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**A GENERAL RELAXATION THEORY
OF SIMPLE LIQUIDS**

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16. Abstract A relatively simple relaxation theory to account for the behavior of liquids under dynamic conditions has been proposed. Though rigorous kinetic theory has not been employed, the theory is, nevertheless, based on a molecular viewpoint. The general dynamical equations obtained are similar in form to the phenomenological relaxation equations used in theories of viscoelasticity; however, they differ in that all the coefficients of the present equations are expressed in terms of thermodynamic and molecular quantities. The theory is based on the concept that flow in a liquid distorts both the radial and the velocity distribution functions, and that relaxation equations describing the return of these functions to their isotropic distributions, characterizing a stationary liquid, can be written. The theory has been applied to the problems of steady and oscillatory shear flows and to the propagation of longitudinal waves. In all cases classical results are predicted for low strain rates, and an expression for the viscosity of a liquid, similar to the Macedo-Litovitz equation, is obtained. At high strain rates viscoelastic behavior is predicted, and for steady shear both normal stresses and a reduction in the apparent viscosity are obtained. The reduction in apparent viscosity is attributed to the enhanced jump probability of a molecule in a strained liquid. For high frequency oscillatory flows the behavior of a liquid in the measurable frequency range is found to be characterized by a single relaxation time. To account for the observed width of the relaxation region and the measured excess absorption in monatomic liquids it will probably be necessary to add the effects of molecular clusters to the theory.			
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NOMENCLATURE

(Other symbols defined in text as needed)

a	Constant in potential energy term
A	Coefficient for the molecular strain caused by the direct strain rate
A_0	Pre-exponential term in Macedo-Litovitz equation
b	Half width of the contact region
B	Coefficient for the molecular strain caused by the normal strain rate
c	Sound speed
c_0	Low frequency sound speed
c_i	Component of the random speed
c_v	Specific heat at constant volume
\underline{c}	Cauchy deformation tensor
d	Hard sphere diameter
d_{ij}	Component of the strain rate tensor
D	Shear rate
e_{ij}	Component of the strain tensor
E	Internal energy
E_i	Energy of each system of an ensemble
E_v	Energy barrier for molecular jump
E_α	Energy barrier for molecular jump in the α direction

f_i	Component of a body force
f_c	Collision frequency
F	Helmholtz free energy
g_{ij}	Component of the metric tensor
G^*	$= G' + iG''$, complex shear modulus
G_∞	High frequency shear modulus
h	Planck's constant
k	Boltzmann's constant
\hat{k}	Thermal conductivity
l	Molecular spacing
l	Molecular spacing in an arbitrary reference state
l_α	Molecular spacing in the α direction
m	Mass of a molecule
M^*	$= M' + iM''$, complex longitudinal modulus
n	Index for variation of potential energy with volume
\bar{n}	Particle density
N	Number of molecules
p_j	Probability for a molecular jump
P_{ij}	Pressure tensor
P	Thermodynamic pressure
P_k	Kinetic contribution to the thermodynamic pressure
P_m	Maximum pressure in the Hertzian region
P_p	Potential contribution to the thermodynamic pressure

Q	Configurational partition function
\underline{r}	Position vector
R	Gas constant
R_s	Real part of the shear impedance
$s_{o\alpha}$	Unstrained length of line in α direction
s_α	Length of line in α direction
S_{ij}	Component of the stress tensor
t	Time
T	Temperature
T_{ij}	Component of the translational temperature tensor
T_o	Mean temperature
u_i	Component of velocity
v	Volume per molecule
v_o	Volume required for a molecular jump
v_f	Free volume
v_{fc}	Free volume for the center of a molecule
w_i	Component of the random velocity
W	Average molecular speed
\underline{x}	Coordinates in deformed material
\underline{X}	Coordinates in undeformed material
X_s	Imaginary component, or reactance, of the shear impedance
Z_s	Complex shear impedance
Z	Canonical partition function

α	Absorption coefficient
γ	Ratio of specific heats
γ_α	Elongation in α direction
δ_{ij}	Kronecker delta
ϵ_{ij}	Molecular strain tensor
ϵ	Determinant of $\epsilon_j^i + \delta_j^i$
θ_{ij}	Component of the deviatoric translational temperature tensor
κ	Molecular strain relaxation time
λ	Gap size between molecules
μ	Viscosity coefficient
$\bar{\mu}_{\text{mean}}$	Mean viscosity coefficient
v_{ij}	Component of the molecular gap tensor
ξ	Displacement
Π_{ij}	Potential stress tensor
ρ	Density
σ_{ij}	Deviatoric stress tensor
τ	Translational relaxation time
τ	Collision time
T_{ij}	Component of the rate of change of strain energy
ϕ	Potential energy in cell
ϕ_L	Total lattice potential energy
Ψ	Dimensionless slope of the variation of the energy barrier with molecular spacing

ω Frequency

ω_{ij} Component of vorticity

Subscripts (unless otherwise specified among the main symbols)

e Equilibrium

m Melting point value

o Mean value

α A principal direction. There is no summation over this subscript

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CHAPTER I

INTRODUCTION

The liquid state is still the least understood of the three states of matter. The behavior of gases at low pressures can be well explained in terms of kinetic theory (Ref. 1). This is possible because the molecules of a dilute gas are so widely separated that they are unaffected by molecular forces, except for very brief encounters or "collisions".

Solids are affected strongly by intermolecular forces. However, because they possess an ordered structure with the only motion of the molecules occurring as thermal vibrations, the mathematics required to analyze them is still tractable.

Liquids, due to their close spacing, are characterized by strong interactions between molecules, yet they do not possess long range order, hence neither of the basic simplifications applicable to solids or gases can be used over the entire liquid range.

Above the critical pressure, it becomes impossible to distinguish between the liquid and gaseous states.

This has led to the approach of viewing liquids as dense gases, and much formal work on statistical mechanics and

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kinetic theory has been done from this viewpoint.
(Refs. 1, 2, 3).

Near the melting point, the molecules of a liquid exhibit close packing similar to the solid case. The difference between the two states concerns the molecular arrangement. In a crystalline solid the molecules vibrate about their centers, which are located in a regular geometrical pattern or space lattice. Therefore solids are said to possess long-range order. In a liquid, there is still a tendency for the molecules to exhibit ordering, however, this order does not persist beyond a few molecular diameters. This short range order has led to attempts to approach liquid theories from the solid side. Notable among these are the cell (Ref. 3) and hole (Ref. 4) theories.

The dynamical behavior of fluids has been described with a good degree of success, for over a century, by the Navier-Stokes equations. However, when flow times become comparable to the times required for molecular processes, the equations are hopelessly inadequate. This problem was first encountered in measurements of absorption and dispersion of sound waves in gases. Good agreement between experiment and theory was finally provided by relaxation theory (Ref. 5) which was first

proposed by Herzfeld and Rice (Ref. 6).

The basic premise of relaxation theory is that a finite time is required for excess energy in any one mode to redistribute itself among the other modes. Thus relaxation theory splits up the overall energy equation into separate equations for each mode and couples these equations by relaxation terms. Applying this concept to sound waves propagating through a gas, we see that energy is first imparted to the gas molecules as translational kinetic energy. After a number of collisions, this excess energy in the translational mode is redistributed among the rotational and vibrational modes. This process, known as thermal relaxation, leads to absorption in excess of that predicted by classical theory which considers only viscosity and conduction.

Relaxation like behavior has also been observed in liquids, and in many instances the same relaxation mechanism as was found in gases has been found to apply (Refs. 7, 8). These liquids are sometimes known as Kneser liquids. A further type of thermal relaxation in liquids is caused by the perturbation of molecular equilibrium between different species, brought about by temperature variations.

In addition many liquids, primarily the associated liquids, display a relaxation caused by volume changes. The prime example of this is water, which shows excess absorption at 4°C. This absorption cannot be thermal in origin since at this temperature $c_p = c_v$, and therefore adiabatic compression and rarefaction waves are also isothermal. For this reason the excess absorption in water has been attributed to the presence of both loose and close packed structural forms. The equilibrium amount of each structure is perturbed by changes in volume, and thus this process is referred to as a structural relaxation (Refs. 8, 9).

Relaxation equations for liquids have also been written from purely phenomenological viewpoints to explain the viscoelastic behavior of substances. These are rheological equations of state which have been used to describe non-Newtonian flow, normal stress effects, and the propagation of ultrasonic shear waves. These theories are based on the suggestion by Maxwell (Ref. 10) that the behavior of a fluid can be described in terms of a relaxing solid. Oldroyd (Refs. 11, 12) has written general rules for formulating rheological equations of state, and has found that the simplest equations which are linear in stresses and include terms of second degree

in stresses and velocity gradients taken together, possess eight arbitrary constants. Though equations obtained from strictly phenomenological grounds can describe many observed phenomena, their main weakness is that there is no connection between the molecular properties of the fluid and the arbitrary constants required to describe the continuum behavior. This is in contrast to the relaxation theory of gases where a knowledge of molecular properties is used to obtain the relaxation equations.

It is clear that any theory which hopes to describe the dynamical behavior of liquids must in some form include relaxation effects.

The purpose of this research is to relate the relaxational behavior of liquids to their molecular properties. The approach adopted is to evaluate the thermodynamic properties of the system by statistical mechanics, and to account for dissipative processes by relaxation from non equilibrium states towards equilibrium. This approach is valid as long as the deviation of the radial distribution function from its equilibrium value is small (Ref. 13), and this will be assumed to be the case in the following analysis.

CHAPTER II

THEORETICAL ANALYSIS

In the analysis that follows, two ideas are essential and will receive further attention. One is that a liquid can, to a certain extent, support a recoverable shear strain, and thus a "molecular strain" tensor can and will be defined. This is possible because a finite time is required for a liquid to come to equilibrium following some disturbance, even though this time may be extremely short.

The other important concept is that the random velocity, and thus the translational kinetic energy, of molecules can be a function of direction (Ref. 14). With a slight modification of the definition of temperature, this leads to the possibility of defining a "translational temperature tensor".

Both of these concepts will be used to write the stress tensor as a function of temperature and molecular spacing. Further, since both the strain and temperature will be related to the strain rate through relaxation equations, the stress will show relaxation effects, and be a function of the strain rate.

2.1 Concept of Strain in a Liquid, and the Molecular Strain Tensor

A liquid, which is in static equilibrium with its surroundings has a uniform distribution of molecules throughout its volume. Thus we say that the radial distribution function, which specifies the number of molecules to be found at any distance from an arbitrary reference molecule, is spherically symmetric. If, as the result of some disturbance, the distribution function deviates from spherical symmetry, it will take a finite time for molecular collisions to bring the distribution back to its equilibrium value. Another way of viewing this is to note that as a result of some disturbance the average spacing between molecules can vary with direction.

It is possible to draw some analogies between a liquid with a distorted radial distribution function and a strained solid. In discussing solids, Love (Ref. 15) states that "the state of strain is entirely determined when we know the lengths in strained and unstrained states of corresponding lines". Thus for a solid, in principal axes of a cartesian system, a strain tensor can be defined in terms of extensions of material line

elements, or fibers, along the principal directions. If $s_{o\alpha}$ is the initial unstrained length of a line in the α direction, and s_α is the strained length, the elongation of the fibre or line is defined as

$$\gamma_\alpha = \frac{s_\alpha}{s_{o\alpha}} \quad (2.1)$$

There is no unique measure of strain (Ref. 16), and in fact any function of γ_α can be used provided that it vanishes for $\gamma_\alpha = 1$, reduces to the infinitesimal strain tensor for $|\gamma_\alpha - 1| \ll 1$, and is dimensionless. As a result, many measures of strain appear in the literature. Some of the more common ones are (Ref. 16):

Cauchy measure

$$e_{\alpha\alpha}^c = \gamma_\alpha - 1$$

Hencky measure

$$e_{\alpha\alpha}^H = \ln \gamma_\alpha$$

Green measure

$$e_{\alpha\alpha}^G = \frac{\gamma_\alpha^2 - 1}{2},$$

plus many others associated with the names of Swainger, Alamansi etc. ...

For a liquid, if the length of the material line, or fiber, is replaced by the average distance between molecules in a particular direction, it is possible to describe the distortion of the radial distribution function in terms of the changes in molecular spacing along principal axes. We can then define a "molecular strain" tensor in principal axes, α , as

$$\epsilon_{\alpha\alpha} = \frac{\ell_{\alpha}}{\ell_e} - 1 \quad (2.2)$$

where ℓ_{α} is the average distance between molecules in the α direction and ℓ_e is the average molecular spacing at the local density. Since this tensor is expressed in principal axes of the deformed material, it can be related to the Cauchy deformation tensor (Ref. 17), \underline{c} , by

$$\underline{\epsilon} + \underline{1} = \underline{c}^{-\frac{1}{2}}$$

where $\underline{\epsilon}$ is the molecular strain tensor, and $\underline{1}$ is the unit tensor. The tensor $\underline{c}^{-\frac{1}{2}}$ is convenient because the principal values are exactly the principal elongations, however, in axes other than principal axes, the terms of the tensor are considerably more difficult to evaluate in terms of the deformation gradients. In fact, the components are in general complicated infinite series in

displacement gradients (Ref. 17). The change in volume during a deformation is expressed by

$$dV = \det \left(\bar{c} \right)^{-\frac{1}{2}} dV_0 .$$

Since the molecular strain refers only to distortion, and not to dilatation the condition

$$\det \left(\delta_j^i + \epsilon_j^i \right) = 1 \quad (2.3)$$

must be satisfied.

2.2 The Stress Tensor

From the kinetic theory of dilute gases, the pressure tensor can be expressed as

$$p_{ij} = \bar{n} \langle m w_i w_j \rangle$$

where the subscripts refer to the axes of a cartesian coordinate system, \bar{n} is the number density, m is the mass of the molecule, and w is the random, or peculiar, velocity. The usual kinetic theory definition of temperature is just

$$T = \frac{m}{3k} \langle w_i w_i \rangle \quad (2.4)$$

where k is the Boltzmann constant.

However, this definition can be extended such that a translational temperature tensor can be defined as

$$T_{ij} \equiv \frac{m}{k} \langle w_i w_j \rangle. \quad (2.5)$$

This leads to an equation of state for an ideal gas (Ref. 14)

$$p_{ij} = \rho R T_{ij} \quad (2.6)$$

where ρ is the density and R is the gas constant. The traditional temperature then is just one third of the first invariant of the temperature tensor.

