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DISCUSSION

(*Monday morning*)

BIRD. The discussion opened with comments and opinions on how the kinetic theory equations predicted the behavior of the viscosity coefficient and other viscometric functions of a non-Newtonian fluid. For example, Bird had shown that eq. (4.4), specialized to dumbells, gave very good agreement with experimental data [ref. 25 of his paper]: he also referred to comparisons in his textbook [R.B. Bird, O. Hassager, R.C. Armstrong and C.F. Curtiss, Dynamics of Polymeric Liquids, vol. 2 (Wiley, New York, 1977)] and to the lecture of Curtiss (this Journal) for further information. The behavior of the perhaps not so familiar – at least to the general audience – functions Ψ_1 and Ψ_2 [eqs. (2.4) and (2.5)] was discussed. *Hess* in particular, agreed that Ψ_2 was equal to zero for the Hookean spring model [eqs. (4.1)–(4.5), with $N = 2$] but asked if the same result obtained for finitely extensible springs was nothing more than an artifact of the solution of the relevant kinetic equations. *Bird* pointed out that $\Psi_2 = 0$ for all bead–spring models if hydrodynamic interaction between the beads through the solvent is omitted, or if an equilibrium-averaged hydrodynamic interaction is used. He reported some unpublished studies with rigid "shiskabobs" of N beads in which hydrodynamic interaction is included. Preliminary results show that Ψ_2 is positive for 2, 3 or 4 beads, but negative for 5 beads or more for small values of the hydrodynamic interaction parameter. [R.B. Bird and C.F. Curtiss, Univ. Wisconsin Res. Ctr. Rept., No. 81 (June 1982).]

Clark asked if the result that the elastic response coefficient $\eta''(\omega, \gamma)$ [ref. 1, p. 169: ω is the frequency and γ the shear rate] has been found experimentally to be negative can be explained simply by means of kinetic theory. *Bird* replied by stating that simple explanations were perhaps inappropriate for such questions: one has to look at the details of the theory and identify the significance of the appropriate terms in the expressions. Thus, this result will undoubtedly be as difficult to explain as the phenomenon of thermal diffusion in the traditional kinetic theory of dilute gases.

Andersen asked if a fluid surface would have a memory if it were broken and hence tend to heal itself. *Bird* referred to the work of Prager and Tirrell [J. Chem. Phys. **75** (1981) 5194] and noted that an earlier scaling analysis was done by de Gennes [C. R. Acad. Sci. (Paris) **B291** (1980) 219].

The Principle of Objectivity (defined, for example in ref. 1, p. 294 and section 3 of Bird's text) invoked a lengthy debate which extended throughout the conference. For instance, *Fixman* questioned its general validity and

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wondered if the appearance of generality could not be ascribed to a lack of critical experimentation. He asked if it should be considered a convenient postulate or a basic physical assumption. *Cohen* also queried what reasonable physical arguments could be made to justify the Principle, especially as spatial anistropy has to be present if a material is sheared. *Bird* replied by stating that the Principle should be, and is, considered a postulate and acknowledged its possible controversial nature. He gave the simple argument that if one obtains the stress/strain relation in a rubber band, the relation would be expected to be independent of the orientation of the band with respect to the observer. He also pointed out that the Principle seems to be satisfied by the kinetic theory of gases through the Burnett equations.

