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A study of polymer conformation in turbulent flow

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There have been numerous investigations[1-4] into this problem in conjunction with the study of turbulent drag reduction—adding a minute amount of polymer reduces the drag exerted by a turbulent fluid significantly.

We shall adapt the bead-spring model for the polymer molecules to illustrate the essential features. As the reader will see below, the major contribution of the turbulent field is to reduce the spring force between the beads. We expect that we may safely consider the two-bead case (often called the dumbbell model) without grossly distorting the important detailed mechanism.

Let us consider the motion of the dumbbell molecule in the turbulent core. In accordance with Ref. 5, the equation for the bead probability density (ψ) can be obtained

$$\frac{\partial}{\partial t}\psi = -\sum_{i=1}^{2}\frac{\partial}{\partial \mathbf{r}_i}\cdot\left\{\left[\bar{\mathbf{v}}(\mathbf{r}_i) - \frac{kT}{\zeta}\frac{\partial}{\partial \mathbf{r}_i}\ln\psi + \frac{\mathbf{F}_i^{(c)}}{\zeta}\right]\psi\right\} - \sum_{i=1}^{2}\frac{\partial}{\partial \mathbf{r}_i}\cdot[\mathbf{v}'(\mathbf{r}_i)\psi] \ . \tag{1}$$

Note that we have defined the fluid velocity $\mathbf{v} = \bar{\mathbf{v}} + \mathbf{v}'$, with $\bar{\mathbf{v}}$ standing for the average velocity (deterministic) and with $\mathbf{v}'$ standing for the fluctuating velocity component (random). Without loss of generality,[6] we shall declare $\bar{\mathbf{v}} = 0$.

To make sense out of this turbulent velocity, we can make a fluctuating velocity averaged probability function: $\langle\psi[\mathbf{v}'(\mathbf{r}_i); \mathbf{r}_i, t]\rangle_{\mathbf{v}'} \equiv \bar{\psi}(\mathbf{r}_i, t)$. Here $\langle\ \rangle_{\mathbf{v}'}$ is the average over the fluctuating velocity. Note $\bar{\psi}$, the averaged probability function, is dependent only on the bead position and time explicitly and is not an explicit functional of $\mathbf{v}'$.

These are the general guidelines for calculating $\bar{\psi}$ in a brute-force kind of way. However, the standard procedure[7] is to construct an effective equation for $\bar{\psi}$ and solve it. That is, the random probability equation which is given in Eq. (1) can be properly put into the average probability equation following the recipe given in Ref. 7:

$$\frac{\partial}{\partial t}\bar{\psi} = 2\frac{kT}{\zeta}\frac{\partial^2}{\partial R^2}\bar{\psi} + \frac{2}{\zeta}\frac{\partial}{\partial \mathbf{R}}\cdot\mathbf{F}^{(c)}\bar{\psi} + \frac{\partial}{\partial \mathbf{R}}\cdot\left[\int_0^t ds\ \mathfrak{G}(\mathbf{R}, s)\right]\cdot\frac{\partial}{\partial \mathbf{R}}\bar{\psi} = 0 \ . \tag{2}$$

Here, we have $\mathfrak{G}$ as the second-order cummulant and we have neglected higher-order cummulants. Further, we have converted to center-of-mass coordinates (i.e., $\mathbf{r}_c = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2)$, and $\mathbf{R} = \mathbf{r}_2 - \mathbf{r}_1$), using the isotropic turbulence assumption which leads to no $\mathbf{r}_c$ dependencies in Eq. (2). Also we have defined $\mathbf{F}^{(c)}$ as the connector force (i.e., $\mathbf{F}_1 = -\mathbf{F}_2 = \mathbf{F}^{(c)}$).

