

Fascinating polymeric liquids

Theory and experiment are beginning to tell us why the motion of liquids containing very large molecules is often just the opposite of what we would expect from our experience with normal fluids.

R. Byron Bird and Charles F. Curtiss

*"The time has come," the dolphin said,
"To speak of many things:
Of flowing macromolecules
And little beads and springs."*

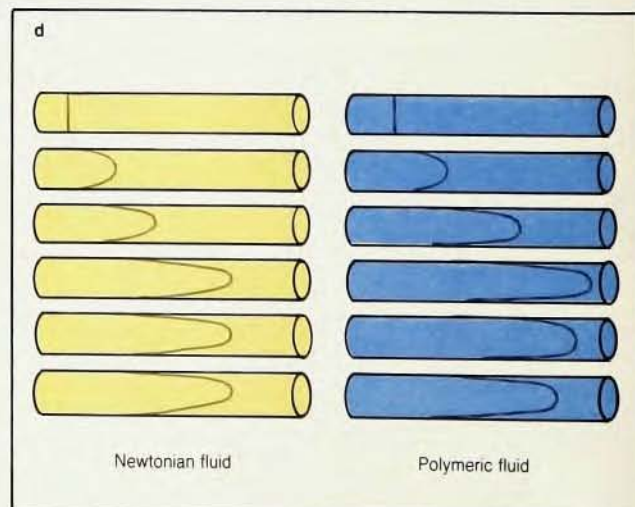
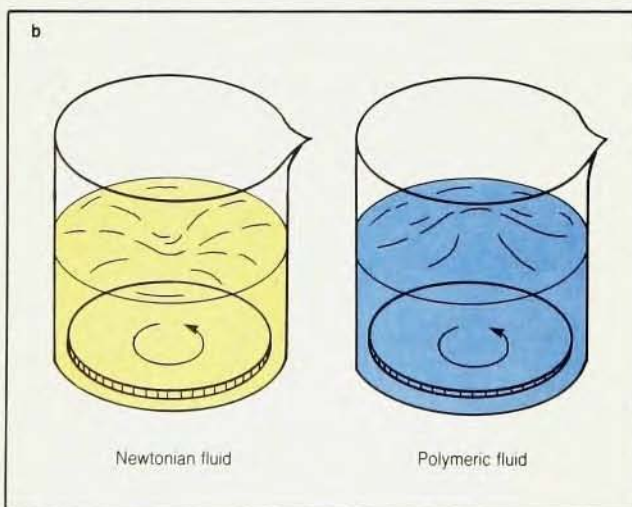
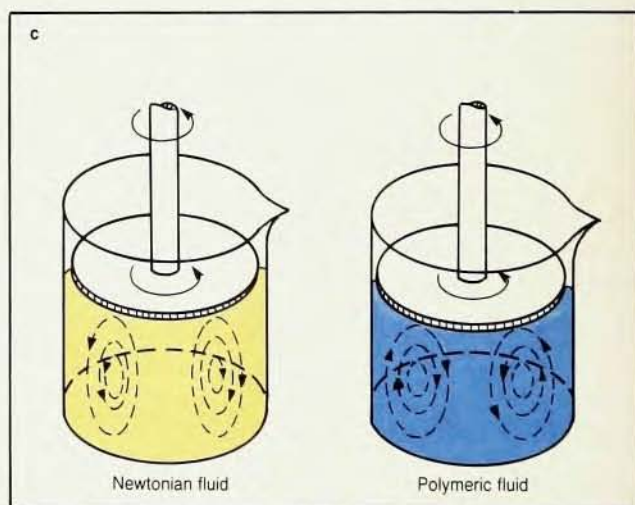
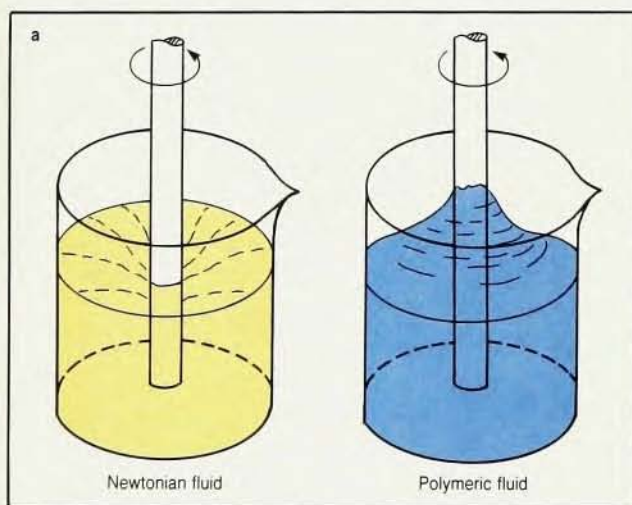
—with apologies to
Lewis Carroll

