaced by additional potentials hindering the free rotation of adjacent polymer segments (§ 5).

5. The influence of the quantum terms on the rheology and on the molecular size appears to be small for both weak and strong flows (§ 5, § 6.3).

6. For weak but rapidly varying flows, an entirely separate difficulty arises in connexion with rigid constraints. A classical analysis demonstrates that at sufficiently high frequency any flexible connector will ultimately move with the applied flow and so exert no stresses. A rigid connector, however, will continue to exert forces on the fluid (§ 6).

In regard to the determination of flow properties for polymer solutions, which provides the motivation for this paper, a more general conclusion is in order. The results for quantum-mechanical systems very rapidly become complex and mathematically intractable. In order that a model be useful it is necessary that it not be too complicated, though, on the other hand, it should still include the important physics. We have seen that the quantized nature of the structure can be important (in the sense that without it the results may not be consistent), but the numerical influence of the parameter Q on the rheology is small. The compromise strongly suggested then is that the self-consistent limit $Q \rightarrow 0$ be employed in polymer modelling: in respect of the thermodynamics rigid constraints must not be used in such a formulation when internal degrees of freedom remain, but must be replaced by stiff springs; nevertheless the computations are rendered far more tractable without substantial loss of accuracy.

Appendix A. Thermodynamic equilibrium for a general system

In § 4 we considered the equilibrium statistics for a system in which the metric tensor g^Q for the quantum modes is a function of the classical co-ordinates q^α. For simplicity, however, the quantum potential V_{AB} was taken as $\epsilon^{-2}\delta_{AB}$. In general, however, we must expect that V_{AB} also varies with the q^α, and the question arises as to how the conclusions are modified.

We note first that for the classical system, with all degrees of freedom present initially, in the limit $\epsilon \to 0$ (4.3) is replaced by

$$\rho \to \text{const.}\,(g^0/\det V_{AB})\exp\left(-\tfrac{1}{2}V_{\alpha\beta}q^\alpha q^\beta\right)\prod_A \delta(q^A). \tag{4.3$'$}$$

Of course the classical expression for the case when the q^A never appear is unaffected by the dependence of V_{AB} on q^α. It follows that the discrepancy between the two classical approaches is even greater here, for only when

$$g' = g^0/\det V_{AB}$$

(to within a multiplicative constant) do they agree.

On the other hand, the introduction of quantum mechanics resolves this difficulty too, for now the eigenfrequencies of vibration ν_A satisfy

$$\det\left(g^{QAB}-(\nu^2/\epsilon^2)\,V_{AB}\right) = 0, \tag{4.9$'$}$$

and hence $$\Pi\nu_A = (g^0/g')^{\frac{1}{2}}/(\det V_{AB})^{\frac{1}{2}}.$$

In consequence, in the limit $Q \to 0$, the result (4.3)$'$ is recovered.

Appendix B. Determination of the probability distribution for a nearly fully extended chain immersed in a strong flow

Determination of the equilibrium distribution ρ_e. It is convenient to rescale the included angles θ_i between the rods so that

$$\theta_i = \pi - \mathscr{P}^{-\frac{1}{2}}\psi_i$$

and then (4.15) becomes

$$g^{QAB} = \Lambda^{AB} + \begin{cases} \tfrac{1}{2}\psi_A^2, & B = A \pm 1,\\ 0 & \text{otherwise.}\end{cases}$$

At leading order, the eigenfrequencies of vibration ν_n ($n = M+1, \ldots, N$) are those of Λ, and the perturbations can be calculated by means of an eigenmode decomposition of Λ. This gives

$$\nu_n = 2\sin n\lambda\left\{1+\frac{1}{4(N+1)\sin^2 n\lambda}\left[\psi_1^2\sin 2n\lambda\sin 4n\lambda + \ldots \right.\right.$$
$$\left.\left. + \psi_{N-1}^2\sin 2\overline{N-1}\,n\lambda\,\sin 2Nn\lambda\right]\right\},$$

where $\lambda = \pi/2(N+1)$. ρ_e is then given by (4.11).

