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Turbulence induced change in the conformation of polymer molecules

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An investigation into the conformation of a polymer molecule exposed to a stochastic flow field is made utilizing a cumulant expansion. The study begins by considering the full Kirkwood-Riseman n -bead chain with an arbitrary connector potential as a model for the polymer molecule, digressing to the two-bead dumbbell molecule for detailed calculations. It is found that the effect of the stochastic velocity field on the molecule can be interpreted as a "renormalization" of the connector potential. The introduction of this renormalized potential greatly simplifies the mathematics and lends an intuitive understanding to the effect of the turbulence on the polymer. It is shown that this analysis will recover the anomalous tendency of the radius of gyration to become infinite for the special case of a Hookean potential which has been observed by previous investigators. Further, this study involves the Eulerian velocity-velocity correlation function rather than the Lagrangian correlation used in the previous studies.

I. INTRODUCTION

Since both turbulence and polymer dynamics are not well understood, the study of these two in combination is particularly challenging. The object of this paper is to provide a systematic study of the polymer conformation when exposed to a turbulent flow.

When a small amount of polymer is added to a solvent undergoing turbulent flow, reductions in frictional drag of upwards of 70% are commonly achieved.¹ It has been recognized for quite some time that the conformation of a polymer subjected to such a flow is of primary importance. Precisely what this conformation looks like has been the subject of a great deal of speculation in the past.² In this paper we intend to apply the bead-spring model to this problem, using a general connector potential for the spring.

We will employ the bead-spring model without hydrodynamic interaction and we will claim that the polymer molecule is well modeled by considering a chain of identical spheres (beads) linked together by some arbitrary spring potential which is immersed in an otherwise Newtonian solvent. In addition we will say that the solvent can exert (Stokes) forces on the beads but the fluid is in no way modified by the polymer (no hydrodynamic interaction). Put simply, we say that the polymer "sees" the solvent but the solvent does not see the polymer. As broad as these assumptions are, they are quite common in the literature and discussion on their relative merits can be found elsewhere.³ It suffices to say that without these assumptions the problem would be a great deal less tractable and the necessary complications might obscure some of the points we want to make in this paper. To further this end we will digress to the dumbbell model (two beads connected by a single spring) before actually calculating a result, though the problem is solvable for an arbitrary number of beads.

The usual method for determining the conformation of bead spring models even for deterministic flows is to formulate an all-encompassing probability density. Previous investigations involving turbulent flows used

the statistically averaged second moment of the probability density (an indication of the polymer size).⁴ In one such case⁵ a new probability density was formulated for the second moment of the probability density for a deterministic flow. In our judgment this type of rearrangement may be philosophically dangerous and may lead to limited or misleading results. We will therefore formulate a single probability density incorporating the statistics of the Brownian forces as well as the turbulence. Another problem with the second moment methods is that it is almost impossible to deal with nonlinear (non-Hookean) spring potentials. The ability to incorporate such a potential into the model is necessary because Hookean potentials have the disconcerting property of allowing the polymer model to become infinitely extended (the beads become infinitely far apart) for deterministic flows even for quite reasonable values of strain rate. The Hookean spring apparently^{4,5} shares this property with nondeterministic turbulent flows also. Accordingly then, we will keep an arbitrary spring potential for the model throughout our calculations.

In order to facilitate our derivation we will formulate a cumulant expansion keeping only the second-order term (the first nontrivial term). This truncation is equivalent to assuming that the ratio of the time scale of the flow to the time scale of the polymer molecule is small. We expect that this approximation becomes more accurate as the Reynolds number of the flow increases because the flow time scale decreases with increasing Reynolds number.⁶ In any case, this approximation is common in the study of turbulent convection of scalar quantities (such as concentration of some passive solute) and is a problem closely related to the one at hand. For deterministic flows it is normally necessary to express the velocity field as the first two terms in a truncated Taylor series. Here we will represent the velocity-velocity correlation as the first two terms in a truncated Taylor series. This assumption should be exceptionally good because the polymer size is a few orders of magnitude below the size of even the smallest eddies occurring in turbulence.²

From the groundwork laid out above we will derive

an explicit equation for the probability density of a dumbbell molecule with an arbitrary connector potential. An important feature of this probability function will be that it is formulated in terms of Eulerian statistics of the flow. Eulerian statistics are based on sampling data by an observer who is stationary with respect to the flow, and understandably most existing data and theory is in this frame of reference. The previous theories mentioned above used the Lagrangian frame of reference where sampling is done by an observer traveling with the fluid. Little is understood of the theory and little experimental data exist in the Lagrangian frame.