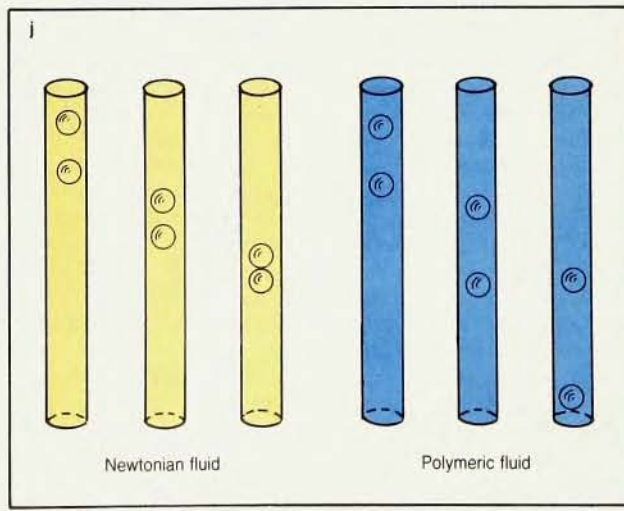
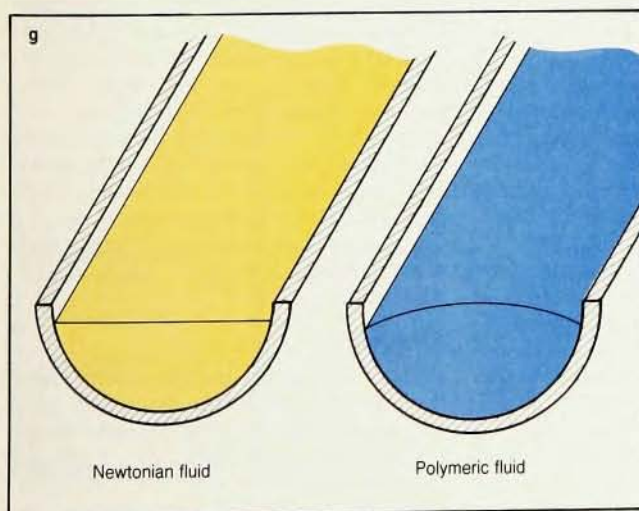
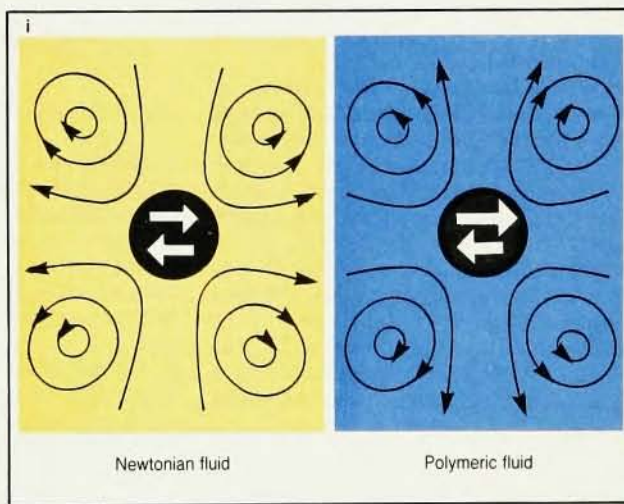
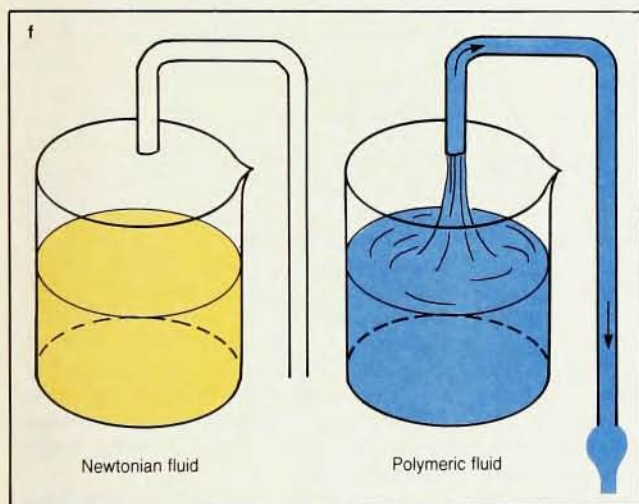
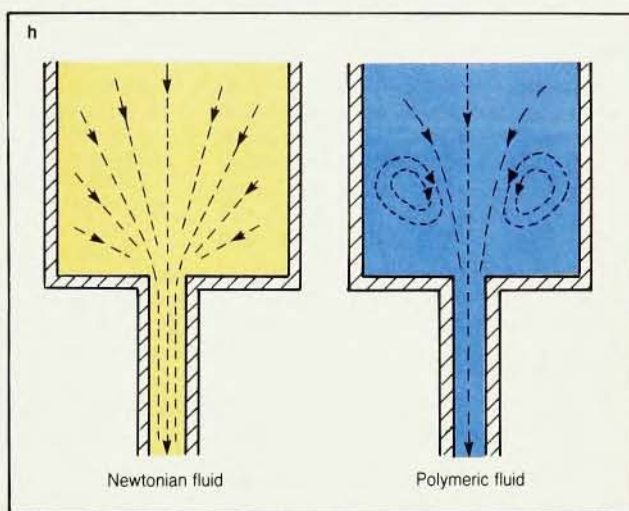
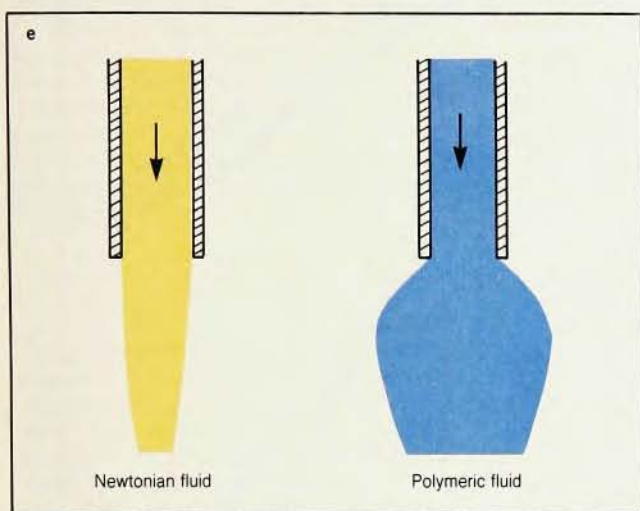
Fluid dynamics is an old subject. In 1687, Isaac Newton wrote a simple equation defining the viscosity of a fluid as the coefficient of proportionality between the shear stress and the velocity gradient. Newton's equation does well at describing gases and liquids made up of "light" molecules—those of molecular weight less than about 1000. By the middle of the last

century the mathematical description of the flow of such "Newtonian" fluids was well established. This description is based on use of the laws of conservation of mass and momentum.^{1,2}

However, neither Newton's equation nor its generalization for more complicated flows (see the box on page 39), describes the flow of liquids containing polymers.³⁻⁶ Here we are dealing with very large molecules—typical molecular weights range from 10^5 to 10^6 —made up of repeating chemical units. Both polymer solutions and undiluted polymers, called "melts," are "non-Newtonian."