Similar equations of state can be written for a liquid, incorporating the effects of the attractive forces and the finite size of the molecules.

Since directionally dependent molecular spacings and temperatures must, if not acted upon by external forces, eventually equalize, we see that we are in fact dealing with a non-equilibrium situation. The usual approach in studying non-equilibrium statistical mechanics is to investigate the change of the distribution function towards canonical form as a solution of the time dependent Liouville equation. The main problem, so far, has been to calculate the distortion of the equilibrium radial distribution function for specific non-

uniformities. Due to the complexity of methods based on the Liouville equation, there is not yet available a complete theory of simple non-uniform liquids that leads to results which can unambiguously be compared with experiment. With the hope of achieving mathematical tractability this approach is abandoned in favor of a simpler, more intuitive procedure. To describe the directionally dependent temperatures, Morgan and Kern (Ref. 14) hypothesized that the non-equilibrium distribution function could be specified by a quasi-Maxwellian distribution which has the property that it is an equilibrium distribution in each direction taken separately. In this way it is possible to talk about thermodynamic quantities as functions of direction. From this viewpoint, the irreversibility of the flow arises from the coupling of the different directional modes by relaxation terms, and allowing the system to return towards the isotropic equilibrium distribution.

The results obtained by Morgan and Kern, for the directional dependence of temperature, are used here. Further, we postulate a quasi-equilibrium molecular spacing in the principal axes of deformation, an assumption which allows us to use the powerful techniques of equilibrium statistical mechanics. There are two

distinct but equivalent procedures which may be applied. One calculates the thermodynamic properties through the partition function, and the other through the radial distribution function. The former approach will be used here.

There are a number of ensembles which are used for thermodynamic calculations, depending on what the independent variables are, and the types of contact the systems make with the surroundings. It can be shown (Ref. 18), however, that away from critical regions, where fluctuations in thermodynamic properties are small, the ensemble to be used can be chosen for mathematical convenience. Generally, the simplest and therefore most commonly used one is the canonical ensemble.

The canonical partition function is

$$Z_N(V,T) = \sum_i \exp - \left(\frac{E_i}{kT} \right) \quad (2.7)$$

where N is the number of molecules, V is the volume, and E_i is the energy of each system of the ensemble. The summation is taken over all systems of the ensemble.

Once the partition function is known, it is possible to obtain all the thermodynamic properties from it. In particular, the Helmholtz free energy is given by

$$F = - kT \ln Z . \quad (2.8)$$

From this, the thermodynamic pressure can be expressed as

$$P = - \left(\frac{\partial F}{\partial V} \right)_T \quad (2.9)$$

The term pressure will only be used for the case of an unstrained liquid. When the liquid is strained, since the molecular strain is recoverable, elasticity theory can be used. Truesdell (Ref. 19) has pointed out that there really is no satisfactory thermodynamical treatment of the foundation of elasticity theory, therefore it is necessary to postulate that a stress tensor obtained from an "elastic potential" or "strain energy" is in fact equivalent to the stress tensor obtained from the principles of mechanics. When this is done, the elastic potential for an isothermal deformation is given by the Helmholtz free energy (Ref. 19), and the stress tensor, S_j^i , can be expressed as

$$S_j^i = \frac{1}{V} x_{,K}^i \frac{\partial F}{\partial x_{,K}^j} \quad (2.10)$$

Here $x_{,K}^i$ is the displacement or deformation gradient defined by

$$x_{,K}^i \equiv \frac{\partial x^i}{\partial X^K}$$

where \underline{X} and \underline{x} are coordinates in the undeformed and

deformed material respectively. In principal axes we can relate the molecular spacing to the displacement gradient with the expression

$$x_{,\alpha}^{\alpha} = \frac{\partial x^{\alpha}}{\partial X^{\alpha}} = \frac{\ell^{\alpha}}{\ell_0^{\alpha}}$$

where ℓ_0 is the equilibrium spacing in some arbitrary reference state. Thus it is possible to relate the stress tensor, through the Helmholtz free energy and the partition function, to the molecular properties of the liquid.

2.3 The Momentum Equation

The momentum equation is used in its usual form

$$\rho \frac{Du^i}{Dt} = S^{ij}_{,j} + \rho f^i \quad (2.11)$$

where u^i is the velocity component, and f^i is the component of any body force in the i direction. The comma refers to covariant differentiation, and the material or substantial derivative is defined as

$$\frac{Da^{i..}}{Dt} = \frac{\partial a^{i..}}{\partial t} + u^k a^{i..}_{..j.,k} \quad (2.12)$$

2.4 The Molecular Strain Relaxation Equations

Equations which express relationships between the stress tensor and the kinematic variables, such as velocity and acceleration, at any point of the body are called rheological equations of state. Since the stress tensor can be expressed in terms of the molecular strain tensor and the temperature tensor, the relationships connecting these tensors to the strain rate tensor can properly be called rheological equations of state. These equations describe the properties of an arbitrary material element moving as part of a continuum and as such must be independent of the frame of reference.

An arbitrary fluid element in motion is continuously translating, rotating and deforming, however, the stress in the element should only be affected by the strain. If this were not the case, the stress distribution would be a function of the rigid body motion even if inertia and body forces were neglected. To avoid the effects of rigid body motion, the physical behavior should be expressed in a coordinate system which is rotating and translating with the element. The only motion which would be seen in this system is a pure deformation, and thus strain and relaxation effects could be more easily

expressed. It is not very convenient to solve problems in this system, however, thus the results should be transformed into standard Eulerian coordinates. To summarize, the procedure to follow is to state a physical law, or hypothesis, in a coordinate system following a fluid element, and then to transform this to a fixed coordinate system for solving problems.

This transformation is easily accomplished by replacing the time derivatives appearing in the moving system by the Jaumann derivative defined as (Refs. 12, 20)

$$\frac{Da^{..j.}}{Dt} \cdot i.. \equiv \frac{\partial a^{..j.}}{\partial t} \cdot i.. + u^k a^{..j.} \cdot i..,k - \sum \omega_i^m a^{..j.} \cdot m.. - \sum' \omega_m^j a^{..m.} \cdot i.. \quad (2.13)$$

where \sum denotes that the summation over m must be performed for each covariant index and \sum' denotes the same for each contravariant index. The vorticity is defined in the usual manner as

$$\omega_{ij} \equiv \frac{1}{2} (u_{i,j} - u_{j,i}) \quad (2.14)$$

The Jaumann derivative can also be written in terms of the more familiar material derivative. It is

$$\frac{Da^{..j.}}{Dt} \cdot i.. = \frac{Da^{..j.}}{Dt} \cdot i.. - \sum \omega_i^m a^{..j.} \cdot m.. - \sum' \omega_m^j a^{..m.} \cdot i.. \quad (2.15)$$

where the extra terms account for the rotation of the fluid element. It should be noted that for a scalar quantity the last two terms of equation (2.15) vanish, and the Jaumann derivative reduces to the common material derivative.

The strain of a body can be described by the relative motion of two points when the rigid body motions have been removed. This motion can be considered to consist of three strains along the principal axes of the strain-rate tensor. Thus it can be shown (Ref. 21) that if δs is the distance between the points, its relationship with the strain-rate tensor is just

$$\frac{1}{\delta s} \frac{D}{Dt} (\delta s) = d_{\alpha\alpha} \quad (\text{no summation}) \quad (2.16)$$

where $d_{\alpha\alpha}$ is the $\alpha\alpha$ component of the strain-rate tensor defined as

$$d_{ij} = \frac{1}{2} (u_{i,j} + u_{j,i}) \quad (2.17)$$

This equation, as it stands, shows that a medium with a constant strain rate imposed on it can deform, or strain, indefinitely. However, the molecular strain, except for the case of pure dilatation can not. This is because the molecular strain depends only upon the mean configuration of molecules about a given reference molecule, irrespec-

tive of the identity of the surrounding molecules. Thus when two molecules are separating from each other because of a strain-rate, and another molecule moves between them, the strain is effectively relieved since the new neighbor determines the radial distribution. Upon cessation of the strain-rate, the radial distribution function will after a finite time revert back to its spherical symmetry, and thus the molecular strain will relax to zero.

If in equation (2.16) the length δs_α is replaced by the average distance between molecules in the α direction, l_α , extra terms must be added to account for the relaxation behavior. We shall postulate that the relaxation can be expressed by terms which are linear in the deviation from equilibrium. We further make the assumption that the molecular spacing in one direction can be a function not only of the strain rates in the same direction, but also of those normal to it. Then, in a cartesian system, in principal axes of the strain, we can write

$$\frac{1}{l_\alpha} \frac{Dl_\alpha}{Dt} + \frac{1}{\kappa} \left(\frac{l_\alpha - l_x}{l_o} + \frac{l_\alpha - l_y}{l_o} + \frac{l_\alpha - l_z}{l_o} \right) =$$

$$= (A-B)d_{\alpha\alpha} + B(d_{xx} + d_{yy} + d_{zz}) \quad (2.18)$$

where κ is the relaxation time for the equilibration of molecular strain and A and B are coefficients for the effects on molecular spacing caused by direct and normal strain rates respectively. One would expect that for simple liquids cross strain effects should be small, thus A should be much larger than B. We see that when $\dot{\ell}_x = \dot{\ell}_y = \dot{\ell}_z$, the relaxation term is zero. However, when there is a difference in spacing in different directions, relaxation will occur to decrease this inequality. In terms of the molecular strain tensor, equation (2.18) can be expressed as

$$\zeta_{\alpha}^{\alpha} \frac{D\epsilon^{\alpha\alpha}}{Dt} + \frac{3\epsilon^{\alpha\alpha} - \epsilon_k^k}{\kappa} = (A-B)d^{\alpha\alpha} + Bd_k^k + \frac{1}{3\rho} \frac{D\rho}{Dt} \quad (2.19)$$

where ζ_j^i is the inverse of $(\epsilon_j^i + \delta_j^i)$. It is evaluated from the expression

$$\zeta_j^i = \frac{E_j^i}{\epsilon} \quad (2.20)$$

where E_j^i is the cofactor of the element $\epsilon_i^j + \delta_i^j$ in the determinant $(\epsilon_i^j + \delta_i^j) \equiv \epsilon$. In an arbitrary coordinate system equation (2.19) becomes

$$\frac{1}{2} \left\{ \zeta_k^i \frac{D\epsilon^{kj}}{Dt} + \zeta_k^j \frac{D\epsilon^{ki}}{Dt} \right\} + \frac{3\epsilon^{ij} - g^{ij} \epsilon_k^k}{\kappa} - \frac{g^{ij}}{3\rho} \frac{D\rho}{Dt} = (A-B)d^{ij} + Bg^{ij} d_k^k, \quad (2.21)$$

and if we lower j , set $i = j$ and contract we get

$$\frac{1}{\varepsilon} \frac{D\varepsilon}{Dt} - \frac{1}{\rho} \frac{D\rho}{Dt} = (A + 2B) d_k^k \quad (2.22)$$

But from equation (2.3) we have $\varepsilon = 1$, therefore equation (2.22) becomes

$$\frac{1}{\rho} \frac{D\rho}{Dt} + (A + 2B) d_k^k = 0, \quad (2.23)$$

and for this to satisfy continuity we must impose the condition

$$A + 2B = 1. \quad (2.24)$$

Since we expect that $A \gg B$, A should be almost unity and B should be close to zero.

2.5 The Energy Relaxation Equations

If in a stationary gas the random translational kinetic energies of the molecules are unequal in different directions, molecular collisions would eventually redistribute the energy until the inequality vanished. Differences in the temperatures would thus relax to zero.

Morgan and Kern (Ref. 14) have shown from a kinetic theory analysis that in principal axes of the strain rate, separate energy relaxation equations can be written, for a gas, in each of the principal directions. In a

cartesian coordinate system where α represents any principal direction, their expression with their simplified conduction terms is

$$\frac{\rho c_v}{3} \left\{ \frac{DT_{\alpha\alpha}}{Dt} + \frac{(T_{\alpha\alpha} - T_{xx}) + (T_{\alpha\alpha} - T_{yy}) + (T_{\alpha\alpha} - T_{zz})}{\tau} \right\} =$$

$$= S_{\alpha\alpha} u_{\alpha,\alpha} + \frac{1}{3} (\hat{k} T_{\alpha\alpha,i})_{,i} \quad (2.25)$$

where τ is the relaxation time for energy exchange between translational modes, c_v is the specific heat at constant volume, and k is the thermal conductivity. It should be noted that if the three equations in the three principal directions are added, the usual energy equation for an ideal gas is recovered. The form of the energy equation for this case is contingent on the fact that the internal energy for an ideal gas is a function of temperature alone. If, as is the case for a liquid, the internal energy depends also upon the density and the strain, the form of the energy equation is altered by the addition of several new terms.

The usual form of the energy equation is

$$\rho \frac{D\hat{E}}{Dt} = + (\hat{k} T_{,i})_{,i} + S^{ij} u_{j,i} \quad (2.26)$$

where \hat{E} is the internal energy per unit mass.

For $\hat{E} = \hat{E}(\rho, T, \epsilon_{ij})$, the left-hand side of equation (2.26) can be expanded as

$$\frac{D\hat{E}}{Dt} = \left(\frac{\partial \hat{E}}{\partial \rho} \right)_{T, \epsilon_{ij}} \frac{D\rho}{Dt} + \left(\frac{\partial \hat{E}}{\partial T} \right)_{\rho, \epsilon_{ij}} \frac{DT}{Dt} + \left(\frac{\partial \hat{E}}{\partial \epsilon_{ij}} \right)_{\rho, T} \frac{D\epsilon_{ij}}{Dt}. \quad (2.27)$$

If we make the assumption that for small strains

$$\left(\frac{\partial \hat{E}}{\partial T} \right)_{\rho, \epsilon_{ij}} \approx \left(\frac{\partial \hat{E}}{\partial T} \right)_{\rho, \epsilon_{ij}=0} = c_v \quad (2.28)$$

and

$$\left(\frac{\partial \hat{E}}{\partial \rho} \right)_{T, \epsilon_{ij}} \approx \left(\frac{\partial \hat{E}}{\partial \rho} \right)_{T, \epsilon_{ij}=0} = \frac{1}{\rho^2} \left[P - T \left(\frac{\partial P}{\partial T} \right)_{\rho} \right], \quad (2.29)$$

and if we define Π_j^i as

$$\Pi_j^i \equiv \rho (\delta_j^k + \epsilon_j^k) \left(\frac{\partial \hat{E}}{\partial \epsilon_i^k} \right)_{\rho, T}, \quad (2.30)$$

then, if we also make use of the continuity equation the left-hand side of equation (2.26) can be rewritten as

$$\rho \frac{D\hat{E}}{Dt} = \rho c_v \frac{DT}{Dt} + \left[P - T \left(\frac{\partial P}{\partial T} \right)_{\rho} \right] d_k^k + \Pi^{ik} \zeta_k^l \frac{D\epsilon_{li}}{Dt} \quad (2.31)$$

Equation (2.30) is seen to define a stress tensor whose elastic potential is just the internal energy.