$\mathfrak{G}$ involves the turbulent flow information and can be expressed in terms of the correlation function of the fluctuating velocity field and

$$\mathfrak{G}(\mathbf{R}; s) = 2[\boldsymbol{\Gamma}(0; s) - \boldsymbol{\Gamma}(R; s)] = G(R, s)\boldsymbol{\delta}^{8} \tag{3}$$

with

$$\boldsymbol{\Gamma}(|\mathbf{r} - \mathbf{r}'|; t - t') \equiv \langle\mathbf{v}'(\mathbf{r}, t)\mathbf{v}'(\mathbf{r}', t')\rangle_{\mathbf{v}'} \ .$$

Without resorting to the detailed information of turbulence, we shall draw a conclusion based on the general properties of $\mathfrak{G}$.

Since the correlation decays with increasing R,[9] we have

$$\Gamma(0, s) > \Gamma(R, s) \quad \text{or} \quad G(R, s) > 0 \ . \tag{4}$$

We shall study the steady-state limit ($t \to \infty$) of Eq. (2), by defining the "turbulent strength" $\alpha(R)$ as

$$\int_0^\infty ds\ \mathfrak{G}(R, s) \equiv \frac{2kT}{\zeta}\alpha(R)\boldsymbol{\delta} \tag{5}$$

with $\alpha(R) > 0$ (positive definite). Then from Eqs. (2) and (5) we have ($t \to \infty$)

$$\left\{2\frac{kT}{\zeta}\frac{\partial}{\partial \mathbf{R}}\cdot[1 + \alpha(R)]\boldsymbol{\delta}\cdot\frac{\partial}{\partial \mathbf{R}} + \frac{2}{\zeta}\frac{\partial}{\partial \mathbf{R}}\cdot\mathbf{F}^{(c)}\right\}\psi = 0 \ . \tag{6}$$

This is an effective equation for the polymer distribution function in turbulent flow and is the central result of the present communication. To have some intuitive appreciation for this approach we shall give the result for a Hookean dumbbell with $\mathbf{F}^{(c)} = H\mathbf{R}$ and use an equilibrium preaveraged $\alpha(R)$.[10] We will define the equilibrium preaveraged $\alpha(R) \doteq \int d^3R\,\alpha(R)\psi_{eq}(R) \equiv \epsilon > 0$. Here, $\psi_{eq}(R)$ is the solution of Eq. (6) when $\alpha(R) = 0$ and under the constraint $\int d^3R\,\psi_{eq} = 1$. That is, $\psi_{eq} = (2\pi kT/H)^{3/2} \times \exp(-HR^2/2kT)$. We will call ϵ the "preaveraged turbulent strength." If one calculates the average of the end-to-end vector distance with and without turbulent flow, we have

$$\langle R^2\rangle_{\text{turbulent}} = \int d^3R\,R^2\,\bar{\psi}(R) = 3\frac{kT}{H}(1 + \epsilon) > 3\frac{kT}{H} = \int d^3R\,R^2\psi_{eq}(R) = \langle R^2\rangle_{eq} \ . \tag{7}$$

Therefore, the polymer (dumbbell in this example) is elongated in the turbulent flow and the parameter $\epsilon = \langle R^2\rangle_{\text{turbulent}}/\langle R^2\rangle_{eq} - 1 > 0$, characterizes magnitude of elongation. As we see from Eq. (7), ϵ depends on the statistics of the fluctuating field through $\alpha(R)$ and the nature of the polymer statistics through $\Psi_{eq}(R)$. It seems that the preaveraged turbulent strength may therefore have considerable bearing on semiempirical relationships derived to characterize the onset and the amount of drag reduction involving dilute polymer solutions. We can consider the first term on the right-hand side of Eq. (6) to be an effective diffusive force term and the second to be a spring-force term. We can see that the ratio of these two determines the half-width of

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Ψ and that the turbulent field acts as either an enhancement of the diffusive term or as an effective reduction in the spring force and intuitively we see why the polymer elongates.