Polymer fluid dynamics—the subject of this article—is a relatively new field. Polymers have been known only since about 1930, and the fluid dynamics of polymeric liquids has been studied since about 1950, because of the rapid development of the plastics industry. One of the main challenges in the field of polymer fluid dynamics is to find an appropriate expression for the stress tensor to take the place of that given by Newton's law of viscosity; such an expression is called a "constitutive equation." Another major challenge is the solution of the conservation equations, along with the constitutive equa-





Unusual flows. The ten experiments sketched here show how the behavior of polymeric liquids is qualitatively different from that of Newtonian liquids. A polymeric liquid climbs a rotating rod in **a**; rises above a rotating disc in **b**; moves radially inward along a rotating disc in **c**; recoils in a tube when the pump is turned off in **d**; swells when it

emerges from a tube in **e**; siphons across a gap in **f**; develops a slightly convex surface when flowing down a trough in **g**; develops a vortex when the tube diameter decreases for slow flow in **h**; moves toward a transversely oscillating cylinder along the line of oscillation in **i**; and causes falling spheres to grow further apart in **j**.

Figure 1

tion, to obtain the distributions of velocity and stress in a variety of flow situations. Most industrially important problems involve the additional complications of heat transfer and phase change, but here we discuss only the simpler isothermal problems involving no change of phase.

We begin this article with a look at ten strange flow phenomena exhibited by polymeric liquids. This will lead us to a discussion of some of the experimental approaches that rheologists take to analyze flow. Then, in the second half of the article, we will discuss theoretical efforts to develop the kinetic theory of the rheological properties of polymers.

Ten strange flows

How do we know that Newton's law of viscosity is inadequate for polymeric liquids? There are many fascinating experiments^{3,5,7} that show that the flow of polymeric fluids is qualitatively different from that of Newtonian fluids. Figure 1 shows some of these experiments, the first three of which involve rotation.

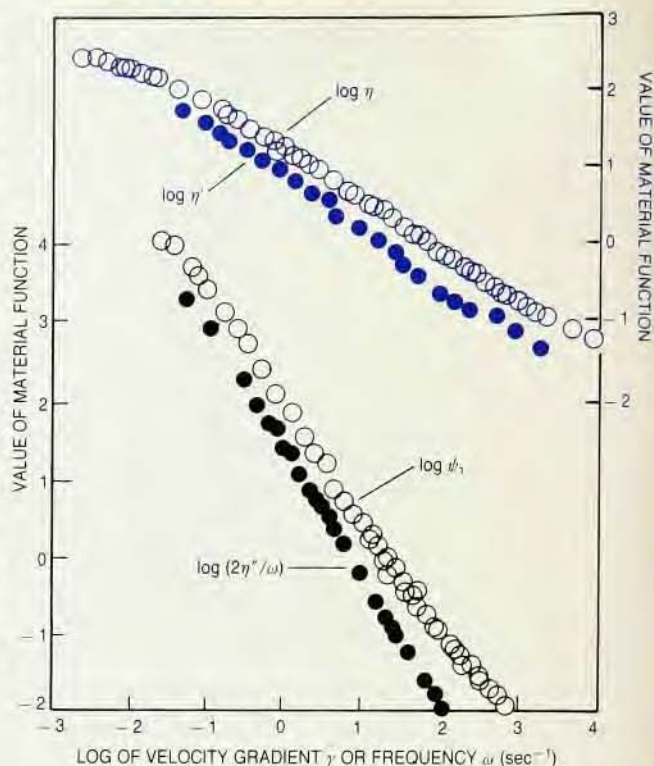
► Figure 1a compares the behavior of Newtonian and polymeric fluids near a rotating rod. The surface of the Newtonian fluid is depressed near the rod, whereas the polymeric liquid tries to climb the rod. This climbing is known as the "Weissenberg effect."

► Figure 1b shows behavior closely related to that of figure 1a. Here a rotating disk at the bottom of the beaker causes a depression in the surface of the Newtonian fluid, but a rise in the surface of the polymeric liquid.

► In figure 1c a rotating disk placed at the surface of either fluid causes a primary flow in the tangential direction, but superposed on this primary flow is a secondary flow. Newtonian fluids are shoved outward by the rotating disk, move downward near the beaker wall and then move upward near the axis of the beaker. Polymeric liquids also have a secondary flow—but in the opposite direction!

► In figure 1d we see how fluids behave as they are pumped down a circular tube. We follow the motion by watching a streak of dye that is inserted before the motion starts; six successive snapshots of the streak are shown. When the pump is turned off at the fourth snapshot, the Newtonian fluid comes to rest, but the polymeric liquid "recoils" as shown in the fifth and sixth snapshots. This illustrates the "memory" of polymeric fluids. Because they do not return all the way to their initial

Material functions for a 1.5% solution of polyacrylamide (Separan AP30) in a 50/50 mixture of water and glycerine. Open circles represent data for steady shear flow: η is the non-Newtonian viscosity and ψ_1 is the first normal-stress coefficient. Solid circles represent data for small-amplitude sinusoidal motion: η' and η'' are the in-phase and out-of-phase coefficients. The colored curves use the scale at the right. The three eta functions have dimensions of pascal seconds, whereas the normal stress coefficient is measured in units of pascal sec². (Data from reference 23.) **Figure 2**



configuration (as a rubber band would after being stretched), we say that these fluids have "fading memory."

► Figure 1e shows how a polymeric liquid swells when it emerges from a tube or slit. The cross-sectional area can increase by as much as a factor of five.

► Figure 1f shows a siphon experiment. For Newtonian fluids, siphons work only as long as the upstream end of the tube is beneath the surface of the liquid. One can siphon polymeric fluids even if there is a gap of several centimeters between the surface of the liquid and the end of the tube!

► In figure 1g we see what happens when a liquid flows down a tilted trough of semi-circular cross section. The flow is laminar in each case. The surface of the Newtonian liquid is flat except for meniscus effects, whereas the surface of the polymeric liquid is slightly convex. This is a small effect, but it is reproducible.

► In figure 1h we see how fluids flow from a large-diameter tube into a small-diameter tube in slow flow. In polymeric liquids a vortex forms upstream. Fluid particles trapped in this vortex do not move on into the small-diameter pipe.

► In figure 1i we see the "acoustical streaming" experiment, in which one observes the flow near a cylinder that is oscillating transversely. High-frequency oscillations produce a steady secondary flow in the surrounding fluid. However, the direction of this flow in a polymeric liquid is just opposite to that

in a Newtonian liquid.

► Finally, figure 1j shows what happens when we drop two spheres, one after the other, into a tube of liquid. In Newtonian fluids, the second sphere always catches up with the first one and collides with it. In polymeric liquids the same thing happens if we drop the second sphere very soon after the first one. However, if we wait longer than a critical time interval, then the spheres tend to move apart while falling.