If we further define the tensor σ^{ij} by

$$s^{ij} = -Pg^{ij} + \sigma^{ij} \quad (2.32)$$

where P is the thermodynamic pressure for the unstrained material at the local mean internal energy and density, the energy equation becomes

$$T_i^i + \rho c_v \frac{DT}{Dt} = -T \left(\frac{\partial P}{\partial T} \right)_\rho d_k^k + (\hat{k} g^{\ell m} T_{,\ell})_{,m} + \sigma^{ij} d_{ji} \quad (2.33)$$

where \hat{k} is the thermal conductivity and

$$T^{ij} = \frac{\rho}{2} \left[\left(\frac{\partial \hat{E}}{\partial \epsilon_{ik}} \right)_{\rho, T} \frac{D\epsilon_k^j}{Dt} + \left(\frac{\partial \hat{E}}{\partial \epsilon_{jk}} \right)_{\rho, T} \frac{D\epsilon_k^i}{Dt} \right] \quad (2.34)$$

is the rate of change of strain energy. Except for the strain energy term, equation (2.33) is a common form of the energy equation (Ref. 21). We now assume that it is possible to write energy relaxation equations for a liquid which are analogous to equation (2.25) derived from kinetic theory by Morgan and Kern. We propose the equation

$$\begin{aligned} \rho \frac{c_v}{3} \left\{ \frac{DT^{ij}}{Dt} + \frac{3T^{ij} - g^{ij} T_k^k}{\tau} \right\} + T^{ij} = -T \left(\frac{\partial P}{\partial T} \right)_\rho d^{ij} + \\ + \frac{1}{3} (\hat{k} g^{\ell m} T_{,\ell}^{ij})_{,m} + \frac{1}{2} (\sigma^{ik} d_k^j + \sigma^{jk} d_k^i) \end{aligned} \quad (2.35)$$

which reduces to equation (2.25) for an ideal gas, and can be transformed into equation (2.33) by lowering j , setting $i = j$, and contracting.

It is sometimes convenient, particularly for isothermal flows, or when conduction can be neglected, to use a non-dimensional deviatoric translational temperature tensor, θ_{ij} , defined by

$$\theta_{ij} \equiv \frac{T_{ij} - g_{ij} T_e}{T_e} \quad (2.36)$$

where

$$T_e = \frac{1}{3} T^k_k \quad (2.37)$$

With this definition we see immediately that

$$\theta^k_k = 0 \quad (2.38)$$

This tensor is useful in that it expresses deviations of temperatures in different directions, rather than the actual temperatures. As such it is analogous to the strain tensor which expresses deviations from the unstrained conditions. Using this definition the energy relaxation equations can be rewritten as

$$\begin{aligned} \frac{\rho c_v T_e}{3} \left\{ \frac{D\theta^{ij}}{Dt} + \frac{3\theta^{ij}}{\tau} + \frac{(g^{ij} + \theta^{ij})}{T_e} \frac{DT_e}{Dt} \right\} + T^{ij} = -T_e \left(\frac{\partial P}{\partial T} \right)_\rho d^{ij} \\ + \frac{1}{3} \left\{ \hat{k} g^{\ell m} [T_e (g^{ij} + \theta^{ij})]_{,\ell} \right\}_{,m} + \frac{1}{2} (\sigma^{ik} d^j_k + \sigma^{jk} d^i_k) \end{aligned} \quad (2.39)$$

It should be noted that these equations do not consider vibrational and rotational energy modes, and should transfer between these and the translational modes be important, relaxation equations connecting these modes should be used.

We have in this chapter expressed twenty-one equations which, in principle at least, can be solved for the twenty-one unknowns describing a general flow problem. The equations consist of six molecular strain relaxation equations, six energy relaxation equations, six stress equations and three momentum equations. The unknowns are six components each of the molecular strain, the temperature, and the stress tensors and three components of velocity. Before a solution to these equations can be obtained, however, it is necessary to evaluate the partition function, and to do this a model for the liquid must be chosen. This will be done in the next chapter where the cell theory approach will be used.

CHAPTER III

THE CELL THEORY APPROXIMATION

To obtain solutions to the equations derived in Chapter 2, it is necessary to evaluate the partition function for a large system of interacting molecules, a task which at present is quite unfeasible. This difficulty is what led Eyring and Hirschfelder (Ref. 22), and Lennard-Jones and Devonshire (Ref. 23) to attempt to simplify the evaluation of the partition function by introducing cell theory. Though the theory was originally proposed as a result of an intuitive approach, Kirkwood (Ref. 24) has placed the theory on a sound statistical mechanical basis by obtaining the partition function for the cell model by successive approximations of the exact partition function.

3.1 The Basis of Cell Theory

The physical arguments leading to the adoption of cell theory emphasize the similarity of the liquid structure to that of a crystalline solid. In a crystal, the molecules are located in a regular geometrical pattern, and therefore the crystalline solid is said to exhibit long range order. In a liquid, for high densities and

for temperatures far below the critical point, X-ray diffraction studies have shown that short range order, extending over a few molecular diameters, still exists. Since the mean molecular spacing is not much greater than the diameter of the molecule, it can be assumed that a molecule is confined to a "cell" or cage consisting of its immediate neighbors. This is a reasonable assumption for thermodynamic calculations provided that the molecules occupy their cells for time periods which are large compared to the time between collisions. A molecule which is restricted to move in its cell, can thus be regarded as an independent thermodynamic system. If it is assumed that the system is homogeneous in the sense that each molecule in a cell is representative of all other molecule-cell combinations, then the partition function for a system of N molecules can be obtained by taking the N th power of the single molecule partition function. In terms of the Helmholtz free energy, this just means that the total free energy is N times the free energy of one molecule in one cell.

In spite of the number of approximations, the cell theories have had outstanding success in obtaining qualitative and, to a lesser extent, quantitative agreement with experimental thermodynamic properties. It is

possible to achieve varying degrees of complexity with cell theories, depending on whether the number of molecules is put equal to the number of cells, whether single or multiple occupancy of the cells is permitted, and depending on the form of the intermolecular potential which is chosen.

3.2 Evaluation of the Partition Function and the Thermodynamic Properties

To facilitate the mathematics, the simplest form of cell theory will be used here. We assume that there are N molecules occupying N cells, with only single occupancy permitted. Attention will be focused on only one molecule, which is allowed to move, while the remaining molecules are assumed to be fixed in their equilibrium positions in a quasi-crystalline lattice. The free molecule or the "wanderer" is restricted to move within its cell, where the potential is assumed to be uniform. Thus the potential energy can be expressed as

$$\left. \begin{aligned} \phi &= \frac{\Phi_L}{N} && \text{(within the cell)} \\ \phi &= \infty && \text{(outside the cell)} \end{aligned} \right\} \quad (3.1)$$

where Φ_L is the total lattice potential energy of the

molecules in their equilibrium positions. It is generally expressed as a function of the specific volume.

The canonical partition function, defined by equation (2.7), can be written as a product of terms including the translational kinetic energy and the potential or configurational energy. Thus

$$Z = Z_{\text{kinetic}} \cdot Q \quad (3.2)$$

where

$$Z_{\text{kinetic}} = \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3N}{2}} \quad (3.3)$$

h is Planck's constant. The configurational partition function for N particles is

$$Q_N(V, T) = \frac{1}{N!} \int_V \dots \int_V \exp \left\{ - \frac{\Phi(\underline{r}_1 \dots \underline{r}_N)}{kT} \right\} d\underline{r}_1 \dots d\underline{r}_N \quad (3.4)$$

where \underline{r}_i is the radius vector of the i 'th molecule, $\Phi(\underline{r}_1 \dots \underline{r}_N)$ is the potential energy of the system in configuration $(\underline{r}_1 \dots \underline{r}_N)$ and the integrations are carried out over the volume V . Utilizing the cell theory assumptions, the configurational partition function for one molecule in its cell is

$$Q_1 = \int_V \exp \left(- \frac{\phi}{kT} \right) d\underline{r} \quad (3.5)$$

where \underline{r} is the position vector of the molecule in its cell. Since ϕ is assumed to be uniform

$$Q_1 = v_{fc} \exp\left(-\frac{\phi}{kT}\right) \quad (3.6)$$

where v_{fc} is the free volume available to the center of the wanderer in its cell. The configurational free energy for one cell is then

$$F_1 = \phi - kT \ln v_{fc} \quad (3.7)$$

and for N particles in N cells

$$F_N = \phi_L - NkT \ln v_{fc} \quad (3.8)$$

If it is assumed that the immediate neighbors making up the cell are fixed in their lattice positions, then for a face centered cubic lattice the volume per molecule is

$$v = \ell^3 / \sqrt{2} \quad (3.9)$$

where ℓ is the distance between nearest neighbors. The free volume available for the center of the moving molecule has a very complicated shape, however, the error introduced is not large if the volume of the largest sphere which fits inside the actual free volume is taken as the free volume (Ref. 25).

Then

$$v_{fc} = \frac{4}{3} \pi (\ell - d)^3 \quad (3.10)$$

where d is the hard sphere diameter. When the lattice is strained, the relative distances between the molecules, and the shape of the free volume are altered. Choosing cartesian axes x , y , and z , coincident with the principal axes of strain for the lattice, the sphere representing the free volume is distorted into an ellipsoid of volume

$$v_{fc} = \frac{4}{3} \pi \lambda_{xx} \lambda_{yy} \lambda_{zz} \quad (3.11)$$

where

$$\lambda_{\alpha\alpha} \equiv (1 + \varepsilon_{\alpha\alpha}) \ell e^{-d} . \quad (3.12)$$

Thus $\lambda_{\alpha\alpha}$ represents the size of the gap between the molecules in the α direction.

To evaluate the partition function, it is necessary to choose an expression for the interaction potential between molecules. There are many forms of the intermolecular potential currently in use, giving good descriptions of gas viscosities, second and third virial coefficients, thermal conductivities and other properties. Unfortunately, since the functions used are only empirical representations of the true interactions, the parameters required to describe them depend on the

property being measured. As an example, the parameters of the Lennard-Jones (6-12) potential required to describe gas viscosities are different from those required for the second virial coefficients. At present, there does not appear to be any potential function which allows consistent information about intermolecular properties to be derived from various physical properties. In view of these uncertainties, a simple form of the potential will be chosen, which does, nevertheless, represent to some extent the actual behavior.

It has been shown (Ref. 3) that a good approximation to the lattice potential energy is given by a function of the form

$$\phi = - \frac{a(T)}{v^n} \quad (3.13)$$

For a liquid which is being strained, a plausible expression which reduces to the above form for no strain is

$$\phi = - \frac{a'}{3} \left(\frac{1}{l_x^{3n}} + \frac{1}{l_y^{3n}} + \frac{1}{l_z^{3n}} \right) \quad (3.14)$$

where

$$a' = 2^{n/2} a \quad (3.15)$$

and l_x , l_y , l_z represent the molecular spacing in the principal x, y, and z directions respectively. It is now possible to evaluate the desired thermodynamic properties.

The stress tensor can be obtained in principal axes as follows,

$$S_{\alpha\alpha} = \frac{\ell_{\alpha}}{V} \left(\frac{\partial F}{\partial \ell_{\alpha}} \right)_T \quad (3.16)$$

Substituting for F from equation (3.8) we get

$$S_{\alpha\alpha} = - \frac{\ell_{\alpha} kT}{v} \left(\frac{\partial \ln v_{fc}}{\partial \ell_{\alpha}} \right)_T + \frac{\ell_{\alpha}}{v} \left(\frac{\partial \phi}{\partial \ell_{\alpha}} \right)_T \quad (3.17)$$

where the effect of temperature variation with direction has been included. When the derivatives are evaluated, the stress becomes simply

$$S_{\alpha\alpha} = - \rho RT_{\alpha\alpha} \left(1 + \frac{d}{\lambda_{\alpha\alpha}} \right) + \frac{na}{v^{n+1}} \frac{1}{(1 + \epsilon_{\alpha\alpha})^{3n}} \quad (3.18)$$

For the case of zero strain, and $n = 1$, we get

$$- S_{\alpha\alpha} = P = \rho RT \left(1 + \frac{d}{\lambda} \right) - \frac{a}{v^2} \quad (3.19)$$

which is one form of the Eyring equation of state (Ref. 4). The identical expression for pressure can be obtained by assuming no strain and using the relation

$$P = - \left(\frac{\partial F}{\partial V} \right)_T \quad (3.20)$$

A closer look at equation (3.19) indicates that in the low density limit, the equation of state for an ideal gas

is recovered. The reason for this behavior is that for a system of non-interacting particles, the introduction of partitions affects the free energy and the entropy, but not the pressure or the internal energy (Ref. 3). Thus equation (3.19) is correct in the high and low density limits, though it can be expected to be in error in between.

The stress and the pressure may be expressed as the sum of kinetic and potential terms. The kinetic contribution is a consequence of the motion of the molecules in their cells, while the potential term results from the potential energy of the molecules located at their respective cell centers. Thus the kinetic pressure is

$$P_k = \rho RT \left(1 + \frac{d}{\lambda} \right) \quad (3.21)$$

and the potential pressure is

$$P_p = \frac{na}{v^{n+1}} \quad (3.22)$$

For small strains, the potential term of the stress tensor can be linearized so that equation (3.18) becomes

$$\bar{S}_{\alpha\alpha} = - \rho RT_{\alpha\alpha} \left(1 + \frac{d}{\lambda_{\alpha\alpha}} \right) + P_p (1 - 3n\epsilon_{\alpha\alpha}) . \quad (3.23)$$

We now define a non-dimensional gap tensor, v_{ij} , as

$$v_{ij} \equiv \frac{\lambda_{ij}}{\lambda} = g_{ij} + \left(1 + \frac{d}{\lambda}\right) \epsilon_{ij} . \quad (3.24)$$

The inverse of v_j^i can be obtained from

$$v_j^i = \frac{N_j^i}{v} \quad (3.25)$$

where N_j^i is the cofactor of v_i^j in $\det(v_i^j) \equiv v$.