The abstract form of the resulting steady-state probability function for the dumbbell system is similar to the probability at equilibrium (no flow) except that the connector potential is "renormalized" by an integral operator that is a function of the statistics of the turbulence and molecular parameters. (Note that this does not mean that the functional form is similar to the equilibrium function. For instance, one can see from the results derived below that for a Hookean potential the probability is highly non-Maxwellian, even though the equilibrium probability is Maxwellian.) This renormalization effectively "screens" some of the potential away. This causes the molecule to behave as if it had a weaker spring than at equilibrium, thus we will find that the dumbbell molecule will be larger in a turbulent flow than at equilibrium. It is rationalized by many^{2,8} that it is this molecular extension that is the primary cause of drag reduction, though we will not repeat their reasoning in this paper. We can however, afford to be a little more precise on the process by which the molecule becomes extended after the following derivation.

II. THE PROBABILITY EQUATION FOR THE N -BEAD CHAIN

When polymer molecules are immersed in a turbulent fluid we have to concern ourselves with two synergistic random processes; those arising from Brownian forces and those arising from the turbulence itself. In this section we will derive an equation that will relate the probability of a particular conformation of the polymer to the random forces external to the molecule and the internal restoring (connector) forces. We will use the n -bead spring model for the mathematical representation of the polymer molecule. The governing probability equation [$\psi(\mathbf{r}_i, t)$] for this system is⁹

$$\frac{\partial}{\partial t} \tilde{\psi} = - \sum_{i=1}^n \frac{\partial}{\partial \mathbf{r}_i} \cdot \left\{ \left[\mathbf{v}(\mathbf{r}_i, t) - \frac{kT}{\zeta} \frac{\partial}{\partial \mathbf{r}_i} \ln \tilde{\psi} - \frac{\mathbf{F}_i^{(c)}}{\zeta} \right] \tilde{\psi} \right\}, \quad (2.1)$$

where \mathbf{r}_i is the position vector of the i th bead, $\mathbf{v}(\mathbf{r}_i, t)$ is the fluctuating fluid velocity at \mathbf{r}_i , and $\mathbf{F}_i^{(c)}$ is the connector (spring) force, with ζ as the Stokes law constant. When we say $\mathbf{v}(\mathbf{r}_i, t)$ is the fluid velocity at \mathbf{r}_i we mean $\mathbf{v}(\mathbf{r}_i, t)$ is measured as if the i th bead was not there. To put it another way, the polymer does not modify the flow field and there is no hydrodynamic interaction. We should point out that we have not made the usual assumption for a Hooke's law form of $\mathbf{F}_i^{(c)}$ being that this assumption has come under a great deal of fire for its tendency to allow the molecule to extend

indefinitely in extensional flows with a finite and reasonable strain. We will keep the arbitrary connector force assumption throughout our analysis.