In the experiments just described, the response of the polymeric liquid is *qualitatively* different from that of the Newtonian liquid. We are thus not dealing with minor variations on an old theme. Rather, we are faced with striking differences that can be explained only by rejecting Newton's law of viscosity and replacing it with some new and more general expression that can account for fading memory, recoil, the reversal of secondary flows, and other bizarre behavior. That is the challenge!

Rheometry

The ten experiments above are thought-provoking, but their flow patterns are a bit too complicated for an introductory scientific study. Polymer rheologists have developed a number of carefully controlled experiments, in which they measure one or more components of the stress tensor in well-defined flows. Such experimental work is referred to as *rheometry*.^{8,9} It is the non-Newtonian analog of *viscometry*.

R. Byron Bird is professor of chemical engineering, and Charles F. Curtiss is professor of chemistry, at the University of Wisconsin, Madison.

In a viscometric experiment one measures a single material constant—the viscosity. In a rheometric experiment one measures a set of “material functions.” Let us examine two rheometric experiments briefly.

We begin with a fluid between two parallel planes. If we move one of the planes with a constant speed in the x direction so that a constant velocity gradient $\dot{\gamma} = dv_x/dy$ is established, then we can measure three quantities—a shear stress and two normal-stress differences:

$$\begin{aligned}\pi_{yx} &= -\eta\dot{\gamma} \\ \pi_{xx} - \pi_{yy} &= -\psi_1\dot{\gamma}^2 \\ \pi_{yy} - \pi_{zz} &= -\psi_2\dot{\gamma}^2\end{aligned}$$

Data on steady shear flow are usually reported in terms of the non-Newtonian viscosity η , the first normal-stress coefficient ψ_1 and the second normal-stress coefficient ψ_2 . All three of these coefficients are strong functions of the velocity gradient $\dot{\gamma}$. Experiments have shown that the non-Newtonian viscosity η and the first normal-stress coefficient ψ_1 are both positive, whereas the second normal-stress coefficient ψ_2 is negative and much smaller in magnitude than ψ_1 . Figure 2 shows one set of data for η and ψ_1 . It is known that the phenomena shown in parts a, b, c and e of figure 1 are closely related to the coefficient ψ_1 , and that the convex surface of fluid in part g of the figure is intimately related to the negative second normal-stress coefficient.

Fundamental equations for incompressible fluids

Newton defined the viscosity μ of a fluid as the coefficient of proportionality between the shear stress π_{yx} and velocity gradient $\partial v_x/\partial y$ in a shear flow:

$$\pi_{yx} = -\mu(\partial v_x/\partial y) \quad (\text{Newton's equation})$$

Here v_x is the x -component of the fluid velocity and π_{yx} is the force per unit area in the x -direction exerted on a fluid surface element perpendicular to the y -direction. In complicated flows, all three velocity components may depend on all three space variables. Then we may generalize the above equation for an incompressible fluid to:

$$\pi_{mn} = p\delta_{mn} - \mu(\partial v_n/\partial x_m + \partial v_m/\partial x_n) \quad m, n = x, y, z$$

(Generalization of Newton's equation)

This expression retains the main idea that the stress tensor components π_{mn} in the fluid at some time t are linear functions of the velocity gradients at the same time t . The term containing the pressure p has to be included to describe the isotropic stresses in a fluid at equilibrium; the Kronecker delta δ_{mn} is zero unless $m = n$.

The description of fluid flow requires the solution of the equations of continuity and motion along with an appropriate constitutive equation:

$$\nabla \cdot \mathbf{v} = 0 \quad (\text{Equation of continuity})$$

$$\rho D\mathbf{v}/Dt = -\nabla \cdot \boldsymbol{\pi} + \rho \mathbf{g} \quad (\text{Equation of motion})$$

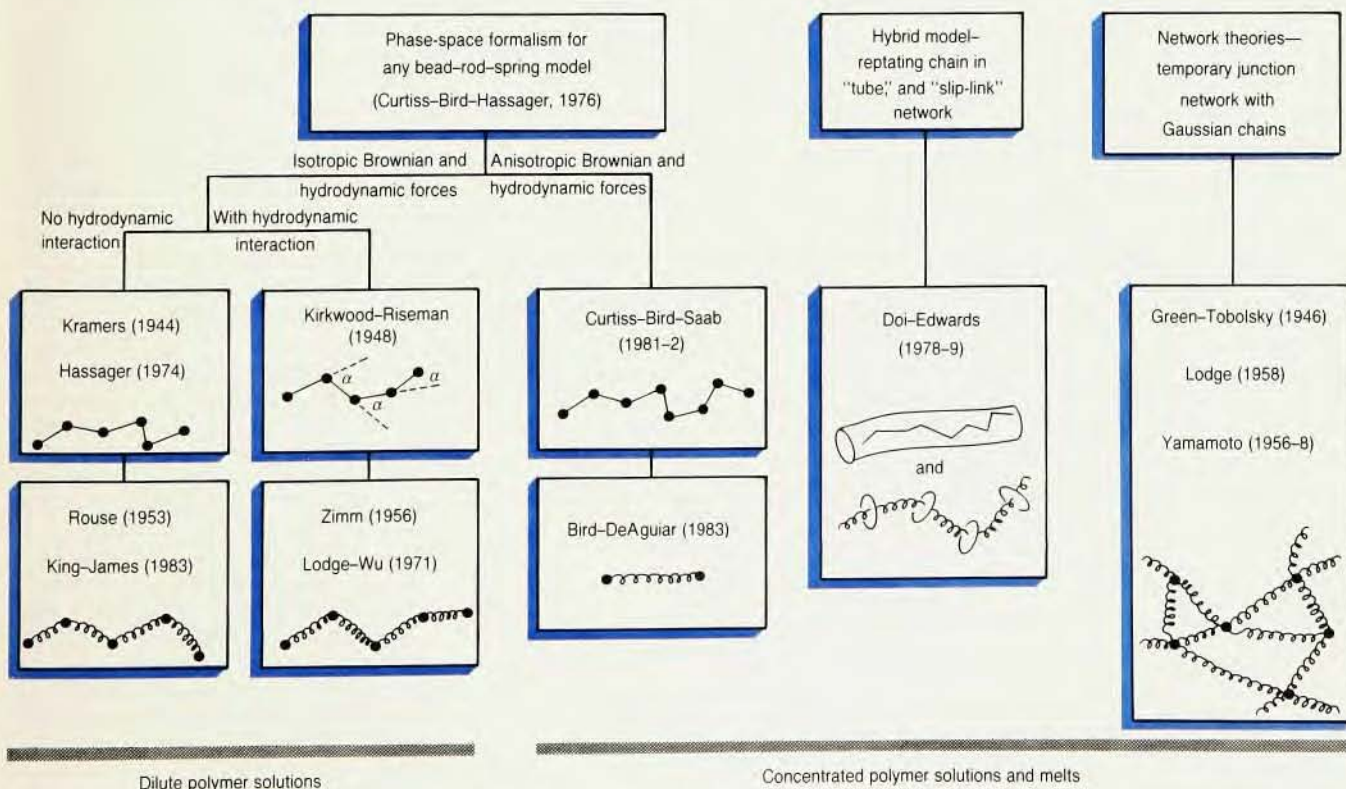
Here ρ is the fluid density, \mathbf{g} is the gravitational acceleration and D/Dt is $\partial/\partial t + \mathbf{v} \cdot \nabla$, the substantial time derivative.