In fact, the connector force term of Eq. (6) may be arranged into an effective force term $\mathbf{F}_{\text{eff}}^{(c)} = \mathbf{F}^{(c)}(R)/[1+\alpha(R)] < \mathbf{F}^{(c)}$. Even though our proof for the reduction of the effective spring force is illustrated for the dumbbell only, the N-bead chain case behaves similarly. Since turbulent flow will effectively reduce the spring force between the N beads, we can expect that the N-bead coil will expand also.

At this point we may speculate somewhat. The idea we want to convey can be viewed as "screened" interaction caused by the turbulent flow. That is, the interaction between the two points in the turbulent flow may be screened and reduced compared to the bare interaction (due to the renormalization process). Such a screening effect in the dumbbell case arises from rapid Brownian-type motion caused by the turbulent flow. Upon closer scrutiny we can see why this formulation may be complementary to ones put forth in the past. Other investigators[1-4] have expanded $\Psi(R, t)$ into a Taylor series truncating at the first term. This yields a correlation function that is probably good at small R but yields the unphysical result that the (Hookean) dumbbell will continue to extend unbounded in time when some statistical flow parameter is exceeded.

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[6]Most of pipe flow averaged velocity profile is plug shaped, i.e., $\bar{\mathbf{v}} = \text{const.}$ in the turbulent core. Since constant velocity does not change the polymer conformation we assume $\bar{\mathbf{v}} = 0$.
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[8]Although the form $\alpha(R)\delta$ is a correct form for an isotropic tensor, for complete generality, the tensor must have the form $\alpha(R)\delta + \beta\,\mathbf{RR}$. This addition does not affect the nature of our final solution (qualitatively). For a thorough treatise on isotropy, see M. E. Gurtin, *An Introduction to Continuum Mechanics* (Academic, New York, 1981).
[9]Rigorous proof can be obtained by using a Schwartz inequality.
[10]Preaveraging has enjoyed widespread popularity in polymer physics, usually in connection with the study of hydrodynamic interaction, cf., H. Yamakawa, *Modern Theory of Polymer Solutions* (Harper and Row, New York, 1971).

Detection of photofragments by multiphoton ionization with direct resolution of angular and time-of-flight distributions

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Molecular beam techniques with moveable universal detectors have played a central role in advancing our fundamental understanding of atomic and molecular scattering processes.[1] Though such experiments are valuable, they are also complex and expensive. Generally it is the physical dimensions and pumping requirements of the detector (usually a rotating, reentrant, electron impact source quadrupole mass spectrometer) that determines the substantial size, complexity, and cost of a scattering apparatus.[2]

With this communication we introduce a new and simpler laser based method. Earlier,[3] we described the first application of a technique of great promise for the universal detection of transient reaction products—resonance enhanced multiphoton ionization (MPI). Of inherently high spatial and temporal resolution, this technique is also state specific, as demonstrated by its wide use as a spectroscopic tool[4] and, in particular, by its application in our estimate of the rotational energy content of nascent NO_2 from the infrared multiphoton dissociation (MPD) of nitromethane in a pulsed jet.[3]

We have now fully exploited the natural time and space resolution of multiphoton ionization in a reactive scattering experiment; using MPI, we have determined angular and flight time distributions for MPD products scattered from a skimmed supersonic molecular beam.

We use a stationary quadrupole mass spectrometer in a small vacuum system to collect the MPI signal for specific fragments as a function of probe laser delay time and focal position. This communication presents the angular distributions for both CH_3 and NO_2 fragments from the multiphoton dissociation of nitromethane.

As described earlier,[3] our apparatus orthogonally crosses a pulsed supersonic molecular beam of CH_3NO_2[5] by the focused outputs of a 1 Hz CO_2 TEA laser and 10 Hz Nd:YAG pumped dye laser, all within the ion collection region of an extranuclear quadrupole mass spectrometer. Pumped by the CO_2 laser to unimolecular dissociation, the CH_3NO_2 yields fragments CH_3 and NO_2,

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