The solution of Eq. (2.1) will, in general, involve functionals of the fluctuating velocity $\mathbf{v}'(\mathbf{r}_i, t)$. To be completely accurate we should write $\mathbf{v} = \langle \mathbf{v} \rangle_{\mathbf{v}} + \mathbf{v}'$ with $\langle \mathbf{v} \rangle_{\mathbf{v}}$ as the average velocity. Here $\langle \rangle_{\mathbf{v}}$ denotes the average over an ensemble of velocity realizations which we presume to be stationary. As we shall see later, the only observable from the flow field in which we will be interested is the gradient of this velocity field: $\nabla \mathbf{v} = \langle \nabla \mathbf{v} \rangle_{\mathbf{v}} + \nabla \mathbf{v}'$. It is a well-established fact⁶ that the fluctuation gradient is much larger than the gradient of the average velocity. So it seems justifiable to assign $\langle \mathbf{v} \rangle_{\mathbf{v}} = 0$ for the rest of our development. To make some sense out of the turbulent velocity field and recast the equation in terms of the statistics of that field, we can make a velocity averaged probability function $\langle \psi(\mathbf{v}'(\mathbf{r}_i, t); \mathbf{r}_i, t) \rangle_{\mathbf{v}} \equiv \psi(\mathbf{r}_i, t)$. Note that ψ is dependent only on the bead positions and time explicitly and dependent only on the statistics of the velocity field.

We will now seek a cumulant expansion¹⁰ of the term involving the stochastic velocity field keeping only the second cumulant (which is nothing more than the second moment since we require $\langle \mathbf{v}'(\mathbf{r}_i, t) \rangle = 0$). In order to avoid convolutions that are a result of the interaction representation and which are unnecessary to our purpose, we will assume that the fluctuations in the velocity field are much faster than the characteristic response time of the polymer molecule. Restating this assumption mathematically, we can say that the Eulerian time scale (T_E) of the velocity field is much smaller, say an order of magnitude smaller, than the relaxation time of the polymer (λ_H). With this assumption the cumulant expansion yields the renormalized differential equation

$$\begin{aligned} \frac{\partial \psi(\mathbf{r}_i, t)}{\partial t} = & \frac{1}{\zeta} \frac{\partial}{\partial \mathbf{r}_i} \cdot (\mathbf{F}_i^{(c)} \psi(\{\mathbf{r}_i\}, t)) + \frac{kT}{\zeta} \frac{\partial^2}{\partial \mathbf{r}_i^2} \psi(\{\mathbf{r}_i\}, t) \\ & + \Gamma(\mathbf{r}_i - \mathbf{r}_j) : \frac{\partial^2 \psi(\{\mathbf{r}_i\}, t)}{\partial \mathbf{r}_i \partial \mathbf{r}_j} \end{aligned} \quad (2.2)$$

(summation implied over repeated indices)

with

$$\left\{ \int_0^\infty ds \langle \mathbf{v}(\mathbf{r}, t) \mathbf{v}(\mathbf{r}', s) \rangle \right\} = \Gamma(\mathbf{r} - \mathbf{r}') . \quad (2.3)$$

This is an effective equation for the polymer probability density and is the central result of this paper. Equation (2.2) represents the probability of a certain conformation in a turbulent fluid and should tend toward a stationary (invariant) probability density at large time since the stochastic velocity field is itself stationary. In the forthcoming development we will therefore seek a solution for $\partial \psi / \partial t = 0$.

Although we have derived the effective probability equation [Eq. (2.2)] from the stochastic probability equation [Eq. (2.1)] by utilizing a cumulant expansion, the same result can be derived from the Langevin equations for the n beads.⁷ The advantage of the cumulant expansion method is that it may point the way toward

loosening the restrictions on the relative time scales of the flow and polymer. It should be said that the previous studies^{4,5} assumed $T_E \ll \lambda_H$ although these were performed by using the second moment of ψ .

The terms in Eq. (2.2) that result from the connector force and the Brownian forces appear as the first and second terms, respectively, and are unchanged from the similar terms arising in the familiar Kirkwood-Riseman equation.³ The third term, however, arises from the stochastic velocity field and behaves as a diffusion term with a spatially dependent diffusion tensor. The fact that the stochastic velocity field manifests itself as diffusion term is not surprising. We have exploited the fact that the velocity field has a correlation time that is short compared with the polymer relaxation time in a manner similar to the derivation of the canonical Fokker-Planck equation. It may appear that we are considering the turbulent and Brownian forces as equivalent, but this could hardly be the case since the progenitors of $kT/\zeta \delta$ and Γ are physically quite different. It cannot be emphasized too strongly that the relative magnitudes of the velocity and Brownian forces (at least six orders of magnitude different) are irrelevant to the validity of Eq. (2.2). Rather, its validity relies on the fact that both random processes have correlation times significantly shorter than the response time of the polymer (n bead chain, in this case). As we will show in the next section, the major contribution of the turbulence is to reduce the connector force between the beads. Because the level of understanding we seek is rather qualitative, we will not try to solve for the general n -bead case. Rather we will digress to the often used dumbbell model—the case of two beads connected by a single spring.