The stress tensor can then be written in arbitrary coordinates as

$$S_{ij} = -\rho R \left\{ T_{ij} + \frac{d}{2\lambda} \left[T_{ik} v_j^k + T_{jk} v_i^k \right] \right\} + P_p (g_{ij} - 3n \epsilon_{ij}) \quad (3.26)$$

It is often more convenient to use the deviatoric stress tensor defined in equation (2.32) and to write it in terms of the deviatoric translational temperature tensor defined in equation (2.36). Equation (3.26) can then be rewritten as

$$\sigma_{ij} = -\rho R T_e \left\{ \theta_{ij} + \frac{d}{2\lambda} \left\{ (\theta_{ik} + g_{ik}) v_j^k + (\theta_{jk} + g_{jk}) v_i^k - 2g_{ij} \right\} \right\} - 3n P_p \epsilon_{ij} . \quad (3.27)$$

To find an expression for Π_{ij} , which was defined by equation (2.30), we must first determine the internal energy, E . This is most easily accomplished by using the Gibbs-Helmholtz equation

$$E = F - T \left(\frac{\partial F}{\partial T} \right)_V \quad (3.28)$$

From the partition function which was obtained earlier, the free energy is

$$F = - \frac{3NkT}{2} \ln \left(\frac{2\pi mkT}{h^2} \right) - NkT \ln (v_{fc}) + \Phi_L \quad (3.29)$$

and the internal energy becomes simply

$$\begin{aligned} E &= \frac{3}{2} NkT + \Phi_L \\ &= c_v T + \Phi_L \end{aligned} \quad (3.30)$$

Using the definition for Π_{ij} , we have in principal cartesian axes that

$$\Pi_{\alpha\alpha} = \frac{\ell_\alpha}{V} \left(\frac{\partial \Phi_L}{\partial \ell_\alpha} \right)_{T, \rho} \quad (3.31)$$

which turns out to be simply the potential part of the stress tensor

$$\Pi_{ij} = P_p (g_{ij} - 3n\varepsilon_{ij}) \quad , \quad (3.32)$$

and for no strain

$$\Pi_{\alpha\alpha} = P_p . \quad (3.33)$$

3.3 The Relaxation Times

In the preceding chapter, two relaxation times were postulated, one for equilibration of translational energy and the other for equilibration of molecular spacing, but no indication was given of how they may be obtained. The time required for equipartition of translational energy for molecules of equal mass should be of the order of the collision time. Morgan and Kern (Ref. 14) have shown that in a gas the translational relaxation time is just

$$\tau = \frac{3\mu}{P} , \quad (3.34)$$

thus if the kinetic theory result for the viscosity of a hard sphere gas is used, it is found that

$$\tau = 3.813 \tau_c \quad (3.35)$$

where τ_c is the collision time. It will be assumed that the same relationship between the relaxation and collision times will apply for a hard sphere liquid.

The collision time for a liquid is a very difficult quantity to determine. Herzfeld and Litovitz (Ref. 5)

have shown that collision times computed under various assumptions for some common liquids disagree by factors of up to thirty. In view of this uncertainty, the collision time will be calculated using a convenient though relatively simple approach. The average collision frequency for molecules in a liquid can roughly be expressed as

$$f_c = \frac{c_x}{2\lambda_x} + \frac{c_y}{2\lambda_y} + \frac{c_z}{2\lambda_z} \quad (3.36)$$

where c_α is the component of the average random speed of the molecules in the α direction. By the component of the random speed we mean the component of the absolute value of the random velocity. Since the velocity distribution in a liquid, as in a gas is Maxwellian (Ref. 33), the average speed is

$$W = \sqrt{\frac{8kT}{\pi m}} \quad (3.37)$$

At equilibrium, the average speed is independent of direction, thus the component of the speed in any direction is obtained by averaging the component for the velocity vector varying over all angles, thus

$$\bar{c}_\alpha = \frac{4}{\pi^2} W \quad (3.38)$$

The spacing is also uniform at equilibrium, thus the

collision time can be expressed as

$$\tau_c = \frac{1}{f_c} = \frac{\pi^2}{12} \lambda \sqrt{\frac{\pi m}{2kT}} \quad (3.39)$$

When the liquid is strained, the spacing between the molecules in different directions is altered and, as may be seen from equation (3.36), the collision frequency is changed.

The ratio of the equilibrium to the strained collision frequency is

$$\frac{f_{ce}}{f_c} = \frac{3\bar{c}/\lambda}{\frac{c_x}{\lambda_x} + \frac{c_y}{\lambda_y} + \frac{c_z}{\lambda_z}} \quad (3.40)$$

It will be shown later that in most liquids $\tau \ll \kappa$, and therefore $\theta_{ij} \ll \epsilon_{ij} < \nu_{ij}$. Since the molecular speeds vary as the square root of the temperature, the effect of strain on the collision time is much greater than the effects of the temperature variations. Thus it can be assumed that the molecular speeds have their average value even in the strained liquid, and

$$\frac{f_{ce}}{f_c} = \frac{3}{\frac{1}{v_{xx}} + \frac{1}{v_{yy}} + \frac{1}{v_{zz}}} \quad (3.41)$$

In any axes

$$\frac{\tau_c}{\tau_{ce}} = \frac{f_{ce}}{f_c} = \frac{3 \text{ III}_v}{\text{II}_v} \quad (3.42)$$

where the invariants of the gap tensor are

$$\text{II}_v = \frac{1}{2} \left(v_i^i v_j^j - v_j^i v_i^j \right) \quad (3.43)$$

and

$$\text{III}_v = \det \left(v_j^i \right) . \quad (3.44)$$

The structural relaxation process is considerably more complicated than the thermal one. When a material is strained, the separation between molecules is altered. The size of these separations fluctuates continuously such that at some time a vacancy large enough to accommodate a molecule is formed. When a molecule jumps into this available space the strain is relieved. Therefore it is possible to identify the relaxation time for molecular strain with the time required for a molecular jump.

Two conditions are required for a jump to occur. First, there must be a sufficiently large volume available, and second, the molecule must have enough energy to leave its position and surmount the potential barrier formed by the neighboring molecules.

Chung (Ref. 26), using statistical mechanical argu-

ments has derived the expression for the jump probability, P_j , as

$$P_j = \left[\frac{1}{2} \left(\frac{E_v}{kT} \right)^2 + \frac{E_v}{kT} + 1 \right] \exp \left[- \frac{E_v}{kT} - \frac{v_o}{v_f} \right] \quad (3.45)$$

where E_v is the energy required for the molecule to jump, and v_o is the required volume. Note that the free volume, v_f , here is not the same one used in deriving the equation of state, but is instead the difference between the actual and close packed volumes per molecule.

Since during the traverse of a sphere into a neighboring vacancy, the travelling sphere makes on the average three glancing collisions (Ref. 27), it is possible to write for the molecular strain relaxation time

$$\kappa = \frac{3\tau_c}{P_j} \quad (3.46)$$

or

$$\kappa = 3\tau_c \left\{ \frac{1}{2} \left(\frac{E_v}{kT} \right)^2 + \frac{E_v}{kT} + 1 \right\}^{-1} \exp \left[\frac{E_v}{kT} + \frac{v_o}{v_f} \right]. \quad (3.47)$$

Brummer (Ref. 28), and Gubbins and Tham (Ref. 29) have shown that the energy required for a jump is a strong function of the density of the fluid. This is to be expected since a molecule must squeeze through the extremely steep repulsive potential of its neighbors. In

a strained liquid then, where a molecule sees a density varying with direction, the total jump probability is obtained by integrating over all directions. Thus

$$P_j = \frac{1}{4\pi} \iiint \left[\frac{1}{2} \left(\frac{E_v(\phi, \psi)}{kT} \right)^2 + \frac{E_v(\phi, \psi)}{kT} + 1 \right]^{-1} \exp \left(- \frac{E_v(\phi, \psi)}{kT} - \frac{v_o}{v_f(\phi, \psi)} \right) \sin\phi d\phi d\psi \quad (3.48)$$

where ϕ and ψ are the angles measured in spherical coordinates.

3.4 Limitations of the Simple Cell Theory

Although cell theory has been shown to give a useful description of the liquid state, there are nevertheless several limitations introduced by the many assumptions which are made.

One of the main problems is that cell theory is really a description of the solid state, introducing a degree of long range order which does not exist in a liquid. The introduction of cells implies that molecules in one cell do not affect molecules in neighboring cells and thus correlation effects are neglected. Both of the above assumptions lead to predictions of entropy which are too low, since order has artificially been

introduced to the system.

The supposition that the virtual lattice, defining the equilibrium molecular positions, expands uniformly with volume appears to be incorrect. X-ray and neutron diffraction studies have shown that there is no appreciable change in the nearest neighbor distance when the volume is altered. This implies that the volume change should be attributed to the decrease in the number of molecules in the first coordination shell. Cell theory can be improved here by introducing a larger number of cells than molecules (Ref. 30), and allowing for multiple occupancy (Ref. 31).

The range of applicability of cell theory is limited by the specification of the cell center as the preferred position for a molecule. Calculations for molecules with a Lennard-Jones (6-12) potential indicate that at reduced density

$$\rho^* \equiv \bar{n}d^3 < 0.69 \quad (3.49)$$

where \bar{n} is the molecular number density, there is a potential maximum at the center of the cell (Ref. 32). Since for this case the ground state no longer corresponds to a regular arrangement of molecules, it is difficult in this range to justify cell theory. If the

energy of the molecule is less than the energy of the central hump, the effect would be for molecules to cluster, and in a sense behave like larger more complicated molecules.

A common problem for theories of the liquid state arises when the potential contributions to the pressure become of the same order as the thermal or kinetic terms. Then it becomes necessary to subtract large terms of equal magnitude, leading to a magnification of any errors. Physically the effects of this delicate balance are shown dramatically by the phenomenon of critical opalescence, an occurrence which is brought about by large scale fluctuations in density. The density fluctuations are in turn a manifestation of the formation of clusters by attractive forces and their subsequent dispersion by molecular collisions. The clusters are found to contain of the order of millions of molecules (Ref. 33). Clustering to a lesser extent must occur in liquids even away from the critical point, thus, in particular, near the saturation curve the cell theory cannot be expected to be accurate.

~~The limitations imposed by the adoption of cell~~
theory must be kept in mind when interpreting the solutions obtained for various problems.

CHAPTER IV

SOME SOLUTIONS AND COMPARISONS WITH EXPERIMENTS

The problem with the present equations, as with most rheological equations of state, is that they are too complex to solve for any but the simplest of flows. The general approach in problems of rheology is to postulate a flow pattern, and then attempt to calculate the stress pattern necessary to maintain this flow. This procedure is used because the inverse problem of calculating the flow from the stress pattern, while difficult for Newtonian flow, becomes quite impracticable for more complicated flows.

4.1 Steady Shearing Flow at Low Strain Rates

Consider a flow such that in cartesian coordinates the velocity field is given by

$$\left. \begin{aligned} u_x &= Dy \\ u_y &= u_z = 0 \end{aligned} \right\} \quad (4.1)$$

where D is called the rate of shear. The coordinate system is shown in figure (1).

Since the flow is described in cartesian coordinates,

it is no longer necessary to differentiate between the covariant and contravariant components of the tensors. Also, the metric tensor can just be replaced by the Kronecker delta.

For this flow, the strain rate and vorticity tensors can be represented by

$$d_{ij} = \begin{bmatrix} 0 & D/2 & 0 \\ D/2 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (4.2)$$

and

$$\omega_{ij} = \begin{bmatrix} 0 & D/2 & 0 \\ -D/2 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (4.3)$$

respectively. The flow is further assumed to be steady

$$\frac{\partial}{\partial t} = 0 \quad , \quad (4.4)$$

isochoric (constant volume)

$$d_{kk} = 0 \quad , \quad (4.5)$$

and isothermal.

It is instructive to solve the equations at first for the case

$$D \rightarrow 0,$$

since then the terms of the strain and deviatoric temperature tensors are small, and the relaxation equations can be linearized.

Equation (2.21), describing the relaxation of molecular strain, becomes

$$\frac{D\epsilon_{ij}}{Dt} + \frac{3\epsilon_{ij} - \delta_{ij} \epsilon_{kk}}{\kappa} = (A-B)d_{ij} + \delta_{ij} B d_{kk} , \quad (4.6)$$

since for low shear rates, and thus small strains

$$\zeta_{ij} = \delta_{ij} .$$

In terms of the individual components we can write for

$i = x, j = x$

$$- D \epsilon_{xy} + \frac{(\epsilon_{xx} - \epsilon_{yy}) + (\epsilon_{xx} - \epsilon_{zz})}{\kappa} = 0 , \quad (4.7)$$

for $i = y, j = y$

$$D \epsilon_{xy} + \frac{(\epsilon_{yy} - \epsilon_{xx}) + (\epsilon_{yy} - \epsilon_{zz})}{\kappa} = 0 , \quad (4.8)$$

for $i = z, j = z$

$$(\epsilon_{zz} - \epsilon_{xx}) + (\epsilon_{zz} - \epsilon_{yy}) = 0 , \quad (4.9)$$

and for $i = x, j = y$

$$\frac{D}{2} (\epsilon_{xx} - \epsilon_{yy}) + \frac{3 \epsilon_{xy}}{\kappa} = (A-B) \frac{D}{2} . \quad (4.10)$$

The z axis remains a principal axis, therefore the off-diagonal terms with a z component are all zero. When the expression obtained from equation (4.9) for ϵ_{zz} is substituted into equations (4.7) and (4.8), the latter become identical. This happens because the molecular strains are not independent, but must satisfy equation (2.3). For small strains this gives

$$\epsilon_{xy}^2 = \epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz} \quad (4.11)$$

Solving equations (4.7), (4.9), (4.10) and (4.11), the components of the molecular strain tensor can be expressed by the array

$$\epsilon_{ij} = \frac{A-B}{2} \begin{bmatrix} \left(\frac{A-B}{6} + 1\right) \left(\frac{\kappa D}{3}\right)^2 & \frac{\kappa D}{3} & 0 \\ \frac{\kappa D}{3} & \left(\frac{A-B}{6} - 1\right) \left(\frac{\kappa D}{3}\right)^2 & 0 \\ 0 & 0 & \left(\frac{A-B}{6}\right) \left(\frac{\kappa D}{3}\right)^2 \end{bmatrix} \quad (4.12)$$

We see that the magnitude of the molecular strain is determined by the dimensionless product κD , a number which essentially expresses the ratio of the time required for molecular rearrangement to the time scale of the imposed fluid deformation. Using this number we are in a position to state that a requirement for a

shear rate to be considered slow is that the condition $\kappa D \ll 1$ must be fulfilled. For most simple liquids under normal conditions, κ is extremely small, generally being less than 10^{-8} seconds.