Next, let us place the fluid between two parallel planes, but now cause one of the planes to oscillate back and forth in the x direction with infinitesimally small amplitude,⁹ so that there is a velocity gradient $\dot{\gamma} = \dot{\gamma}^0 \cos \omega t$. Here $\dot{\gamma}^0$ is the amplitude and ω is the frequency. The shear stress in this system has an

in-phase component and an out-of-phase component:

$$\pi_{yx} = -\eta' \dot{\gamma}^0 \cos \omega t - \eta'' \dot{\gamma}^0 \sin \omega t$$

The quantity η' is related to the dissipation of energy, whereas η'' is related to the storage of elastic energy; both are strong functions of the frequency. Fig-



Models and theories. The chart summarizes molecular models and outlines the development of kinetic theories of polymer liquids. The

sketches show some simple physical pictures that form the basis of theoretical models describing molecular motion in flowing systems. Figure 3

ure 2 shows some sample data for these quantities. Note the similarity of the curves for the viscosity η and the in-phase coefficient η' , and also of the curves for the first normal-stress coefficient ψ_1 and the ratio $2\eta''/\omega$, which involves the out-of-phase coefficient. Many fluids obey rather well the empirical "Cox-Merz rule," which says that the curves of η versus $\dot{\gamma}$ and $(\eta'^2 + \eta''^2)^{1/2}$ versus ω should superpose.

Another twelve to fifteen rheometric experiments are currently under study. These involve stress relaxation, recoil, elongational flows, and so on. Each experiment yields one or more material functions. Polymer fluid dynamicists feel that if a constitutive equation can describe the data of a half-dozen or so rheometric experiments, then it can in principle describe all the phenomena in the ten experiments discussed earlier.

Now we come to the question: Can we develop a molecular theory capable of describing the material functions obtained in rheometric experiments? Anyone who has peeked into a book on the kinetic theory of gases has doubtless been aghast at the incredibly complicated mathematical gyrations required just to calculate the viscosity of a dilute monatomic gas. One might think that the calculation of the various material functions for a liquid made up of macromolecules with thousands of internal degrees of freedom

would be hopeless. However, in the last three decades a small band of dedicated researchers has been trying to scale this Mount Everest of kinetic theory, and with considerable success. After we discuss the question of polymer molecule modeling, we will proceed to the discussion of molecular theory.

Modeling the polymer molecule

There are many kinds of synthetic and biological polymers—long chain-like molecules, chains with side branches, rigid molecules, and so on. To simplify our discussion of modeling^{10,11} here we consider only the first of these: long flexible chains with repeating units. Examples of such molecules are polyethylene $(-\text{CH}_2-)_n$, polystyrene $(-\text{CH}_2-\text{CH}(\text{C}_6\text{H}_5)-)_n$, and polyisoprene (natural rubber) $(-\text{CH}_2-\text{C}(\text{CH}_3)=\text{CH}-\text{CH}_2-)_n$, where n is a very large number, say 10^3 to 10^6 . To study the kinetic theory of polymeric liquids, one has to select some kind of mechanical model that represents the actual polymer molecule. Paul Flory, in his study¹⁰ of the configurations of polymer molecules in systems at equilibrium, actually uses rather detailed models that account for chemical bond lengths, bond angles and rotational isomeric states. However, we cannot permit ourselves the luxury of such realistic molecular modeling in rheolo-

gical studies, because the motion of molecules in flowing systems is so much more complicated than that in equilibrium systems. Therefore, theorists have used a number of simpler models, a few of which are listed in figure 3.

In the Kirkwood-Riseman model¹² the molecular backbone is represented by a series of mass points, or "beads," and each succeeding link is required to lie on a cone with a prescribed angle. Less realistic is the model¹³ used by Hendrik A. Kramers, based on a linear arrangement of freely jointed rigid rods that link together a series of beads. Here the beads do not represent the atoms on the backbone of the molecule, but rather some finite portion of the polymer molecule. Other investigators have chosen to use a freely jointed chain of beads and springs, thereby avoiding the constraints imposed by rigid rods and the necessity of using generalized coordinates. A degenerate case of the bead-spring chain is the elastic dumbbell, a terribly oversimplified model that has nonetheless proven quite useful in exploratory calculations. These models simulate with varying degrees of fidelity the salient mechanical features of the chain: its great length, its stretchability, its orientability and its many degrees of freedom.