III. THE DETAILS CONCERNING A TWO-BEAD SYSTEM

The system for two beads then becomes

$$\begin{aligned} \frac{\partial \psi}{\partial t} = & \frac{1}{\zeta} \frac{\partial}{\partial \mathbf{r}_1} \cdot (\mathbf{F}_1^{(c)} \psi) + \frac{1}{\zeta} \frac{\partial}{\partial \mathbf{r}_2} \cdot (\mathbf{F}_2^{(c)} \psi) + \Gamma(0) : \frac{\partial}{\partial \mathbf{r}_1} \frac{\partial}{\partial \mathbf{r}_1} \psi \\ & + \Gamma(0) : \frac{\partial}{\partial \mathbf{r}_2} \frac{\partial}{\partial \mathbf{r}_2} \psi + 2\Gamma(\mathbf{r}_2 - \mathbf{r}_1) : \frac{\partial}{\partial \mathbf{r}_1} \frac{\partial}{\partial \mathbf{r}_2} \psi \\ & + \frac{kT}{\zeta} \left\{ \frac{\partial}{\partial \mathbf{r}_1} \cdot \frac{\partial}{\partial \mathbf{r}_1} + \frac{\partial}{\partial \mathbf{r}_2} \cdot \frac{\partial}{\partial \mathbf{r}_2} \right\} \psi. \end{aligned} \quad (3.1)$$

By adopting a connector potential (ϕ) that depends only on the scalar distance of separation such that $\mathbf{F}_1^{(c)} = -(\partial/\partial \mathbf{r}_1)\phi(|\mathbf{r}_1 - \mathbf{r}_2|) = -\mathbf{F}_2^{(c)}$. We can recast Eq. (3.1) into the center of mass ($\mathbf{r}_c = (\mathbf{r}_2 + \mathbf{r}_1)/2$) and relative ($\mathbf{R} = \mathbf{r}_2 - \mathbf{r}_1$) coordinates

$$\begin{aligned} \frac{\partial \psi}{\partial t} = & \frac{2}{\zeta} \frac{\partial}{\partial \mathbf{R}} \cdot \left\{ \frac{\partial \phi}{\partial \mathbf{R}} \psi \right\} + 2(\Gamma(0) - \Gamma(\mathbf{R})) : \frac{\partial}{\partial \mathbf{R}} \frac{\partial}{\partial \mathbf{R}} \psi + \frac{2kT}{\zeta} \frac{\partial}{\partial \mathbf{R}} \cdot \frac{\partial}{\partial \mathbf{R}} \psi \\ & + \frac{1}{2}(\Gamma(0) + \Gamma(\mathbf{R})) : \frac{\partial}{\partial \mathbf{r}_c} \frac{\partial}{\partial \mathbf{r}_c} \psi + \frac{kT}{2\zeta} \frac{\partial}{\partial \mathbf{r}_c} \cdot \frac{\partial}{\partial \mathbf{r}_c} \psi. \end{aligned} \quad (3.2)$$

Since Γ and ϕ are independent of \mathbf{r}_c , we can see that if at some time during the evolution of the system ψ becomes homogeneous (independent of \mathbf{r}_c), then it will remain forever after homogeneous. If, then, we assume that ψ is initially homogeneous we can neglect

terms involving derivatives of \mathbf{r}_c in Eq. (3.2):

$$\begin{aligned} \frac{\partial \psi}{\partial t} = & \frac{2}{\zeta} \frac{\partial}{\partial \mathbf{R}} \cdot \left\{ \left(\frac{\partial \phi}{\partial \mathbf{R}} \right) \psi \right\} + \frac{2kT}{\zeta} \frac{\partial}{\partial \mathbf{R}} \cdot \frac{\partial}{\partial \mathbf{R}} \psi \\ & + 2(\Gamma(0) - \Gamma(\mathbf{R})) : \frac{\partial}{\partial \mathbf{R}} \frac{\partial}{\partial \mathbf{R}} \psi. \end{aligned} \quad (3.3)$$