De Gennes submitted the following comment:

I enjoyed this review enormously, but I remain unhappy with the presentation of the "Principle of Objectivity." This Principle is in fact an approximation, based on the neglect of centrifugal and coriolis forces at the molecular level. We can make a numerical estimate of the error involved as follows:

a) The order of magnitude of the centrifugal forces for a polymer coil of size R rotating at angular velocity Ω is

$$f_c = \tilde{M}\Omega^2 R, \tag{1}$$

where $\tilde{M}$ is a molecular weight modified by the Archimedes correction in the solvent.

b) For a simple, ideal, coil of r.m.s. R_0 the elastic resolving force is of order

$$f_{el} = kTR/R_0^2. \tag{2}$$

c) The ratio of the two is

$$\kappa = \tilde{M}\Omega^2 R_0^2/kT \tag{3}$$

$$\approx \left(\frac{N\Omega}{\Omega_{th}}\right)^2, \tag{4}$$

where N is the number of monomers per chain, and Ω_{th} is a r.m.s. rotational velocity for a single monomer. Typically $\Omega_{th} \approx 10^{11}$, $\Omega \approx 10^3$ and $N = 10^4$ giving $\kappa \approx 10^{-8}$.

d) A similar estimate can be obtained for the Coriolis force

$$f_{COR} = \tilde{M}V\Omega R_0, \tag{5}$$

where V is a coil velocity, which we estimate from the elastic force eq. (2); thus a friction of the stokes form for an object of size R_0 is

$$V \approx \frac{1}{6\eta R_0} f_{\mathrm{el}}. \tag{6}$$

If we insert eq. (6) into eq. (5) we can compute the ratio

$$y = \frac{f_{\mathrm{COR}}}{f_{\mathrm{el}}} \approx \frac{\tilde{M}\Omega}{\eta R_0}, \tag{7}$$

$$y \approx \Omega N^{1/2} \tau, \tag{8}$$

where τ is a rotational relaxation force for a monomer. Using $t \approx 10^{-11}$ s, $\Omega = 10^2$ and $N = 10^4$ gives $y = 10^{-7}$ – again a small number.

The overall conclusion is that we may neglect all the special forces which occur in a rotating form (centrifugal and Coriolis) when we build up a constitutive equation for usual polymer fluids. But this is an approximation, not a principle. Indeed, with semirigid molecules of very high molecular weight, the approximation could break down.

Bird submitted a response to the above:

The kinetic theories of polymers have traditionally neglected the acceleration terms in the equation of motion for the polymer molecule [see, e.g., M. Fixman, J. Chem. Phys. **42** (1965), 3831; also ref. 19, p. 690]. This is probably the reason that the polymer kinetic theories do give results in accord with the Principle Of Objectivity. Even though this "Principle" is an approximation, as Professor de Gennes correctly points out, it has nonetheless proven to be a sensible and useful one.

Hoover submitted:

There is an interesting violation of the Objectivity Principle which arises at the Burnett level in atomistic kinetic theory. Consider the steady rotation of an annulus, heated on the inner boundary and cooled on the outer boundary. There is a steady flow of heat, and steady radial density and pressure gradients, which balance the centrifugal force. In the comoving (corotating) frame – the "Lagrangian" frame, in which the fluid velocity vanishes – objectivity predicts a purely radial heat flow. Both the Boltzmann equations and molecular dynamics contradict objectivity – the heat flux has a nonvanishing angular part. The *magnitude* of this angular flux, as measured by molecular dynamics, agrees semiquantitatively with Enskog's dense-fluid theory, in the Burnett approximation. The flux is proportional both to the radial temperature gradient and to the angular rotation frequency. See W.G. Hoover, B. Moran, R.M. More, and A.J.C. Ladd, Phys. Rev. **A24** (1981) 2109.

COHEN. Several comments followed Cohen's remarks on problems associated with developing a thermodyamics for a system subjected to a very large gradient; so large that the peculiar velocity changes appreciably over the range of the intermolecular potential. *Keizer* emphasized that a thermodynamic theory for steady states was proposed several years ago and referred to his talk (this Journal). *Eu* also added that since 1980, a theory of generalized thermodynamics has been known even for nonsteady states which is formulated based on the Boltzmann equation and its generalized form. He noted the procedure is discussed at the Poster Session.