Determination of ρ. It remains to find the potential flow term $\mathbf{b}^i\,.\,\mathsf{E}\,.\,\mathbf{b}^j$, and then ρ is given by (5.20). We follow Hassager (1974*a*) and choose spherical polar co-ordinates (γ^i, ϕ^i) relative to the principal axis of extension for each $\mathbf{b}^i$,

$$\mathbf{b}^i = (\cos(\pi-\gamma^i), \sin(\pi-\gamma^i)\cos\phi^i, \sin(\pi-\gamma^i)\sin\phi^i),$$

which again may be simplified on noting that $\gamma^i \ll 1$. Now choosing local Cartesian co-ordinates x_i, y_i with

$$x_i = \mathscr{P}^{\frac{1}{2}}\gamma^i\cos\phi^i, \quad y_i = \mathscr{P}^{\frac{1}{2}}\gamma^i\sin\phi^i, \tag{B 1}$$

we obtain $$\mathbf{b}^i\,.\,\mathsf{E}\,.\,\mathbf{b}^j/2D = (x_i^2+y_i^2+x_j^2+y_j^2+x_i x_j+y_i y_j),$$

and so $$\Lambda^{-1ij}\mathbf{b}^i\,.\,\mathsf{E}\,.\,\mathbf{b}^j/2D = L_{ij}(x_i x_j+y_i y_j),$$

where
$$L_{ij} = \frac{1}{N}\begin{cases}(N+2)\,\Lambda^{-1ij}, & i = j,\\ \Lambda^{-1ij}, & i \neq j.\end{cases} \tag{B 2}$$

Finally in this representation we note that

$$\psi_i^2 = (x_i - x_{i+1})^2 + (y_i - y_{i+1})^2$$

and thus (5.20) gives

$$\begin{aligned}\rho \sim \text{const.}\,(1+\mathscr{P}^{-1}\mathscr{M}_{ij}(x_i x_j + y_i y_j))\exp\mathscr{P}[\mathscr{Q}\textstyle\sum_n N_{ij}(x_i x_j + y_i y_j)\\ + L_{ij}(x_i x_j + y_i y_j)]/\textstyle\prod_n[1-\exp - 2\mathscr{Q}(2\mathscr{P}\sin n\lambda + N_{ij}(x_i x_j + y_i y_j))],\end{aligned} \tag{B 3}$$

where
$$\mathscr{M}_{ij}(x_i x_j + y_i y_j) = \sum_i \Lambda^{-1i\,i+1}[(x_{i+1}-x_i)^2 + (y_{i+1}-y_i)^2] \tag{B 4}$$

and

$$\begin{aligned}N_{ij}(x_i x_j + y_i y_j) = \frac{1}{2(N+1)\sin n\lambda}\{[(x_2-x_1)^2 + (y_2-y_1)^2]\sin 2n\lambda \sin 4n\lambda\\ + \ldots + [(x_N - x_{N-1})^2 + (y_N - y_{N-1})^2 \sin 2\overline{N-1}n\lambda \sin 2Nn\lambda]\}.\end{aligned} \tag{B 5}$$

Asymptotic forms for ρ. The exponent in each term of the denominator of (B 3) has the form $-2\mathscr{Q}(2\sin n\lambda\mathscr{P} + N_{ij}(x_i x_j + y_i y_j))$ with $N_{ij} \sim O(1)$. Thus if $\mathscr{Q} \ll 1$, the dependence on x and y can be expanded. This is the physically realistic case. In addition, when $Q \gg 1$ the denominator becomes unity. In either case, ρ has the particularly simple form

$$\rho \sim \text{const.}\,(1+\mathscr{P}^{-1}\mathscr{M}'_{ij}(x_i x_j + y_i y_j))\exp\mathscr{P}[R_{ij}(x_i x_j + y_i y_j)] \tag{B 6}$$

where
$$R_{ij} = L_{ij} + \mathscr{Q}\sum_n N_{ij}. \tag{B 7}$$

Appendix C. Evaluation of geometrical and rheological functions for an almost fully extended Rouse chain

1. *Quantities of interest*. We first simplify the forms of the rheological functions when the chain is almost fully extended.