It may seem that we are overemphasizing the aspect of homogeneity, but this is where the development in this paper clearly diverges from those given in the past. Previously, investigators developed an equation for the moment of a probability density that moved with the fluid particles.⁵ These types of analyses invoke the additional hardship of needing to use convected (Lagrangian) statistics for the turbulent field. Apparently there is no need to look at the molecule in the convected frame in order to get detailed knowledge about its conformation.

One of the few well accepted facts in the area of drag reduction is that the size of the smallest eddies appearing in the turbulence are many times larger than the equilibrium conformation of the molecule.² Even if the molecule is stretched out to the greatest length its monomeric conformation will allow (an unlikely possibility), it might only then be on the order of the size of the *smallest* eddies in a high Reynolds number flow. In light of this, it is clear that we can represent the velocity field well by assuming a truncated Taylor series expansion

$$\Gamma(\mathbf{R}) = \Gamma(0) + \frac{\mathbf{R}\mathbf{R}}{2} : \left[\frac{\partial}{\partial \mathbf{R}'} \frac{\partial}{\partial \mathbf{R}'} \Gamma(\mathbf{R}') \right]_{\mathbf{R}'=0}. \quad (3.4)$$

Now using Eq. (3.4) and the assumption of the isotropy of the turbulence, we find

$$\frac{\partial \psi}{\partial t} = \frac{2}{\zeta} \frac{\partial}{\partial \mathbf{R}} \cdot \left(\frac{\partial \phi}{\partial \mathbf{R}} \psi \right) + \frac{2kT}{\zeta} \frac{\partial}{\partial \mathbf{R}} \cdot \frac{\partial}{\partial \mathbf{R}} \psi + \Delta(\mathbf{R}) : \frac{\partial}{\partial \mathbf{R}} \frac{\partial}{\partial \mathbf{R}} \psi, \quad (3.5)$$

with

$$\Delta = -\mathbf{R}\mathbf{R} : \left[\frac{\partial}{\partial \mathbf{R}'} \frac{\partial}{\partial \mathbf{R}'} \Gamma(\mathbf{R}') \right]_{\mathbf{R}'=0} = A[2R^2 \delta - \mathbf{R}\mathbf{R}],$$

where

$$A = -u'^2 \int_0^\infty dt \left[\frac{\partial}{\partial \mathbf{R}'} \cdot \frac{\partial}{\partial \mathbf{R}'} f \right]_{\mathbf{R}'=0} \quad (\text{a positive number}),$$

with u' as the rms velocity fluctuation and f as the so-called coefficient of the longitudinal velocity correlation.⁶ We are now in a position to solve for the steady-state case when $\partial \psi / \partial t = 0$. Due to the symmetry of the situation, ψ can be integrated by components to obtain

$$\frac{\partial \ln \psi}{\partial \mathbf{R}} = -\frac{2}{\zeta} \left(\Delta(\mathbf{R}) + \frac{2kT}{\zeta} \delta \right)^{-1} \cdot \frac{\partial \phi}{\partial \mathbf{R}}. \quad (3.6)$$

$[\Delta(\mathbf{R}) + (2kT/\zeta)\delta]^{-1}$ has the effect of a spatially dependent diffusion tensor which arises from turbulent and Brownian forces by themselves give rise to a constant diffusion coefficient (diagonal diffusion tensor). The fact that Brownian forces by themselves give rise to a diagonal tensor is due to the rather special characteristics that the statistics of these forces are assumed to have. It is not hard (see the Appendix) to show that

$$\left(\Delta + \frac{2kT}{\zeta}\delta\right)^{-1} = \frac{1}{2A(R^2 + \alpha)(R^2 + 2\alpha)} [(R^2 + 2\alpha)\delta + RR], \quad (3.7)$$

where $\alpha = kT/\zeta A$.