Hess remarked that the moment method of Maxwell and Grid, and used by Waldmann and coworkers, leads to a continued fraction expansion of nonlocal transport coefficients with respect to spatial derivatives or of the wave vector rather than a power series expansion encountered in the higher Chapman–Enskog–Burnett procedure. He pointed out that the analysis and comparison between the two methods is relatively simple for the case of diffusion in a Lorentz gas [S. Hess, Z. Naturforsch. **32a** (1977) 678].

Fixman asked two questions: (1) do the nonequilibrium computer results, which were obtained at high frequency and/or shear rate, extrapolate to zero frequency or shear rate; (2) how do the computer results depend on the box size or the number of particles (N). *Cohen* deferred to subsequent speakers (e.g., Evans, Hoover, Erpenbeck) for details but remarked that the viscosity from nonequilibrium molecular dynamics appeared to extrapolate satisfactorily to equivalent viscosities from the Green Kubo formulas via conventional equilibrium molecular dynamics. *Hoover* added that evidence from many nonequilibrium computer simulations from different investigators and via different algorithms suggests that the N-dependence is weak for $N \geqslant 108$. In fact, extrapolations of results to infinite N did not appear to be of significance, given the computer data at this time.

Yip remarked on the importance of ring collisions in kinetic theory and submitted the following:

I would like to call attention to the essential role of ring collisions in formulating a dynamical theory of *dense* fluids. I have in mind the successful mode-coupling calculations of W. Goetze and collaborators at Munich on fluids with continuous potentials (also more recent work of L. Sjogren and A. Sjolander), and in particular the kinetic theory for hard spheres developed by E. Leutheusser [J. Phys. C **15** (1982) 2801–2827]. Leutheusser has shown how dense fluid properties such as shear wave propagation at finite wave number in the transverse current correlation function and appearance of a second relaxing component (viscoelastic mode) in the density correlation function can be calculated in quantitative agreement with molecular dynamics simulation results. It appears that the ideas of G. Mazeko and others that a tractable microscopic theory of dense fluids can be built on the basis of ring collisions and mode coupling do allow us to begin analyzing dynamical properties at liquid densities.

Clark then asked Yip if Yip's approach gave correct long time tail behavior. The question was addressed by *Leutheusser* who submitted:

I would like to comment on the enhanced long time tail of the shear viscosity observed in molecular dynamics experiments. Preliminary results of a selfconsistent kinetic ring theory for the hard sphere liquid (J. Phys. **C15** (1982) 2801) show that there is a potential contribution to the power law long time coefficient which at the density $V/V_0 = 1.6$ is roughly 14 times the known kinetic contribution. Though this already is a considerable enhancement it does not account for the observed factor of roughly 370. However, based on recent work on the Lorentz-gas, I believe that at this high density near the fluid–solid transition this observed strong enhancement is due to a new physical effect, namely the freezing of the fluid. In the Lorentz-gas the new effect is even more spectacular since not only the prefactors of the long time tail of the velocity correlation function are quite different in the low density regime and the critical regime of the diffusion–localization transition, but also the power law exponents are different.

Editors Note. As remarked in the Preface, Bird and Cohen set the stage for the later talks and discussion and it was interesting and gratifying how many points raised by them, and asked or implied in the discussion, were indeed followed up later. Some of these points included:

1. The Principle of Objectivity and its violations.
2. The concept of correlated motion in some form for example: ring collisions, vortex motion, and hydrodynamic interactions between the solvent and particles of interest.

2a. The consequences of correlated motion, for instance on the pair correlation function, reptation ideas, non-Newtonian behavior.

3. The credibility of recent nonequilibrium molecular dynamics (NEMD) computer simulations.

3a. The consequences of the NEMD results, e.g., interpretation of experimental results from a real non-Newtonian fluid; the ability of kinetic theory to handle the simulation data; basic questions of definition for a system under a large shear gradient.

4. The general validity of the Green–Kubo relations.
5. A thermodynamic description of a system far from equilibrium and, in general, basic thermodynamic concepts for any state other than the equilibrium state.