Another important point to note is that the shear strain is of order κD , while the normal strains are of order $(\kappa D)^2$. This means that the expression obtained for volume changes in linear theory (Ref. 17),

$$\frac{dV - dV_0}{dV_0} = \epsilon_{kk} \quad , \quad (4.13)$$

cannot be used even for small strains, since ϵ_{xy}^2 is of the same order as ϵ_{kk} . This is the reason for the ϵ_{xy}^2 term appearing in equation (4.11).

The linearized energy relaxation equation can be written as

$$\frac{\rho c_v}{3} \left\{ \frac{D\theta}{Dt}{}_{ij} + \frac{3\theta}{\tau}{}_{ij} \right\} = - \frac{P}{T} \frac{D\epsilon}{Dt}{}_{ij} - \left(\frac{\partial P}{\partial T} \right)_v d_{ij} \quad (4.14)$$

where it has been assumed that the dissipation term is of order D^2 , and can thus be neglected. This assumption is verified a posteriori. In terms of the individual components, equation (4.14) can be expressed as,

for $i = x, j = x$

$$\theta_{xx} - \frac{\tau D}{3} \theta_{xy} = + \left(\frac{P}{\rho c_v T} \right) \tau D \epsilon_{xy} , \quad (4.15)$$

for $i = y, j = y$

$$\theta_{yy} + \frac{\tau D}{3} \theta_{xy} = - \left(\frac{P}{\rho c_v T} \right) \tau D \epsilon_{xy} , \quad (4.16)$$

for $i = z, j = z$

$$\theta_{zz} = 0 , \quad (4.17)$$

and for $i = x, j = y$

$$\begin{aligned} \theta_{xy} + \frac{\tau D}{6} (\theta_{xx} - \theta_{yy}) = & - \left(\frac{P}{\rho c_v T} \right) \frac{\tau D}{2} (\epsilon_{xx} - \epsilon_{yy}) - \\ & - \frac{1}{\rho c_v} \left(\frac{\partial P}{\partial T} \right)_v \frac{\tau D}{2} . \end{aligned} \quad (4.18)$$

The equations for $i \neq j$ and either i or $j = z$, become identically zero since z remains a principal axis. From equations (2.38) and (4.17) we find that

$$\theta_{xx} = - \theta_{yy} . \quad (4.19)$$

With this substitution equations (4.15) and (4.16) become identical. This happens because, to this order, the overall energy equation is satisfied trivially by the specification of isothermal and isochoric flow.

The solution for the translational temperature tensor becomes

$$\theta_{ij} = - \frac{3}{2\rho c_v} \left(\frac{\partial P}{\partial T} \right)_v \begin{bmatrix} \left(\frac{\tau D}{3} \right)^2 & \frac{\tau D}{3} & 0 \\ \frac{\tau D}{3} & - \left(\frac{\tau D}{3} \right)^2 & 0 \\ 0 & 0 & 0 \end{bmatrix} \quad (4.20)$$

The deviation of the translational temperature from isotropy is determined by the dimensionless product τD , which expresses the ratio of the time required for thermal equilibration to the inverse of the strain rate. τD plays the same role in the energy relaxation equation as κD does in the molecular strain relaxation equation.

The stress field required to maintain this flow can be obtained from equation (3.27). With the present approximations, in terms of the individual components we have for the shear stress

$$\sigma_{xy} = - P_k \theta_{xy} + \left(\frac{d}{\lambda} P_k - 3n P_p \right) \epsilon_{xy} \quad (4.21)$$

and for the normal stresses

$$\sigma_{xx} = - P_k \theta_{xx} + \left(\frac{d}{\lambda} P_k - 3n P_p \right) \epsilon_{xx} + \frac{d}{\lambda} P_k (\theta_{xy} - \nu_{xy}) \epsilon_{xy} \quad (4.22)$$

$$\sigma_{yy} = -P_k \theta_{yy} + \left(\frac{d}{\lambda} P_k - 3n P_p \right) \epsilon_{yy} + \frac{d}{\lambda} P_k (\theta_{xy} - v_{xy}) \epsilon_{xy} \quad (4.23)$$

$$\sigma_{zz} = \left(\frac{d}{\lambda} P_k - 3n P_p \right) \epsilon_{zz} \quad (4.24)$$

Substituting the solutions obtained for θ_{ij} and ϵ_{ij} , the shear stress becomes

$$\sigma_{xy} = \frac{P_k}{2\rho c_v} \left(\frac{\partial P}{\partial T} \right)_v \tau D + \frac{A-B}{6} \left(\frac{d}{\lambda} P_k - 3n P_p \right) \kappa D, \quad (4.25)$$

and the normal stresses become

$$\begin{aligned} \sigma_{xx} = & \frac{3P_k}{2\rho c_v} \left(\frac{\partial P}{\partial T} \right)_v \left(\frac{\tau D}{3} \right)^2 + \frac{A-B}{2} \left[\frac{A-B}{6} + 1 \right] \left[\frac{d}{\lambda} P_k - 3n P_p \right] \left(\frac{\kappa D}{3} \right)^2 \\ & - \frac{A-B}{6} \frac{d}{\lambda} P_k \left[\frac{A-B}{6} \left(1 + \frac{d}{\lambda} \right) \kappa D + \frac{1}{2\rho c_v} \left(\frac{\partial P}{\partial T} \right)_v \tau D \right] \kappa D \quad (4.26) \end{aligned}$$

$$\begin{aligned} \sigma_{yy} = & - \frac{3P_k}{2\rho c_v} \left(\frac{\partial P}{\partial T} \right)_v \left(\frac{\tau D}{3} \right)^2 + \frac{A-B}{2} \left[\frac{A-B}{6} - 1 \right] \left[\frac{d}{\lambda} P_k - 3n P_p \right] \left(\frac{\kappa D}{3} \right)^2 \\ & - \frac{A-B}{6} \frac{d}{\lambda} P_k \left[\frac{A-B}{6} \left(1 + \frac{d}{\lambda} \right) \kappa D + \frac{1}{2\rho c_v} \left(\frac{\partial P}{\partial T} \right)_v \tau D \right] \kappa D \quad (4.27) \end{aligned}$$

and

$$\sigma_{zz} = \frac{(A-B)^2}{12} \left[\frac{d}{\lambda} P_k - 3n P_p \right] \left(\frac{\kappa D}{3} \right)^2 \quad (4.28)$$

Since the shear rate is low, we have

$$\tau D \ll 1$$

and $\kappa D \ll 1$.

Thus the normal stresses can be seen to be of higher order than the shear stresses.

For a dilute gas, because of the wide separation between molecules, the attractive forces become negligible, and

$$\frac{d}{\lambda} \ll 1 .$$

The stress field then becomes simply

$$\sigma_{xy} = P \frac{\tau D}{3} \quad (4.29)$$

$$\sigma_{xx} = P \left(\frac{\tau D}{3} \right)^2 \quad (4.30)$$

$$\sigma_{yy} = - P \left(\frac{\tau D}{3} \right)^2 \quad (4.31)$$

$$\sigma_{zz} = 0 \quad (4.32)$$

This is seen to be identical to the results obtained for a Maxwell fluid (Ref. 46). Though the strain rates required to generate them would be extremely high, these results indicate that normal stress effects can be expected in gases as well as in liquids.

Normal stress effects in gases have also been calculated by Morgan and Kern (Ref. 14), who obtained off-diagonal terms of the stress tensor in axes coincident

with the principal axes of the strain rate tensor, and by Truesdell (Ref. 34), who did a kinetic theory analysis of Maxwell molecules. Reiner (Refs. 35, 36) claims to have measured normal stress effects in air, however, there is still some question concerning the interpretation of his results (Ref. 20).

The result for the shear stress, equation (4.25), indicates that for slow shear rates the behavior of the fluid is Newtonian, with a viscosity

$$\mu = \frac{\sigma_{xy}}{D} = \frac{1}{2\rho c_v} \left(\frac{\partial P}{\partial T} \right) P_k \tau + \frac{A-B}{6} \left[\frac{d}{\lambda} P_k - 3n P_p \right] \kappa \quad (4.33)$$

The first term represents the kinetic contribution and is proportional to the square root of the temperature. This is identical to the kinetic theory result for a gas composed of rigid elastic spheres.

The second term is a combination of kinetic and intermolecular force contributions and decreases exponentially with temperature. For most liquids it is expected that the gas type contribution to the viscosity is small and that therefore the second term dominates the first. The viscosity can then be represented as

$$\mu = \frac{\frac{A-B}{2} \left[\frac{d}{\lambda} P_k - 3n P_p \right] \tau_c}{\frac{1}{2} \left(\frac{E_v}{kT} \right)^2 + \frac{E_v}{kT} + 1} \exp \left[\frac{E_v}{kT} + \frac{v_o}{v_f} \right], \quad (4.34)$$

an expression which is very similar in form to the hybrid equation for viscosity advanced by Macedo and Litovitz (Ref. 37). Their equation,

$$\mu = A_o \exp \left[\frac{E_v}{kT} + \gamma \frac{v_o}{v_f} \right] \quad (4.35)$$

where γ is a correction factor required to correct for the overlap of free volume, was proposed to combine the desirable aspects of the free volume theory of Cohen and Turnbull (Ref. 38) with the reaction rate theory of Eyring (Ref. 39), both of which have proven to be very successful in predicting the behavior of different liquids. Considerable success has been achieved by the application of the Macedo-Litovitz equation to the temperature and pressure dependence of a wide variety of liquids, both organic and inorganic. The main difference between the Macedo-Litovitz equation and equation (4.34) arises in the pre-exponential factor, which for the Macedo-Litovitz equation is an adjustable parameter. A table, listing the values of E_v and v_o/v_f required to fit the viscosity of many liquids, is presented by Macedo and Litovitz.

From these values it can be seen that the exponential term is in general very large, and that for most liquids, therefore, $\kappa \gg \tau$. This justifies the neglect of the gas-like term in the viscosity of liquids.

It is important to note that the expression obtained for viscosity, particularly the pre-exponential term, is subject to all the previously enumerated limitations of cell theory and the equation of state. Further, it is necessary to account for the fact that the hard sphere volume is not a constant, but decreases with increasing temperature, since more energetic molecules can approach each other more closely than those with low energy.

Equation (4.34) has been applied to two oils, for which the variation of viscosity and density have carefully been measured over a wide range of pressure and temperature. These are oils 17-D and 29-F of the ASME Pressure Viscosity Report (1953). The main reason for choosing these particular oils was because of their similarity to the oils used by Crook (Ref. 40) and Smith (Ref. 41) in their elastohydrodynamic lubrication experiments which are discussed in the next section. The molecules of the oils are certainly not spherical, however, the presence of large proportions of cyclic hydrocarbons, such as the naphthenes and the aromatics, could make this

a reasonable first approximation. The success of the Cohen and Turnbull equation, which is a special case of equation (4.35) in describing the viscosity data of high molecular weight hydrocarbons to within the accuracy of the experimental data is certainly encouraging in this respect.

The molecular weight of oil 29-F was not available, consequently, it was estimated by the method of Hirschler (Ref. 42), to be approximately 440. The index n , for the variation of the potential energy with volume was taken equal to one, since this has been found to be a good approximation for many liquids (Ref. 3). It was further assumed that the cross-strains produced by the strain rate are small, and therefore A was put equal to one and B to zero.

The energy barrier, E_v , and the close packed volume, v_o , were not known, and were therefore treated as adjustable parameters. It has been found (Ref. 29) that E_v is an increasing function of density, and that v_o decreases with increasing temperature, accordingly, simple linear relationships displaying these characteristics were used.

Gubbins and Tham (Ref. 29) have shown a reduced plot of the "activation energy", E_v , as a function of the

volume for several liquids, and their curve, together with the points obtained for the two oils, is presented in figure (2). For the oils, the pour point parameters were used for the reduction of the data since the melting point parameters used by Gubbins and Tham were unavailable. Nevertheless, the agreement of the values for the oils with those obtained for other liquids is quite good.

The experimental and calculated variation of viscosity with temperature and pressure is shown for the two oils in figures (3) and (4). The agreement is very good, except for high temperature and low pressures, which is precisely the region where cell theory cannot be expected to apply.

4.2 Steady Shearing Flow at Arbitrary Strain Rates

The analysis presented in the previous section is applicable to infinitesimally small strain rates. When the restriction, $\kappa D \ll 1$, is removed, the equations are no longer linear. In this case we can expect that the stress will no longer be linear in the strain rate, and thus the flow will be non-Newtonian.

Non-Newtonian behavior has been observed in liquid crystals (Ref. 43), colloidal suspensions (Ref. 44),

polymer melts and solutions (Ref. 45), and mineral oils in elastohydrodynamic (EHD) lubrication (Ref. 46). The theory, as developed so far, cannot be expected to hold for the first three cases, since for liquid crystals and polymers the molecules are extremely complicated and orientation effects play a large role, and for colloidal suspensions the flow of the particles making up the suspension must be considered (Ref. 47). There is hope, however, that the high shear rate flow of mineral oils can be described adequately by the present theory. This hope is reinforced by the success achieved in describing the oil viscosities over a wide range of temperature and pressure.