From Eq. (3.6) and (3.7) we obtain

$$\psi = C \exp \left\{ -\frac{2\alpha}{kT} \int_0^R \frac{1}{R'^2 + 2\alpha} \frac{d\phi(R')}{dR'} dR' \right\}. \quad (3.8)$$

Note that C is left as a normalization constant and note also that the term on the right-hand side involves only scalar quantities.

It is clear that if $A = 0$ ($\alpha \rightarrow \infty$), we recover the equilibrium solution

$$\lim_{A \rightarrow 0} \psi = \psi_{eq} = C \exp[-\phi/kT]. \quad (3.9)$$

We can see that the presence of turbulence has caused a change or a "renormalization" in the connector potential, or schematically

$$\phi \rightarrow \phi_R = \int_0^R dR' \frac{1}{\left(\frac{R'}{\sqrt{2\alpha}}\right)^2 + 1} \frac{d\phi(R')}{dR'} \quad (3.10)$$

(bare potential) (renormalized potential)

Of course, the negative gradient of this potential is what really counts in the dynamics of the polymer molecule itself,

$$-\nabla\phi = -\hat{\mathbf{R}} \frac{d\phi(R)}{dR} \rightarrow -\nabla\phi_R = -\hat{\mathbf{R}} \frac{2kT}{A\zeta R^2 + 2kT} \frac{d\phi(R)}{dR}, \quad (3.11)$$

(bare force) (renormalized force)

where $\hat{\mathbf{R}}$ is the unit vector in the \mathbf{R} direction. We see that the magnitude of the force has been reduced everywhere except at $\mathbf{R} = 0$. It is clear that turbulence produces a screening effect on the force, reducing its magnitude but not its direction.

It seems then that turbulence introduces a new spatially dependent diffusion tensor reducing the interaction force between the beads. This will cause the molecule to expand and, we expect, cause a reduction in the drag produced by the flow. It should be emphasized that this idea of a renormalized potential is pictorial in nature and results solely from an additional diffusive term contributed by the presence of the turbulence. In addition we ought to say that we regard this extra turbulence term as "diffusive" only by its mathematical structure and we do not mean to imply that it has some physical relation to the Brownian motion. It is clear that Eq. (2.2) is a variant of the Fokker-Planck equation and the turbulence term can be considered a diffusion caused by the stochastic fluid, which is physically unrelated to normal Brownian diffusion.

We will illustrate these results with the simple example of a dumbbell molecule with a Hookean potential; $\phi = \frac{1}{2}HR^2$ where H is the Hooke's law constant. We can see what turbulence will do to this molecule by inserting the potential into Eq. (3.8). We find

$$\psi = C \left[1 + \frac{R^2}{2\alpha} \right]^{-H/\zeta A}, \quad (3.12)$$

where C is a normalization constant. An interesting mathematical detail with regard to this equation is that for A (turbulent strength) large enough ψ will cease to be normalized. In other words, the integral

$$\int_0^\infty R^2 \left[1 + \frac{R^2}{2\alpha} \right]^{-H/\zeta A} dR$$

will not converge for $H/\zeta A < 3/2$. By a similar procedure we can find that $\langle RR \rangle$, the second moment of ψ , will not converge for $H/\zeta A < 5/2$ and it is this result that was observed in the previous analysis done by Lumley.⁴ It is clear that this anomaly has no basis in the physics of the problem since we expect the potential in a real polymer molecule to go to much higher orders in R even though the Hookean potential is a good approximation for small perturbations from equilibrium. A simple fix would be to use the FENE³ potential,

$$\phi = -\frac{1}{2}HR_0^2 \ln \left[1 - \left(\frac{R}{R_0} \right)^2 \right] \text{ for } R < R_0, \quad (3.13)$$

where H and R_0 both serve as adjustable parameters. This formulation has the advantage of never allowing the dumbbell to stretch past R_0 . When this potential is fed into Eq. (3.8), we obtain the following result:

$$\psi = C \left[\frac{R_0^2 - R^2}{R^2 + 2\alpha} \right]^{H/\zeta A (1 + 2\alpha/R_0^2)}. \quad (3.14)$$