(*a*) *Extensional viscosity*. As in § 5.2 we have that

$$\hat{\mu}_e = \tfrac{1}{12}\Lambda^{-1ij}\langle 4b_1^i b_1^j + b_2^i b_2^j + b_3^i b_3^j\rangle$$

and so simplifying with our choice of the $\mathbf{b}^i$ we obtain

$$\hat{\mu}_e = \tfrac{1}{36}N(N+1)(N+2)\langle 1 + \mathscr{P}^{-1}T_{ij}^{(2)}(x_i x_j + y_i y_j) + O(\mathscr{P}^{-2})\rangle,$$

where
$$T_{ij}^{(1)} = \frac{3}{N(N+1)(N+2)}\begin{cases}-(2N+1)\,\Lambda^{-1ij}, & i = j,\\ \Lambda^{-1ij}, & i \neq j.\end{cases} \tag{C 1}$$

(*b*) *The overall length*. Similarly from (5.18) we obtain

$$\langle r_{\parallel}\rangle/Nl = \langle 1 + \mathscr{P}^{-1}T_{ij}^{(2)}(x_i x_j + y_i y_j) + O(\mathscr{P}^{-2})\rangle$$

with
$$T_{ij}^{(2)} = -\frac{1}{2N}\delta_{ij}. \tag{C 2}$$

(*c*) *The mean square displacement*

$$\langle r_\perp^p \rangle / l = \mathscr{P}^{-1} T_{ij}^{(3)} (x_i x_j + y_i y_j) + O(\mathscr{P}^{-2})$$

and, by the same technique,

$$T_{ij}^{(3)} = \delta_{ip} \delta_{jp} \quad \text{(no sum).} \tag{C 3}$$

2. *Lemma on Gaussian integrals*. The integrals which must be performed to evaluate the averages in the expressions above are all of Gaussian type as $\mathscr{P} \to \infty$. We therefore write down an important lemma:

If $I(\mathbf{A})$ is defined by

$$I(A_{ij}) = \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} (1 + A_{ij} x_i x_j + \ldots) \exp[-\mathscr{P} B_{ij} (x_i x_j + \ldots)] \prod_n dx_n,$$

where each expansion is asymptotic as $|\mathbf{x}| \to 0$, then

$$I(\mathbf{A}^{(1)}) / I(\mathbf{A}^{(2)}) = 1 + \tfrac{1}{2} \mathscr{P}^{-1} B_{ij}^{-1} (A_{ij}^{(1)} - A_{ij}^{(2)}) + O(\mathscr{P}^{-2}) \quad \text{as} \quad \mathscr{P} \to \infty.$$

3. *Evaluation of properties*. By use of the lemma, the coefficients in the expressions (5.17–5.19) may now be calculated with the form for ρ derived as (B 6). These are

$$a_0(N) = \tfrac{1}{36} N (N+1)(N+2); \quad a_1(\mathscr{Q}, N) = a_0(N) R_{ij}^{-1} T_{ij}^{(1)},$$
$$b(\mathscr{Q}, N) = R_{ij}^{-1} T_{ij}^{(2)}; \quad c^p(\mathscr{Q}, N) = R_{ij}^{-1} T_{ij}^{(3)}. \tag{C 4}$$

The problem has thus been reduced to one entirely of matrix algebra: given N and $\mathscr{Q}$, $\mathbf{R}$ is determined by (B 7), and the matrices $\mathbf{L}$, $\mathbf{N}$ are given by (B 2) and (B 7); $\mathbf{R}$ may be inverted numerically, and the functions a, b, c^p are then easily determined.

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