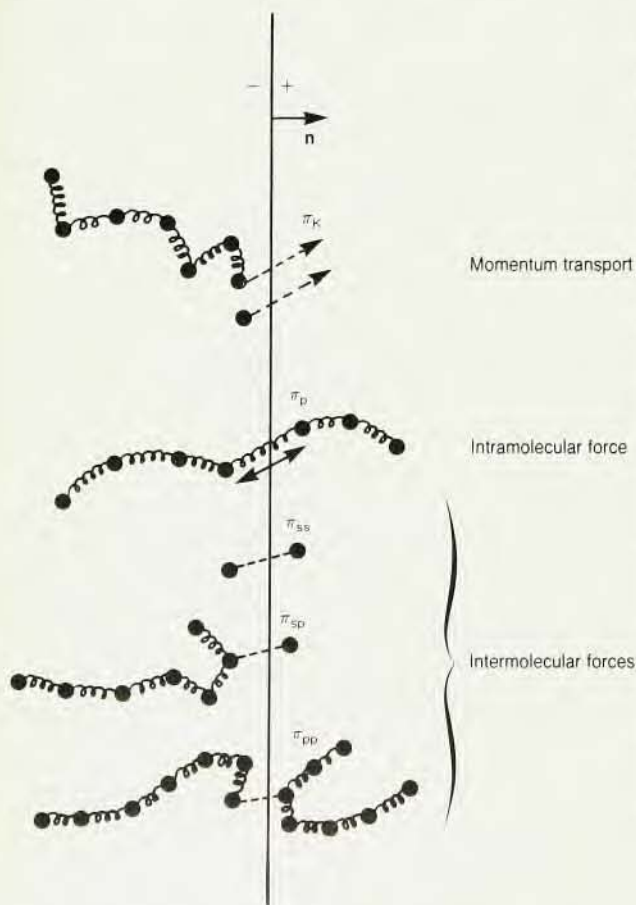
The various models contain a number of constants, such as the number of beads, the spring constants and the length of rods. These are, of course, empirical parameters, and are not unlike the constants in the Lennard-Jones potential used widely in the statistical mechanics of gases. In many instances one can eliminate these parameters in favor of more fundamental molecular constants or parameters derived experimentally from bulk properties.

Molecular theories

There are two main parts in the kinetic theory of the rheological properties of polymers:^{4,6,12,14,15} the development of an expression for the stress tensor, and the derivation of an equation for the configurational distribution function. Although some of the details are lengthy and difficult, the basic physical ideas embodied in the theory are actually rather simple.

The stress tensor π describes the force transmitted across an arbitrary mathematical plane moving with the fluid (the force per unit area from the negative side to the positive side across a plane with unit normal vector \mathbf{n} is just $\mathbf{n} \cdot \pi$). As figure 4 shows, there are five mechanisms contributing to the force:

► the momentum transfer as the solvent or polymer "beads" cross the surface



Molecular mechanisms that contribute to the stresses in a polymeric liquid. The diagram depicts five mechanisms for transmitting a force across a plane that moves with the average velocity of the fluid. Single beads represent solvent molecules; bead-spring chains represent polymer molecules. Symbols for the terms that contribute to the total stress tensor appear in the appropriate places. From top to bottom, the five mechanisms are: momentum transfer as solvent or polymer molecules cross the plane; tension in polymer molecules that straddle the plane; forces between solvent or polymer molecules on opposite sides of the plane.

Figure 4

Constitutive equation for a polymer melt

The expression for the stress tensor π given below was derived recently for polymer molecules modeled as freely-jointed chains, each chain having N beads and $N-1$ links of length a .

$$\pi = p\delta + NnkT \left[\frac{1}{3} \delta - \int_{-\infty}^t \mu(t-t') \mathbf{A} dt' - \epsilon \int_{-\infty}^t \nu(t-t') \mathbf{B} dt' \right]$$

In this constitutive equation, \mathbf{A} and \mathbf{B} are tensors^{3,4} depending on a finite strain tensor $\gamma^{(0)}$.

$$\mathbf{A} = (4\pi)^{-1} \int [1 + \gamma^{(0)} : \mathbf{u}\mathbf{u}]^{-3/2} \mathbf{u}\mathbf{u} d\mathbf{u}$$

$$\mathbf{B} = \frac{1}{2} \lambda \dot{\gamma} : (4\pi)^{-1} \int [1 + \gamma^{(0)} : \mathbf{u}\mathbf{u}]^{-3/2} \mathbf{u}\mathbf{u}\mathbf{u}\mathbf{u} d\mathbf{u}$$

Here $\dot{\gamma}$ is the rate-of-deformation tensor, \mathbf{u} is a unit vector, δ is the unit tensor and n is the number density of the polymer chains. The function $\nu(s)$ is given by

$$\nu(s) = (16/\pi^2 \lambda) \sum_{j \text{ odd}} j^{-2} \exp(-\pi^2 j^2 s / \lambda)$$

and $\mu(s) = -(\lambda/2)(d\nu/ds)$. The time constant λ contains some of the constants of the model:

$$\lambda = N^{3+\beta} \xi a^2 / 2kT$$

Here β is an empirical constant. The final expression contains only four adjustable parameters: N , λ , β and ϵ . For some concentrated solutions and melts of linear, monodisperse polymers, we found β to be about $1/3$, ϵ to be about $3/8$, and λ in the range from 0.1 sec to 1000 sec. Note that in the constitutive equation, one can factor each integrand into the product of a function depending on the fluid response (μ or ν) and a function of the kinematics of the flow field (\mathbf{A} or \mathbf{B}). The constitutive equation can describe the shapes of curves obtained from steady or oscillatory shear experiments, such as those in figure 2. The constitutive equation also gives a relationship between the two normal-stress coefficients: $\psi_2 = -(\frac{2}{7})(1-\epsilon)\psi_1$, and it gives the Cox-Merz rule up to values of $\lambda\dot{\gamma}$ (or $\lambda\omega$) of about 50. The functions $\mu(s)$ and $\nu(s)$ describe the "fading memory" of the fluid. The Doi-Edwards constitutive equation corresponds to $\epsilon=0$ and $\beta=0$.

- the tension in a polymer molecule that straddles the surface
- the force between two solvent molecules on opposite sides of the surface
- the force between a solvent molecule and a polymer molecule
- the force between two polymer molecules.

Hence the total expression for the stress tensor is

$$\pi = \pi_K + \pi_p + \pi_{ss} + \pi_{sp} + \pi_{pp}$$

By means of elementary physical arguments one can write down approximate expressions for each of these contributions. The expression for π_p involves the contribution of intramolecular forces. Here one must average over all possible configurations of the macromolecule in the particular flow system being studied, that is, one has to know the "configurational distribution function" Ψ , which tells the probability of each of the very numerous configurations of the polymer chain. Similarly, to calculate the kinetic contribution π_K , we have to know the velocity distribution of the beads. To get the intermolecular force contributions π_{ss} , π_{sp} and π_{pp} , we need the various pair distribution functions. To date, no one

has obtained these last two distribution functions, so work has proceeded through the use of some assumptions, which we will describe. The configurational distribution function, however, is very important, so we discuss first how it is obtained.