Now all integrations are carried out over the interval $(0, R_0)$, and as a consequence the normalization constant and all the moments of ψ converge. It seems that a nonlinear potential is a necessary prerequisite to any detailed study of the response of polymers to a turbulent flow.

IV. SUMMARY AND CONCLUSION

We have derived an equation for the probability density for an n -bead molecule using the approximation that the fluid time scale is much shorter than the molecular time scale ($T_E \ll \lambda_H$) which should become more accurate as the Reynolds number increases. The form of the equation so obtained is familiar to the extent that the terms involving Brownian and connector forces are identical to those found in the Kirkwood-Riseman equation. The turbulence has the effect of contributing a diffusive-like term that involves a spatially depending diffusion tensor. To do the explicit calculations we digressed to the two-bead (dumbbell) model and found that the turbulence manifests itself in the probability density by renormalizing the connector force between the beads. This has the effect of reducing the connector force, allowing the beads to extend further than they otherwise would. In other words, the molecule expands when exposed to the turbulent flow.

Although we derived the dumbbell probability density for an arbitrary connector potential, we discovered that for a Hookean potential the probability density would have an infinite second moment at some value of the turbulent strength (A). This is a result found previously by others by the indirect means of analyzing the second moment of the probability density.^{4,5} It should also be pointed out that the analysis done here employed

Eulerian statistics of the turbulence which are somewhat more tenable than the Lagrangian statistics used by these previous investigators. It appears that the probability density, rather than its second moment, is the appropriate way of treating the problem, and in conjunction with the approximation, $T_E \ll \lambda_H$, it yields a particularly elegant and intuitive result.

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APPENDIX: THE DETAILS PERTAINING TO EQ. (3.7)

We can save ourselves a great deal of effort by taking note that the tensor to be inverted is isotropically invariant in the R coordinate, and that the inverse of such a tensor must preserve this invariance. That is, the inverse of $(\Delta + 2kT/\zeta \delta)$ must be of the form

$$C_1(R)\delta + C_2(R)RR \quad (A1)$$

or

$$[C_1(R)\delta + C_2(R)RR] \cdot (\Delta + 2kT/\zeta \delta) = \delta \quad (A2)$$

and we find $C_1(R)$ and $C_2(R)$ by comparing terms:

$$C_1(R) = \frac{1}{2A(R^2 + \alpha)},$$

$$C_2(R) = \frac{1}{2A(R^2 + \alpha)(R^2 + 2\alpha)}.$$

By taking advantage of the invariance property we have converted a two or three-page calculation by more pedestrian methods to a two- or three-line calculation.

¹P. S. Virk, A. I. Chem. E. J. 21, 625 (1975).

²E. J. Hinch, Phys. Fluids 20, 522 (1977).

³R. B. Bird, R. C. Armstrong, O. Hassager, and C. F. Curtiss, *Dynamics of Polymeric Liquids* (Wiley, New York, 1977), Vols. I and II.

⁴J. L. Lumley, Symp. Math. 9, 315 (1972).

⁵N. Phan-Thien and R. I. Tanner, Phys. Fluids 21, 311 (1978).

⁶J. O. Hinze, *Turbulence*, 2nd ed. (McGraw-Hill, New York 1975).

⁷V. I. Klyatskin and V. I. Tatarskii, Sov. Phys. Usp. 16, 494 (1974).

⁸R. Armstrong and M. S. Jhon, J. Chem. Phys. 77, 4256 (1982).

⁹N. S. Berman, Annu. Rev. Fluid Mech. 10, 47 (1974).

¹⁰N. G. van Kampen, Phys. Lett. C 24, 171 (1976).