The elastohydrodynamic problem consists of the combination of the elastic deformation of the lubricating surfaces and the hydrodynamic behavior of the lubricant film. The shape of the film is determined by the deformation of the contacting surfaces, and since this film is generally very thin, the strain rates are extremely high. Figure (5) shows the shape and thickness of the lubricant film between two discs, measured by capacitance techniques (Ref. 40). The thickness is seen to be constant to within 10% in the region where the discs are deformed or in the Hertzian band. The ratio of the length of the

contact area to the film thickness is of order 100, and the width of the area is often 10^3 to 10^4 times greater than the film thickness. The extremely high pressures encountered raise the viscosity of the oil in the contact zone by factors of 10^4 or more, thus reducing the escape of lubricant from the sides and front. These considerations indicate that the EHD flow of lubricants can be approximated quite well by plane Couette flow.

To analyze this flow, we make the same assumptions as in the previous sections, except that we remove the restriction $\kappa D \ll 1$. Also, since it was shown that the viscosity of the liquid is primarily determined by the molecular strain, the energy relaxation equations are not considered.

The molecular strain relaxation equations now become

for $i = x, j = x$

$$\begin{aligned}
 & - (1 + \epsilon_{yy})(1 + \epsilon_{zz}) D \epsilon_{xy} + \epsilon_{xy} (1 + \epsilon_{zz}) \frac{D}{2} (\epsilon_{yy} - \epsilon_{xx}) \\
 & + \frac{(\epsilon_{xx} - \epsilon_{yy}) + (\epsilon_{xx} - \epsilon_{zz})}{\kappa} = 0 \quad (4.36)
 \end{aligned}$$

for $i = y, j = y$

$$(1 + \epsilon_{xx})(1 + \epsilon_{zz}) D \epsilon_{xy} + \epsilon_{xy}(1 + \epsilon_{zz}) \frac{D}{2} (\epsilon_{yy} - \epsilon_{xx}) + \frac{(\epsilon_{yy} - \epsilon_{xx}) + (\epsilon_{yy} - \epsilon_{zz})}{\kappa} = 0 \quad (4.37)$$

for $i = z, j = z$

$$\frac{(\epsilon_{zz} - \epsilon_{xx}) + (\epsilon_{zz} - \epsilon_{yy})}{\kappa} = 0 \quad (4.38)$$

and for $i = x, j = y$

$$(1 + \epsilon_{zz})(2 + \epsilon_{xx} + \epsilon_{yy}) \frac{D}{4} (\epsilon_{xx} - \epsilon_{yy}) + \frac{3\epsilon_{xy}}{\kappa} = \frac{A-B}{2} D \quad (4.39)$$

Substituting the expression obtained for ϵ_{zz} from equation (4.38) into equation (4.36) and (4.37) makes the latter equations identical for the same reason which was discussed in the previous section, therefore we again use equation (2.3).

With some algebraic manipulations, the equations to be solved can be written as

$$\epsilon_{zz} = (\epsilon_{xx} + \epsilon_{yy})/2 \quad (4.40)$$

$$\epsilon_{xy}(1 + \epsilon_{zz})^2 = \frac{3}{2} \frac{(\epsilon_{xx} - \epsilon_{yy})}{\kappa D} \quad (4.41)$$

$$(\epsilon_{xx} - \epsilon_{yy})(1 + \epsilon_{zz})^2 = (A-B) - \frac{6 \epsilon_{xy}}{\kappa D} \quad (4.42)$$

and

$$(1 + \epsilon_{zz}) \{ (1 + \epsilon_{xx})(1 + \epsilon_{yy}) - \epsilon_{xy}^2 \} = 1 \quad (4.43)$$

In these expressions, κ is still a function of the molecular strain, and this relationship is yet to be determined.

Gubbins and Tham (Ref. 29) give the following description of the jump of a molecule into a neighboring hole. In figure (6), for the molecule at 1 to jump to 3, it is necessary to overcome the energy barrier at 2 caused by the steep repulsive potentials of the neighboring molecules. This barrier is clearly a function of the molecular spacing in the directions normal to the direction of the jump. Thus for a jump to occur in the z direction, the energy required should be a function of the spacing in the x and y directions. A plausible assumption would be that E_v depends on the area of the gap as seen by the jumping molecule and thus the variation of E_v can be expressed as a function of the product $l_x l_y$. In principal axes, α , we can then write for small strains that

$$E_{\alpha} = E_{ve} - \frac{\lambda_e}{2} \frac{dE_v}{d\lambda_e} \epsilon_{\alpha\alpha} \quad (4.44)$$

where $dE_v/d\lambda_e$ can be determined from figure (2).

For pure shear, a sphere is distorted into an ellipsoid whose axes correspond to the principal axes of strain. We therefore assume that the energy required for a jump in a particular direction is also distributed ellipsoidally. Hence we can write

$$E_v(\phi, \psi) = E_{ve} + \frac{\lambda_e}{2} \frac{dE_v}{d\lambda_e} \left\{ 1 - \left[\frac{\sin^2 \phi \cos^2 \psi}{(1 + \epsilon_1^*)^2} + \frac{\sin^2 \phi \sin^2 \psi}{(1 + \epsilon_2^*)^2} + \frac{\cos^2 \phi}{(1 + \epsilon_3^*)^2} \right]^{-\frac{1}{2}} \right\} \quad (4.45)$$

where ϵ_1^* , ϵ_2^* , and ϵ_3^* are the principal strains obtained from the roots of the equation

$$\epsilon^{*3} - I_{\epsilon} \epsilon^{*2} - II_{\epsilon} \epsilon^* - III_{\epsilon} = 0 \quad (4.46)$$

The invariants of the tensor $(\epsilon_{ij} + \delta_{ij})$ are

$$I_{\epsilon} = \epsilon_{ii} + \delta_{ii}$$

$$II_{\epsilon} = \frac{1}{2} \{ (\epsilon_{ii} + \delta_{ii})(\epsilon_{jj} + \delta_{jj}) - (\epsilon_{ij} + \delta_{ij})(\epsilon_{ij} + \delta_{ij}) \}$$

and

$$III_{\epsilon} = \det(\epsilon_{ij} + \delta_{ij}).$$

This expression for $E(\phi, \psi)$ can be used in equation (3.48) to integrate for the jump probability over all directions. Similar arguments can be used to determine the change in the probability of finding sufficient free volume for a jump, as a function of direction, and the same ellipsoidal distribution is used for $v_o/v_f(\phi, \psi)$ in equation (3.48).

Equations (4.40-43) can be solved numerically to obtain the strains as a function of $\kappa_e D$, where κ_e is the molecular strain relaxation time for the unstrained liquid.

The solutions are obtained by the following procedure. First, a small value for $\kappa_e D$, typically 10^{-4} , is chosen, and the strains are computed with the low strain rate assumption, equation (4.12). These strains are used as a first approximation in solving equations (4.40-43) by a Newton-Raphson technique for systems, where κD is assumed constant. With the new strains, a new κD is calculated from equations (3.46) and (3.48) and compared with the previous κD . If the two values for κD are close, it is assumed that the method has converged to the required solution, if not, the new value for κD is used to obtain another approximation to the strains. This procedure can be continued until convergence is obtained.

When a higher $\kappa_e D$ is chosen next, the previous solution is used as the first guess for the strains.

Once the required strains have been obtained, the stress field can be calculated from the following expressions.

$$\sigma_{xy} = \left(\frac{d}{\lambda} P_k \frac{v_{zz}}{v} - 3nP_p \right) \epsilon_{xy} \quad (4.47)$$

$$\sigma_{xx} = - \frac{d}{\lambda} \frac{P_k}{(1 + d/\lambda)} \left(\frac{v_{yy} v_{zz}}{v} - 1 \right) - 3nP_p \epsilon_{xx} \quad (4.48)$$

$$\sigma_{yy} = - \frac{d}{\lambda} \frac{P_k}{(1 + d/\lambda)} \left(\frac{v_{xx} v_{zz}}{v} - 1 \right) - 3nP_p \epsilon_{yy} \quad (4.49)$$

and

$$\epsilon_{zz} = - \frac{d}{\lambda} \frac{P_k}{(1 + d/\lambda)} \left(\frac{1}{v_{zz}} - 1 \right) - 3nP_p \epsilon_{zz} \quad (4.50)$$

It is convenient to non-dimensionalize the stresses by dividing them by the expression

$$\frac{G_\infty}{3} = \frac{\mu}{\kappa_e} = \frac{A-B}{6} \left(\frac{d}{\lambda} P_k - 3nP_p \right) \quad (4.51)$$

where G_∞ is later found to be the limiting high frequency shear rigidity. For a Newtonian fluid the dimensionless shear stress is just given by

$$\frac{c_{xy}}{G_\infty} = \frac{\kappa D}{3} \quad (4.52)$$

The numerical solutions obtained for the variation of shear stress with shear rate are compared with Dyson's (Ref. 46) interpretation of the EHD lubrication experiments performed by Smith (Ref. 41) and Crook (Ref. 40).

Smith's experimental apparatus consisted of a motor driven cylindrical roller in contact with a spherical roller which was allowed to rotate freely in ball bearings. The axes of the two rollers could be skewed relative to each other, thus varying the sliding speed between them. Measurements of the axial force on the spherical roller were used to determine the frictional force. Heating elements inside the housings of the rollers, and a thermocouple in the air space near the point of contact of the rollers were used to maintain and regulate the temperature of the system. The film thicknesses were not measured, however, Dyson calculated them using the approximate theory of Grubin (Ref. 48). He estimates that this theory should be sufficiently accurate to give the film thicknesses to within a factor of three.

Dyson further introduced corrections to the experimental points for temperature variations in the contact zone, determining what the results would have been if the

conditions had been isothermal.

Crook performed his experiments by loading together pairs of discs, and measuring the frictional force as the sliding speed was varied. The film thicknesses were determined from the measured capacitance between the discs, and the surface temperatures were measured with thermocouples. Dyson also corrected Crook's results for thermal effects.

There is yet another correction which must be made before the calculated and experimental results can be compared, and that is to account for the variation of pressure in the contact zone.

It can be shown that under high loads, the pressure distribution in the contact region during EHD lubrication is very close to that which would exist for static loading with no lubricating film. This "Hertzian" pressure distribution is given by

$$P = P_m \left(1 - \frac{x^2}{b^2} \right)^{\frac{1}{2}} \quad (4.53)$$

where b is the half width of the contact region. Using Grubin's assumption that the viscosity variation with pressure is nearly exponential,

$$\mu = \mu_0 \exp(\beta P) \quad (4.54)$$

where β depends only on temperature, it is possible to develop a relationship between the mean effective viscosity, and the viscosity at the maximum Hertzian pressure. The ratio between the two can be expressed as

$$\frac{\bar{\mu}_{\text{mean}}}{\mu_{\text{max}}} = \frac{\int_0^1 \exp\left\{\beta P_m \left(1 - \frac{x^2}{b^2}\right)^{\frac{1}{2}}\right\} d\left(\frac{x}{b}\right)}{\exp(\beta P_m)} \quad (4.55)$$

The experimental results were all adjusted to the conditions prevailing at the maximum Hertzian pressure, which were also the conditions for which the calculations were performed.

The properties of the mineral oils studied by Smith and Crook were not available, therefore the oils showing the greatest similarity to the actual ones used were chosen from the ASME Pressure Viscosity Report (1953). Oil 17-D of the report was chosen to be representative of Smith's oil, while Crook states that oil 29-F was most similar to his.

The experimental conditions were all out of the range of the ASME data, however, some cases were close enough for a reasonable extrapolation to be attempted. For this reason some of Smith's high pressure data could

not be compared with the theory. The most difficult quantity to find an extrapolated value for is

$$\Psi \equiv \frac{\ell_e}{2kT} \frac{dE_v}{d\ell} \quad (4.56)$$

which is required to evaluate the change in the jump probability due to the molecular strain. From figure (2) we see that E_v rises very rapidly as V/V_m is decreased, consequently it is extremely difficult to extrapolate to small values of V/V_m . This problem is compounded further by attempting to determine an extrapolated value for the slope of the curve. For this reason, Ψ is treated as an adjustable parameter in the calculations. The values for the hard sphere diameters and close packed volumes are obtained from the relationships used to fit the low shear rate viscosity data. The conditions of the experiments, and the quantities used for the calculations are shown in Table I.

The experimental results obtained by Smith and Crook, for the variation of shear stress as a function of strain rate are shown plotted in dimensionless form in figure (7). Since the theory shows that in addition to being a function of the dimensionless strain rate, $\kappa_e D$, the stress also depends upon the dimensionless quantities

Ψ , d/λ , E_v/kT , and $P_k/3nP_p$, it is surprising that the results appear, within the scatter of the data, to fall on a single curve. This is particularly unexpected in view of the dissimilarity of the two oils used in the experiments and the fact that yet two other oils were used for the reduction of the data. This result may be fortuitous since the data plotted in dimensional form is originally close to a single curve, however, reduction to dimensionless form reduces the range of scatter from a factor of three to a factor of two, or roughly thirty per cent.

The general features of Smith's results may be seen in figure (8) where the data obtained using steel rollers is plotted in dimensional form. An increase in the pressure at constant temperature or a decrease in the temperature at constant pressure raises the stress level at which departure from Newtonian flow occurs. The behavior of the stress level is similar to that of G_∞ , therefore non-dimensionalizing the stresses with G_∞ can be expected to bring the results together, though there is no *a priori* reason for expecting them to collapse onto a single curve.

The experimental conditions for all but the lowest pressure and highest temperature were too far out of the range of the ASME data to permit extrapolation with any

degree of confidence, accordingly, only this case is shown in dimensionless form in figure (9). The calculated curve, together with the value of Ψ required to match the data is also displayed, and the fit is seen to be quite good.

In figure (10) Smith's results for a spherical aluminum free roller rolling on a cylindrical steel driven roller are shown. These results indicate that the shear stress at which departure from Newtonian flow occurs is independent of the rolling speed, even though, as has been discussed by Dyson, the rolling speed does affect the apparent viscosity. The reason for this behavior is still not understood. The calculated curve can again be fitted quite well to the measured data.

Crook's results, together with calculated curves for his average conditions, are shown in figure (11). Since these measurements were taken over a much narrower range of strain rates than Smith's, the effect of the scatter is much more pronounced.

In figure (12) we show the calculated results for the change in shear stress when some of the non-dimensional parameters are varied. A decrease in the values of Ψ , E_v/kT and d/λ produce an increase in the dimensionless stress at which departure from Newtonian flow takes place,

however, the variation of E_v/kT and d/λ , throughout the entire range encountered in the experiments, is insufficient to shift the calculated results out of the range of scatter of the data. This indicates that, in this range, the stresses are fairly insensitive to changes in E_v/kT and d/λ , and that the largest variation occurs as a result of changes in Ψ . Altering the ratio of the kinetic to potential pressure is found to have a negligible effect on the calculated results. The value of Ψ required to match the experimental data is a strong function of the values of G_∞ used to non-dimensionalize the stresses, thus any inaccuracies in G_∞ produce a corresponding error in Ψ .