We can write down an equation of continuity for the distribution function $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, t)$, which gives the probability that the polymer molecule finds itself in the configuration $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N$ at time t :

$$\frac{\partial \Psi}{\partial t} = - \sum_{v=1}^N \left(\frac{\partial}{\partial \mathbf{r}_v} \cdot \dot{\mathbf{r}}_v \Psi \right) \quad (1)$$

Here \mathbf{r}_v is the position of the v th bead and $\dot{\mathbf{r}}_v$ is its velocity. This equation simply states that when a polymer molecule leaves one configuration it must turn up in another. This equation by itself is of little interest—what we need is an expression for the bead velocity $\dot{\mathbf{r}}_v$. We obtain this by writing down an equation of motion for each of the N beads of the bead-spring model:

$$m_v \ddot{\mathbf{r}}_v = \mathbf{F}_v^{(h)} + \mathbf{F}_v^{(Br)} + \mathbf{F}_v^{(\phi)} \quad v = 1, 2, \dots, N \quad (2)$$

This says that the product of bead mass and bead acceleration is equal to the

sum of the various forces acting on a bead—the hydrodynamic drag force, the Brownian motion force and the spring force associated with the intramolecular potential. It is usually permissible to omit the acceleration terms on the left side of the equation so that the equation represents just a balance of forces. After one introduces specific expressions for the various forces (including a form of Stokes's law for the hydrodynamic drag, which involves the bead velocity $\dot{\mathbf{r}}_v$), one can solve equation 2 for the bead velocity and substitute the result into equation 1 to obtain a second-order partial differential equation for Ψ .

Traditionally, physicists have used rather elementary physical arguments in their work on the two parts of kinetic theory discussed above—the stress tensor and the configurational distribution function. By and large, the intuitive approaches used by the earlier investigators were correct and led to useful results, but it also left many unresolved questions as to the procedure for averaging certain quantities, the completeness of the expressions, the existence of hidden assumptions, and the internal consistency of the theory. In our own research, we recently redeveloped the kinetic theory of polymeric liquids by taking a more fundamental point of view.^{4,16} Let us examine this systematic approach as an example of current research in polymer flows.

Phase-space molecular theory

We begin by writing down the classical equations of motion for all the "beads" in a polymer solution or melt. The polymer molecule in our model may have any kind of internal constraints, such as rigid rods or fixed bond angles. Next we write the Liouville equation for the phase-space distribution function, the latter giving the probability that each of the beads has a particular position and momentum. From the Liouville equation we obtain a "general equation of change" for any function of the phase-space variables. By choosing specific functions of the phase-space variables, we can get, after considerable manipulation, two main results:

- An expression giving the *stress tensor* of the polymeric fluid as the sum of five integrals. These integrals correspond to the five basic mechanisms listed in figure 4. No previous theoretical studies have given these integrals.
- The *equation of continuity* in the configuration space (a generalization of equation 1) and an *equation of motion* for each internal degree of freedom (a generalization of equation 2). In the latter, we obtain detailed expressions for the hydrodynamic drag force in terms of pair distribution functions,

and we obtain expressions for the force due to Brownian motion in terms of the velocity distribution function; we believe that these expressions are new.

Up to this point, the development is purely formal, and we have made no assumptions other than that the molecules are modeled by bead-rod-spring assemblies. To proceed, we need expressions for the hydrodynamic drag and Brownian motion forces, but these involve distribution functions that we do not know and would prefer not to have to derive. Hence, at this point we introduce empiricisms.

For *dilute solutions*, in which the parts of the polymer molecule can move freely through the surrounding sea of solvent molecules as indicated in figure 5a, it has been traditional to approximate the hydrodynamic drag by Stokes's law:

$$\mathbf{F}_v^{(h)} = -\zeta(\dot{\mathbf{r}}_v - \mathbf{v}_v)$$

That is, the drag force on the v th bead is just proportional to the difference between the velocity of bead v and the unperturbed solvent velocity at bead v . The coefficient of proportionality ζ is taken to be a scalar, usually called the "friction coefficient." For the Brownian force, our formula contains the velocity distribution function. In all theories of dilute solutions it is tacitly assumed that the velocity distribution is Maxwellian about the solvent velocity at the center of mass of the polymer molecule. With this assumption, our general formula gives for the force due to Brownian motion the well-known expression

$$\mathbf{F}_v^{(Br)} = -kT \frac{\partial}{\partial \mathbf{r}_v} \ln \Psi$$

For *concentrated polymer solutions* or polymer melts, the physical situation is quite different, as illustrated in figure 5b. In the concentrated systems one expects much more drag in the direction perpendicular to the chain backbone than in the direction of the chain backbone. Such anisotropy in the drag requires modification of Stokes's law,^{17,18} which contains a parameter ϵ that tells how anisotropic the drag force is. As far as Brownian motion is concerned, because of the constraints imposed by the surrounding polymer molecules, the main fluctuations will be along the backbone direction. This snakelike wriggling back and forth, called "reptation,"¹⁹ is consistent with an observed large deviation from the isotropic Maxwellian velocity distribution.

It should be evident that from a single starting point—the phase-space molecular theory—we can set up theories for dilute solutions and for concentrated solutions and melts. The only difference between the theories of di-

lute and concentrated solutions is that in the latter we must take the hydrodynamic and Brownian forces to be anisotropic. As figure 3 indicates, we can obtain all of the older results for dilute solutions as special cases and also obtain new results for concentrated systems.

