

NOTE

Constitutive Equation or Stress Calculator?

Various molecular theories of dilute polymer solutions use models in which bead-rod or bead-spring systems immersed in an incompressible Newtonian solvent are subject to thermal motion forces. In the absence of polymer, it is assumed that a homogeneous velocity field

$$\mathbf{v}(\mathbf{r}, t) = \mathbf{v}_0 + \mathbf{r} \cdot \mathbf{K}(t) \quad (1)$$

can be imposed, for instance, by moving apparatus walls. $\mathbf{v}(\mathbf{r}, t)$ denotes the solvent velocity at a place of position vector \mathbf{r} (relative to an origin 0 fixed in space) at time t ; the velocity gradient tensor \mathbf{K} is independent of \mathbf{r} . \mathbf{v}_0 denotes the solvent velocity at 0 .

If, as is usually assumed, inertial forces in the stress equation of motion can be neglected, addition of polymer results in addition of extra terms to (1), yielding an equation of the form

$$\mathbf{v}(\mathbf{r}, t) = \mathbf{v}_0 + \mathbf{r} \cdot \mathbf{K}(t) + \Sigma \mathbf{v}_i(\mathbf{r}, \mathbf{r}_i, t), \quad (2)$$

where $\mathbf{v}_i(\mathbf{r}, \mathbf{r}_i, t)$ denotes the contribution to solvent velocity at \mathbf{r}, t arising from bead i located instantaneously at \mathbf{r}_i . Σ denotes a summation over all beads in the solution sample considered.

According to the bead-spring theory of Rouse^{1,2}, it is assumed that *the effects of bead forces acting on the solvent can be neglected* and that the solution (macroscopic) velocity gradient tensor is equal to $\mathbf{K}(t)$. It is, however, assumed that the solvent exerts forces on the beads and thereby alters the bead-spring distribution function and hence also the stress. This paradoxical treatment seems to be not unreasonable *provided that $\mathbf{K}(t)$ is not zero*; in particular, it gives an at least approximate value for the polymer contribution to stress in the most useful experimental cases (steady and oscillatory shear); the equation² for calculating the solution stress tensor \mathbf{p} may be written in the form

$$\mathbf{p}(\mathbf{r}, t) + p(\mathbf{r}, t)\mathbf{I} = \eta_s[\mathbf{K}(t)] + \int_{-\infty}^t m(t-t')\mathbf{B}(t, t') dt' \quad (3)$$

where $p\mathbf{I}$ denotes an isotropic contribution to stress, η_s denotes the solvent viscosity, $m(t-t')$ is a known sum of exponentials, $\mathbf{B}(t, t')$ denotes the Finger strain tensor constructed from $\mathbf{K}(t'')$ ($t' < t'' < t$), and $[\mathbf{K}]$ denotes the symmetric part of \mathbf{K} . The integration is "at constant particle".

If one puts $\mathbf{p}(\mathbf{r}, t) = 0$ ($t > 0$) in (3) in the hope of calculating free recovery after a flow history $\mathbf{K}(t')$ has been imposed up to $t' = 0$, one obtains non-zero values for $\mathbf{K}(t)$ ($t > 0$). [Similar problems have been solved³ for the "rubberlike liquid" equation obtainable from (3) by putting $\eta_s = 0$; it is a straightforward matter to extend the solution to the case $\eta_s > 0$.] The question arises: what do these non-zero values for $\mathbf{K}(t)$ represent?

According to the Rouse theory in the approximation used in deriving (3), *the beads and springs have no effect on the solvent velocity*. It follows that there can be no elastic recovery, and hence that (3) should be regarded, not as a Rouse theory constitutive equation applicable to all flow problems (including recovery), but rather as a Rouse theory "stress calculator equation" applicable only to those problems for which a non-zero uniform solvent velocity gradient $\mathbf{K}(t)$ is specified. The recovery which one calculates by putting $\mathbf{p} = 0$ in (3) is a fictitious recovery: it is simply that uniform velocity gradient $\mathbf{K}(t)$ which must be imposed by some unrealizable means (and which cannot be generated by retraction of polymer molecules) in order to give zero stress.

For clarity and simplicity, the present arguments have been expressed in terms of the Rouse theory, but similar arguments also apply to the Zimm theory^{2,4} because it is also assumed that the beads have no influence on the macroscopic solution velocity field which is again assumed to be of the form (1). The influence of beads on the solvent field is considered only in connection with the motion of beads on the same polymer molecule.

It should be possible, in principle, to calculate a non-zero free recovery on the basis of the bead-spring model for dilute polymer solutions. It would be essential to abandon the Rouse assumption that the effects of beads on the solvent velocity can be neglected. There would be no term $\mathbf{r} \cdot \mathbf{K}(t)$ because the only contributions to solvent velocity come from the beads, i.e. we would have

$$\mathbf{v}(\mathbf{r}, t) = \Sigma \mathbf{v}_i(\mathbf{r}, \mathbf{r}_i, t) \quad (\text{free recovery}). \quad (4)$$

One would presumably need to consider a large sample of solution, assume some nonspherically symmetric form for the spring distribution function at time $t = 0$ to represent the effect of the flow history imposed prior to recovery, and then calculate the combined effects of the bead forces on the solvent subject to the condition at large distances that the free solvent boundary shall have a zero or uniform normal component of traction and no tangential component. The elastic recovery would presumably be obtainable from the solvent velocity gradient tensor, suitably averaged to give the macroscopic solution velocity gradient tensor. Such a calculation has not been published as far as I am aware; it is certainly not part of the Rouse theory. The importance of recalculating the macroscopic solution velocity gradient tensor by sample-averaging contributions of the type (4) was noted by Lodge and Wu²; such calculations have been performed by Higashitani⁵ and by Schuemmer and Otten⁶.

This simple example serves to show that, in order to explain elastic recovery of polymeric liquids *in molecular terms*, it is essential to specify, not only the retraction mechanism of individual polymer molecules but also the way in which these molecules affect their environment. In the Rouse theory, the actual environment of a given polymer molecule is treated by means of a "mean field" type of assumption, namely that the system of solvent molecules can be replaced by an incompressible Newtonian liquid whose velocity field is restricted to be of the form (1). It appears to be typical of this and certain other "mean field" theories that attention is focused on representing the effects of the environment on a given polymer molecule. The present discussion suggests that such treatments may give "stress calculator" rather than "constitutive" equations, and that if one wishes to calculate free recovery on a molecular basis, it may not be sufficient to put the extra stress zero in "stress calculator" equations: it may be necessary to reexamine

mean field models in order to calculate the effect of the typical polymer molecule on the "mean field" in order to see how some, at least, of the polymer molecule retraction can be transmitted to the outer fluid boundary.

References

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