Neither Crook nor Smith attempted to measure normal stress effects, nevertheless, since the theory predicts their presence, the calculated results are indicated in figure (13). In general, we see that σ_{yy} and σ_{xx} are both negative, suggesting that the flow causes an increase in the mean compressive stress. Further, since $(\sigma_{xx} - \sigma_{yy}) > 0$, the fluid is in tension along streamlines and in compression normal to the stream lines along the velocity gradient, when compared to the mean normal stress. Since σ_{zz} is a factor of approximately a hundred smaller than either σ_{xx} or σ_{yy} , the relative magnitude of

the stresses are very similar to those obtained for a Maxwell fluid. This resemblance to a Maxwell fluid is also shown by the low shear rate results, where it is seen that the normal stresses depend on the square of the strain rate. Changes in E_v/kT have very little effect on the normal stresses, however, decreases in Ψ and d/λ lead to an increase in their magnitude at the corresponding strain rates.

The variation of molecular strain with strain rate is shown in figure (14). The magnitude of the strains, for all the cases considered, is always less than 10^{-2} indicating that the small strain assumption should be valid for an entire range of flow. The stress, however, is a function of $v_{ij} = \delta_{ij} + (1 + d/\lambda)\epsilon_{ij}$, which for large values of d/λ can become large. Thus it is necessary to evaluate ϵ_{ij} without making the small strain assumption.

We can conclude that the present theory is capable of describing non-Newtonian behavior in a hard sphere fluid. In this theory the decrease in apparent viscosity with increasing strain rate can be caused by two effects. One is the increase in the jump probability of a molecule in a strained fluid, which takes place at high densities and high strain rates. This mechanism is characterized

by a high value of Ψ .

The other is that as the strain rate increases, the strain eventually reaches a limiting value. When this value is reached, an increase in the strain rate no longer causes an increase in the potential term of the stress tensor. This mechanism, as can be seen from equation (4.47) is characterized by a low value of $(d/\lambda)(P_k/3nP_p)$.

There is yet another mechanism which could be responsible for non-Newtonian behavior of liquids, but since it entails the addition of some more assumptions, it has not been included in the present theory. In associated liquids it is possible that the rate of making and breaking of hydrogen bonds is a function of the molecular strain or the strain rate. Since the jump probability of a molecule is dependent on whether or not it is hydrogen bonded to others, a decrease in the number of bonded molecules can lead to a decrease in the apparent viscosity of the liquid. Similar arguments could very well apply to any liquid whose molecules form clusters. The sizes and the number of clusters could be dependent on the strain rate, and since a molecule in a cluster would probably have a smaller jump probability than a free molecule, a decrease in the size and number of

clusters would lead to a decrease in the apparent viscosity.

4.3 Oscillatory Shear Flow

Consider the propagation of plane oscillating shear waves in a liquid. Let x be the direction of motion of the liquid and y be the direction of propagation of the shear wave. Assume that the amplitudes of the oscillations are sufficiently small that products of perturbation quantities may be neglected. Then the equations describing the flow can be linearized to give:

the molecular strain relaxation equation

$$\frac{\partial \epsilon_{xy}}{\partial t} + \frac{3\epsilon_{xy}}{\kappa} = \frac{A-B}{2} \frac{\partial u_x}{\partial y}, \quad (4.57)$$

the energy relaxation equation for no conduction

$$\frac{\partial \theta_{xy}}{\partial t} + \frac{3\theta_{xy}}{\tau} + \frac{3P_p}{\rho c_v T} \frac{\partial \epsilon_{xy}}{\partial t} = - \frac{3}{2\rho c_v} \left(\frac{\partial P}{\partial T} \right)_\rho \frac{\partial u_x}{\partial y}, \quad (4.58)$$

the momentum equation

$$\rho \frac{\partial u_x}{\partial t} = \frac{\partial \sigma_{xy}}{\partial y}, \quad (4.59)$$

and the stress

$$\sigma_{xy} = - p_k \epsilon_{xy} + \left[\frac{d}{\lambda} p_k - 3n p_p \right] \epsilon_{xy} \quad (4.60)$$

Assume that any perturbation quantity Q , varies as

$$Q = \tilde{Q} \exp(i\omega t + m^*y) \quad (4.61)$$

where ω is the angular frequency and m^* , is defined as

$$m^* \equiv -\alpha - \frac{i\omega}{c} \quad (4.62)$$

Here α is the absorption coefficient and c is the propagation velocity. It is further convenient to let

$$\kappa' = \kappa/3 \quad (4.63)$$

and

$$\tau' = \tau/3 \quad (4.64)$$

The equations which must be solved then become

$$i\omega\tilde{\epsilon}_{xy} + \tilde{\epsilon}_{xy}/\kappa' = \frac{A-B}{2} m^*\tilde{u}_x \quad (4.65)$$

$$i\omega\tilde{\theta}_{xy} + \tilde{\theta}_{xy}/\tau' + \frac{3P_p}{\rho c_v T} i\omega\tilde{\epsilon}_{xy} = -\frac{3}{2\rho c_v} \left(\frac{\partial P}{\partial T} \right)_\rho m^*\tilde{u}_x \quad (4.66)$$

$$i\omega\rho\tilde{u} = m^*\tilde{\sigma}_{xy} \quad (4.67)$$

and

$$\tilde{\sigma}_{xy} = -P_k \tilde{\theta}_{xy} + \left[\frac{d}{\lambda} P_k - 3nP_p \right] \tilde{\epsilon}_{xy} \quad (4.68)$$

Solving equations (4.65) and (4.66), we find that

$$\tilde{\epsilon}_{xy} = \frac{A-B}{2} \frac{m^*\tilde{u}_x \kappa'}{1 + i\omega\kappa'} \quad (4.69)$$

and

$$\tilde{\theta}_{xy} = - \frac{3}{2\rho c_v} \left(\frac{\partial P}{\partial T} \right)_\rho \frac{m^* \tilde{u}_x \tau'}{1 + i\omega\tau'} - \frac{3P}{\rho c_v T} \tilde{\epsilon}_{xy} \frac{i\omega\tau'}{1 + i\omega\tau'} \quad (4.70)$$

Substituting the expression for the stress, (4.68), in the momentum equation (4.67), and then using the expression obtained above for $\tilde{\epsilon}_{xy}$ and $\tilde{\theta}_{xy}$ we get

$$\begin{aligned} \left(\frac{i\omega}{m^*} \right)^2 = \frac{1}{\rho} \left\{ \frac{3P_k}{2\rho c_v} \left(\frac{\partial P}{\partial T} \right)_\rho \frac{i\omega\tau'}{1 + i\omega\tau'} - \frac{3P_k P}{\rho c_v T} \frac{A-B}{2} \frac{\omega\kappa'}{1 + i\omega\kappa'} \right. \\ \left. \times \frac{\omega\tau'}{1 + i\omega\tau'} + \left[\frac{d}{\lambda} P_k - 3nP_p \right] \frac{A-B}{2} \frac{i\omega\kappa'}{1 + i\omega\kappa'} \right\} \quad (4.71) \end{aligned}$$

In practice the quantity measured in oscillating shear experiments is the shear mechanical impedance, Z_s , defined by

$$Z_s \equiv \frac{\sigma_{xy}}{u_x} = R_s + iX_s \quad (4.72)$$

From the momentum equation we get

$$Z_s = \rho \left(\frac{i\omega}{m^*} \right) \quad (4.73)$$

which can be evaluated in terms of the fluid properties by using equation (4.71). Another commonly used quantity is the shear modulus, G , which is obtained from the

equation of motion for an elastic solid,

$$\rho \frac{\partial^2 \xi}{\partial t^2} = G \frac{\partial^2 \xi}{\partial y^2} \quad , \quad (4.74)$$

where ξ is the displacement in the x direction. To account for dissipation, G is made complex, and solving for oscillatory motion, equation (4.74) gives the complex shear modulus

$$G^* = \rho \left(\frac{i\omega}{m^*} \right)^2 = G' + iG'' \quad (4.75)$$

which can also be obtained from equation (4.71). The real and imaginary parts of the shear mechanical impedance can then be expressed as

$$R_s^2 = \frac{\rho G'}{2} \left\{ \left[1 + \left(\frac{G''}{G'} \right)^2 \right]^{\frac{1}{2}} + 1 \right\} \quad (4.76)$$

and

$$X_s^2 = \frac{\rho G'}{2} \left\{ \left[1 + \left(\frac{G''}{G'} \right)^2 \right]^{\frac{1}{2}} - 1 \right\} \quad (4.77)$$

For a Newtonian fluid, the equation of motion is

$$\rho \frac{\partial u_x}{\partial t} = \mu \frac{\partial^2 u_x}{\partial y^2} \quad , \quad (4.78)$$

and for oscillatory motion this yields

$$\left(\frac{i\omega}{\eta^*}\right)^2 = \frac{i\omega\mu}{\rho} \quad (4.79)$$

Comparing this expression with equation (4.75) we see that for a Newtonian fluid

$$G^* = i\omega\mu \quad (4.80)$$

which is purely imaginary.

For a loss-free solid,

$$G^* = \rho c_s^2 \quad (4.81)$$

which is real. Here c_s is the propagation velocity of the shear wave.

According to the present theory, the complex shea modulus is given by

$$G' = \frac{3}{2} \frac{P_k}{\rho c_v} \left(\frac{\partial P}{\partial T}\right)_\rho \frac{\omega^2 \tau'^2}{1 + \omega^2 \tau'^2} + \frac{A-B}{2} \left[\frac{d}{\lambda} P_k - 3nP_p \right] \frac{\omega^2 \kappa'^2}{1 + \omega^2 \kappa'^2} - \frac{3P_k P_p}{\rho c_v T} \frac{A-B}{2} \frac{\omega \kappa' \omega \tau' (1 - \omega \kappa' \omega \tau')}{(1 + \omega^2 \kappa'^2)(1 + \omega^2 \tau'^2)} \quad (4.82)$$

and

$$G'' = \frac{3}{2} \frac{P_k}{\rho c_v} \left(\frac{\partial P}{\partial T}\right)_\rho \frac{\omega \tau'}{1 + \omega^2 \tau'^2} + \frac{A-B}{2} \left[\frac{d}{\lambda} P_k - 3nP_p \right] \frac{\omega \kappa'}{1 + \omega^2 \kappa'^2} + \frac{3P_k P_p}{\rho c_v T} \frac{A-B}{2} \frac{\omega \kappa' \omega \tau' (\omega \kappa' + \omega \tau')}{(1 + \omega^2 \kappa'^2)(1 + \omega^2 \tau'^2)} \quad (4.83)$$

Taking the low frequency limit, we find that

$$\lim_{\omega \rightarrow 0} G^* = i\omega \left[\frac{3}{2} \frac{P_k}{\rho c_v} \left(\frac{\partial P}{\partial T} \right)_\rho \tau' + \frac{A-B}{2} \left(\frac{d}{\lambda} P_k - 3nP_p \right) \kappa' \right] \quad (4.84)$$

and comparing this to equation (4.33) we see that

$$\lim_{\omega \rightarrow 0} G^* = i\omega\mu \quad (4.85)$$

This expression is the same as equation (4.80), thus in the low frequency limit our theory predicts Newtonian behavior.

In the limit of high frequency, we get

$$\lim_{\omega \rightarrow \infty} G^* = \frac{3}{2} \frac{P_k}{\rho c_v} \left(\frac{\partial P}{\partial T} \right)_\rho + \left(\frac{d}{\lambda} P_k - 3nP_p \right) \frac{A-B}{2} + \frac{3P_k P_p}{\rho c_v T} \frac{A-B}{2} \quad (4.86)$$

which is real, and independent of frequency. Thus in this limit, our theory predicts that the fluid behaves like an elastic solid.

The highest frequencies which can presently be obtained by experiment are in the neighborhood of 1 GHz, and since τ' is of order 10^{-13} seconds, the terms involving the product $\omega\tau'$ are very small. The molecular strain relaxation times of many liquids are of order 10^{-8} or greater, thus these relaxation effects can be measured.

The measurable complex shear modulus is

$$G^* = \frac{A-B}{2} \left(\frac{d}{\lambda} P_k - 3nP_p \right) \left[\frac{\omega^2 \kappa'^2}{1 + \omega^2 \kappa'^2} + i \frac{\omega \kappa'}{1 + \omega^2 \kappa'^2} \right], \quad (4.87)$$

which describes exactly the behavior of a single relaxation time Maxwell fluid whose infinite frequency shear modulus is

$$G_\infty = \frac{A-B}{2} \left(\frac{d}{\lambda} P_k - 3nP_p \right) \quad . \quad (4.88)$$

With this result, the low frequency, or low strain rate, viscosity can be expressed as

$$\mu = G_\infty \tau' \quad . \quad (4.89)$$

The very high frequencies required to study molecular relaxation processes can best be obtained by utilizing piezoelectric crystal transducers. Mason *et al.* (Ref. 49) developed a technique for obtaining the shear mechanical impedance of a liquid by measuring the reflection coefficient of an incident shear wave at the crystal-liquid interface. This method has been employed and modified by many others to perform experiments on a wide variety of liquids (Ref. 9).

So far only two liquids have been found which conform to the single relaxation time behavior predicted by both

the present theory and the Maxwell fluid model. These are molten zinc chloride (Ref. 50) and boric oxide (Ref. 51). The measurements on boric oxide were carried out over a wide range of temperatures, and it was found that above 800°C the fluid exhibits single relaxation time behavior, while below this temperature the width of the relaxation region increases with decreasing temperature.

Up to the present time, all other liquids, on which oscillatory shear experiments have been performed, exhibit a relaxation region which is broader than that predicted for a single relaxation time process. This behavior has generally been analyzed by postulating that the viscoelastic behavior can be represented by the summation of discrete single relaxation time processes, and then determining the spectrum of relaxation times required to fit the data. As has been pointed out by Barlow *et al.* (Ref. 52), this procedure does not yield a unique distribution, nor does it give a physical description of the process. As an alternative approach, Barlow, Erginsav and Lamb (Ref. 53) have suggested that the shear ~~mechanical impedance of a viscoelastic liquid can be~~ represented by a parallel combination of impedances characterizing a solid and a Newtonian fluid. This

procedure has had a fair degree of success in describing the relaxation behavior of some fluids. A comparison of the results obtained, for the real and imaginary parts of the shear mechanical impedance, using this model and the single relaxation time theory is presented in figure (15).