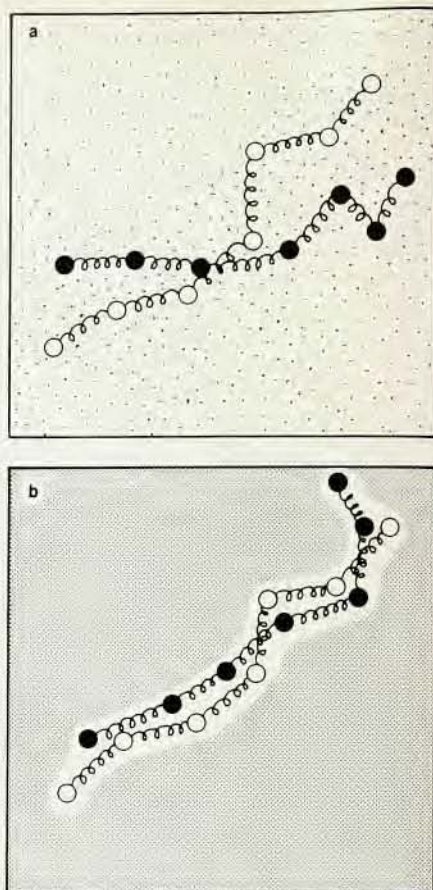
The box on page 41, which contains the constitutive equation¹⁸ that our kinetic theory yields for a polymer melt, gives some idea as to the complexity of the final result.

Network theories

For concentrated solutions and melts there is another group of theories, whose members do not fit into our general scheme. These are the "network theories," which are inspired by the kinetic theory of rubber elasticity.^{5,6,20} Whereas in rubber a permanent network is formed by the chemical crosslinking of polymer chains, in a polymeric liquid there is a temporary network formed by the physical junctions, or "entanglements," of the chains. In most of these theories one has to describe empirically the rate at which junctions form and break, and these empiricisms have led to a wide variety of constitutive equations.

Another theory for concentrated polymer systems has been developed²¹ by Masao Doi and Sam Edwards. They describe their theory as using a "slip-link network model" that allows for slippage of bead-spring chains at the points of entanglement. They account for reptation by applying the theory of fluctuations to a chain of freely-jointed rods trapped in a "tube."¹⁹ Doi and Edwards use a stress tensor formula from the theory of rubber elasticity, and make no mention of Stokes's law. Although their model and theory are quite different from ours, their constitutive equation is similar to the one shown in the box on page 41.

More challenges. Now that the search for constitutive equations based on molecular theory is well under way, the most important challenge lying ahead is the solution of flow problems.²² This involves solving the equations of continuity and motion (see the box on page 39) along with a constitutive equation (such as that shown in the box on page 41). Because of the complexity of this set of equations, the solution will require very large computing facilities and probably some new numerical methods. Those active in this field have all reported great difficulty in solving problems when the "Deborah number" is greater than 1 or 2. This parameter, named after the prophet Deborah (as Denis Evans and his coauthors explain in their article on page 26), is the ratio of some characteristic time for the fluid—such as λ in the box on page 41—to some characteristic



Changing configuration of a polymer chain. The solid-circle chains represent new configurations of the open-circle chains after a brief time interval. **a:** A dilute solution in which polymer chains are free to move in any direction through a sea of solvent molecules. **b:** A concentrated solution or melt, in which polymer chains cannot move "sideways" very much because of all the other polymer molecules (shaded region). Figure 5

time for the flow—usually the time for a typical fluid particle to traverse some obstacle. For large Deborah numbers the fluid particles have difficulty in adapting to imposed external changes; this difficulty in adapting results in "elastic effects."

Although we now can describe the shapes of many material functions and understand qualitatively many of the ten experiments discussed at the beginning of this article, most of the experiments are not yet fully described by solutions of the equations of fluid dynamics. There is still much to be done before we can solve the complex problems of the polymer processing industry, understand the role of polymer additives in lubricants, and unravel the mystery of the locomotion of dolphins and other aquatic creatures that apparently exude polymeric liquids to reduce their hydrodynamic drag while swimming.

* * *

We wish to dedicate this article to professor Hermann Janeschitz-Kriegl of Johannes

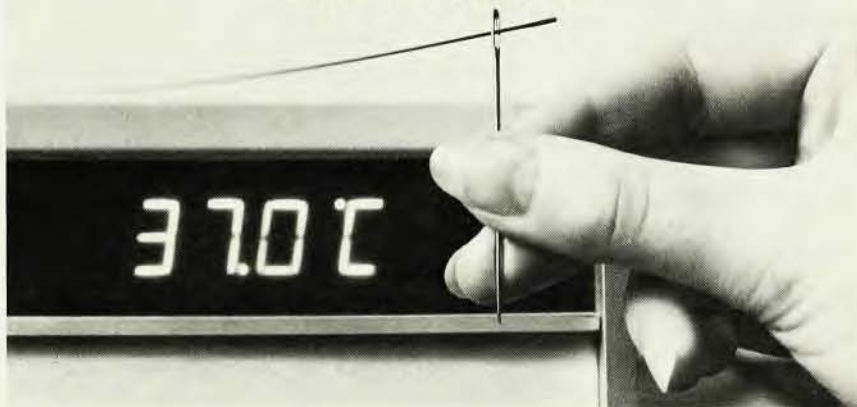
Kepler University, Linz, Austria, on the occasion of his 60th birthday. We acknowledge the National Science Foundation for its financial support of our research on kinetic theory.

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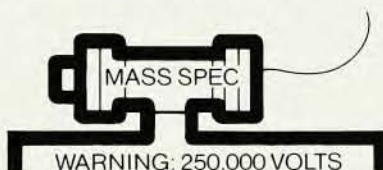
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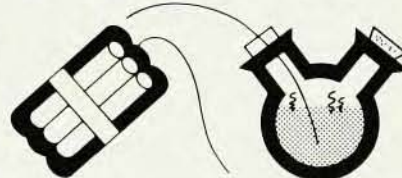
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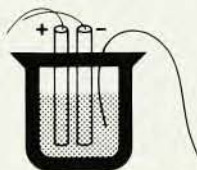
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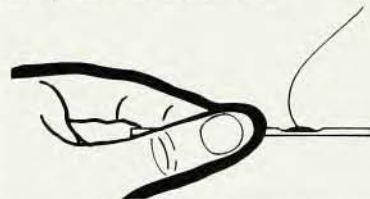
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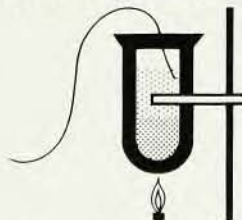
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