An attempt at a physical explanation for the width of the relaxation region has been provided by Litovitz and McDuffie (Ref. 54) who in a qualitative way attribute it to the requirement of cooperative motion of neighboring molecules to provide the free volume necessary for molecular rearrangement.

Another possible explanation for this behavior could be the effect of molecular clusters in the liquid. At high temperatures the number and sizes of the clusters would be small, meaning that all the molecules would essentially be free. This would lead to a single relaxation time behavior. As the temperature is decreased, the number and sizes of clusters would increase, making the liquid a mixture consisting of a wide range of cluster sizes. This would lead to a spread in the range of the relaxation region with decreasing temperature, as observed in B_2O_3 .

There does not yet appear to be a satisfactory quantitative physical explanation of the width of the visco-

elastic relaxation region.

Barlow and Lamb (Ref. 55) have experimentally studied the behavior of three lubricating oils possessing high, medium and low viscosity indices. All of these exhibited a relaxation region which was broader than that predicted by single relaxation time theory, however, it is of interest to see how well the present theory predicts the magnitude of the limiting high frequency shear modulus, G_{∞} . The viscosities, at 30°C, of the high, medium and low viscosity index oils were respectively 3.54, 2.08 and 4.52 poise, while those of oils 29-F and 17-D were 1.6 and 0.12 poise. Thus we would expect oil 29-F to be more similar to the oils used by Barlow and Lamb than oil 17-D, and thus provide a better comparison.

Using the values of d/λ obtained by fitting the low shear rate viscosity data, the calculated results for G_{∞} were 7.2×10^9 and 3.9×10^9 dyne/cm² for oils 29-F and 17-D respectively. The measured values obtained by Barlow and Lamb were 7.0×10^9 , 7.8×10^9 and 7.0×10^9 dyne/cm² for the high, medium and low viscosity index oils in that order. Since there were no adjustable parameters in the calculation of G_{∞} , these results must certainly be considered to be encouraging.

Comparing the experimental results for oscillatory

and steady shear flows it has been noted (Ref. 46) that departure from Newtonian flow occurs at much lower strain rates for the latter case than the former. This feature cannot be explained on the basis of the Maxwell model since the values of G_{∞} required to describe the two flows by this model differ by a factor of about 10^3 . The present theory, however, can account for this disparate behavior on the basis of the difference in magnitude of the molecular strains encountered. One consequence of this is that the behavior of a liquid under conditions of steady shearing flow cannot, on the basis of the present theory, be deduced from oscillatory shear experiments.

4.4 Absorption and Dispersion of Longitudinal Waves

Consider the propagation, in the x-direction, of plane longitudinal periodic waves of infinitesimal amplitude. In most liquids, excluding the liquid metals whose thermal conductivities are high, the effects of conduction are very small compared to the effects of viscosity (Ref. 5). Further, when the period of the sound wave is large compared to the relaxation times of the fluid, the effects of viscosity and thermal conductivity on the absorption add linearly. Therefore, to simplify the analysis, thermal conduction is ignored.

The equations which must be solved are then:

continuity

$$\frac{1}{\rho} \frac{D\rho}{Dt} + \frac{\partial u_x}{\partial x} = 0, \quad (4.90)$$

molecular strain relaxation

$$\frac{\partial \epsilon_{xx}}{\partial t} + \frac{3\epsilon_{xx}}{\kappa} - \frac{1}{3\rho} \frac{D\rho}{Dt} = A \frac{\partial u_x}{\partial x}, \quad (4.91)$$

energy

$$\rho c_v \frac{DT}{Dt} = -T \left(\frac{\partial P}{\partial T} \right)_\rho \frac{\partial u_x}{\partial x}, \quad (4.92)$$

energy relaxation

$$\frac{\partial \theta_{xx}}{\partial t} + \frac{3\theta_{xx}}{\tau} = -\frac{3}{\rho c_v} \left(\frac{\partial P}{\partial T} \right)_\rho \frac{\partial u_x}{\partial x} - \frac{3P}{\rho c_v T} \frac{\partial \epsilon_{xx}}{\partial t} - \frac{1}{T} \frac{DT}{Dt}, \quad (4.93)$$

momentum

$$\rho \frac{Du_x}{Dt} = \frac{\partial S_{xx}}{\partial x}, \quad (4.94)$$

and the dynamical equation of state

$$S_{xx} = -\rho RT_{xx} \left(1 + \frac{d}{\lambda_{xx}} \right) + \frac{P}{(1 + \epsilon_{xx})^{3n}}, \quad (4.95)$$

$$= -P + \sigma_{xx}$$

We now write the local equilibrium quantities as

$$T = T_o(1 + \theta) \quad (4.96)$$

and

$$\rho = \rho_o(1 + s) \quad (4.97)$$

where the subscript o refers to the mean values, and θ and s are much less than one. The derivative of S_{xx} with respect to x , can then be written in terms of the derivatives of the perturbation quantities, and the momentum equation can be expressed as

$$\begin{aligned} \rho_o \frac{\partial u_x}{\partial t} = & - \rho_o \left(\frac{\partial P}{\partial \rho} \right)_T \frac{\partial s}{\partial x} - T_o \left(\frac{\partial P}{\partial T} \right)_\rho \frac{\partial \theta}{\partial x} - \\ & - P_{ko} \frac{\partial \theta_{xx}}{\partial x} + \left[\frac{d}{\lambda_o} P_{ko} - 3n P_{po} \right] \frac{\partial \epsilon_{xx}}{\partial x} . \end{aligned} \quad (4.98)$$

If we now let the perturbation quantities vary as

$$Q = \tilde{Q} \exp(m^*x + i\omega t)$$

and make the substitutions $\kappa' = \kappa/3$ and $\tau' = \tau/3$, the algebraic equations which must be solved are:

continuity

$$i\omega \tilde{s} = - m^* \tilde{u} \quad , \quad (4.99)$$

molecular strain relaxation

$$i\omega \tilde{\epsilon}_{xx} + \frac{\tilde{\epsilon}_{xx}}{\kappa'} = \frac{2}{3} (A-B) m^* \tilde{u}_x, \quad (4.100)$$

energy

$$\rho_o c_v i\omega \tilde{\Theta} = - \left(\frac{\partial P}{\partial T} \right)_\rho m^* \tilde{u}, \quad (4.101)$$

energy relaxation

$$i\omega \tilde{\theta}_{xx} + \frac{\tilde{\theta}_{xx}}{\tau'} = - \frac{2}{\rho_o c_v} \left(\frac{\partial P}{\partial T} \right)_\rho m^* \tilde{u} - \frac{3P \rho_o}{\rho_o c_v T_o} i\omega \tilde{\epsilon}_{xx}, \quad (4.102)$$

and momentum

$$\begin{aligned} \rho_o i\omega \tilde{u}_x = & - \rho_o \left(\frac{\partial P}{\partial \rho} \right)_T m^* \tilde{s} - T_o \left(\frac{\partial P}{\partial T} \right)_\rho m^* \tilde{\Theta} - P_k m^* \tilde{\theta}_{xx} \\ & + \left[\frac{d}{\lambda_o} P_{ko} - 3n P_{po} \right] m^* \tilde{\epsilon}_{xx}. \end{aligned} \quad (4.103)$$

The solutions for the perturbation quantities are easily found to be

$$\tilde{s} = - \left(\frac{m^*}{i\omega} \right) \tilde{u}_x, \quad (4.104)$$

$$\tilde{\epsilon}_{xx} = + \frac{2}{3} (A-B) \frac{\omega \kappa'}{1 + i\omega \kappa'} \left(\frac{m^*}{i\omega} \right) \tilde{u}_x, \quad (4.105)$$

$$\tilde{\Theta} = - \frac{1}{\rho_o c_v} \left(\frac{\partial P}{\partial T} \right)_\rho \left(\frac{m^*}{i\omega} \right) \tilde{u}_x, \quad (4.106)$$

and

$$\tilde{\theta}_{xx} = - \frac{2}{\rho_o c_v} \left(\frac{\partial P}{\partial T} \right)_\rho \frac{i\omega\tau'}{1+i\omega\tau'} \left(\frac{m^*}{i\omega} \right) \tilde{u}_x - \frac{3P_{po}}{\rho_o c_v T_o} \frac{i\omega\tau'}{1+i\omega\tau'} \tilde{\epsilon}_{xx} \quad (4.107)$$

Substituting these expressions into equation (4.103), and separating the real and imaginary parts, the complex longitudinal modulus

$$M^* = M' + iM'' = \rho_o \left(\frac{i\omega}{m^*} \right)^2 \quad (4.108)$$

can be expressed in terms of physical quantities as

$$\begin{aligned} M' = & \rho_o \left(\frac{\partial P}{\partial \rho} \right)_T + \frac{T_o}{\rho_o c_v} \left(\frac{\partial P}{\partial T} \right)_\rho^2 + \frac{2P_{ko}}{\rho_o c_v} \left(\frac{\partial P}{\partial T} \right)_\rho \frac{\omega^2 \tau'^2}{1+\omega^2 \tau'^2} + \\ & (A-B) \frac{2P_{ko} P_{po}}{\rho_o c_v T_o} \frac{\omega\tau'\omega\kappa'(\omega\tau'\omega\kappa' - 1)}{(1+\omega^2 \kappa'^2)(1+\omega^2 \tau'^2)} + \frac{2}{3} (A-B) \times \\ & \times \left(\frac{d}{\lambda} P_{ko} - 3nP_{po} \right) \frac{\omega^2 \kappa'^2}{1+\omega^2 \kappa'^2} \end{aligned} \quad (4.109)$$

and

$$\begin{aligned} M'' = & \frac{2P_{ko}}{\rho_o c_v} \left(\frac{\partial P}{\partial T} \right)_\rho \frac{\omega\tau'}{1+\omega^2 \tau'^2} + \frac{2P_{ko} P_{po}}{\rho_o c_v T_o} (A-B) \frac{\omega\tau'\omega\kappa'(\omega\tau' + \omega\kappa')}{(1+\omega^2 \kappa'^2)(1+\omega^2 \tau'^2)} + \\ & + \frac{2}{3} (A-B) \left(\frac{d}{\lambda_o} P_{ko} - 3nP_{po} \right) \frac{\omega\kappa'}{1+\omega^2 \kappa'^2} \end{aligned} \quad (4.110)$$

The low frequency sound speed is

$$c_o^2 = \lim_{\omega \rightarrow 0} \frac{M'}{\rho_o}$$

$$= \left(\frac{\partial P}{\partial \rho} \right)_T + \frac{T_o}{\rho_o^2 c_v} \left(\frac{\partial P}{\partial T} \right)_\rho^2 \quad (4.111)$$

Using standard thermodynamic relations this can be rewritten in the familiar form

$$c_o^2 = \gamma \left(\frac{\partial P}{\partial \rho} \right)_T \quad (4.112)$$

where γ is the ratio of specific heats.

If we make the approximation

$$\frac{\alpha c}{\omega} \ll 1 \quad ,$$

a condition fulfilled by most liquids (Ref. 9), the propagation velocity can be expressed as

$$c^2 = \frac{M'}{\rho_o} \quad , \quad (4.113)$$

and looking at equation (4.109) we see that velocity dispersion is predicted. Since at the present time measurements cannot be performed at frequencies of comparable magnitude to the collision frequencies in liquids, the terms involving $\omega\tau$ are small and the measurable velocity dispersion is given by

$$c^2 = c_o^2 + \frac{2}{3} \frac{(A-B)}{\rho_o} \left(\frac{d}{\lambda_o} P_{ko} - 3nP_{po} \right) \frac{\omega^2 \kappa'^2}{1 + \omega^2 \kappa'^2} \quad (4.114)$$

which using equation (4.88) can be rewritten as

$$c^2 = c_o^2 + \frac{4}{3} \frac{G_\infty}{\rho_o} \frac{\omega^2 \kappa'^2}{1 + \omega^2 \kappa'^2} \quad (4.115)$$

This is the result for a viscoelastic fluid with no bulk viscosity (Ref. 56).

The absorption, α , can be obtained from the relation

$$\alpha = \frac{\omega}{2c^3} \frac{M''}{\rho_o} \quad (4.116)$$

and it can be seen to exhibit two maxima, one at $\omega\kappa' = 1$ and the other at $\omega\tau' = 1$. For low frequencies the absorption becomes

$$\alpha = \frac{2}{3} \frac{\omega^2}{\rho_o c_o^3} \left(\frac{P_{ko}}{2\rho_o c_v} \left(\frac{\partial P}{\partial T} \right)_\rho \tau + \frac{A-B}{6} \left(\frac{d}{\lambda_o} P_{ko} - 3nP_{po} \right) \kappa \right) \quad (4.117)$$

and comparing this to equation (4.35) we find that

$$\alpha = \frac{2}{3} \frac{\omega^2 \mu}{\rho_o c_o^3} \quad (4.118)$$

which is just the classical result for the case of no heat conduction. We can thus see that the present theory

predicts a zero bulk, or volume viscosity for a hard sphere liquid. This disagrees with experimental results which indicate that monatomic liquids such as liquid argon (Ref. 57) and several liquid metals (Refs. 58, 59) exhibit excess absorption. The reason for this discrepancy is that all the relaxation mechanisms have not been considered in the theory so far.

Generally in nonassociated liquids the major causes of excess absorption are rotational isomerism and vibrational relaxation, whereas in associated liquids the effects of structural relaxation are most important. Structural relaxation has also been suggested to be responsible for the existence of volume viscosity in monatomic liquids (Refs. 9, 58, 59). This effect could arise in the following fashion.

It is well known, through the property of critical opalescence, that liquids near the critical point exhibit large, local density fluctuations caused by the continuous agglomeration and breakup of large clusters of molecules. These clusters often contain on the order of millions of molecules. Away from the critical point, clustering should still occur to some extent in most liquids. The equilibrium numbers and sizes of the clusters are determined by the local thermodynamic conditions, and any

changes in these conditions lead to potential energy changes due to the varying structure of the liquid. There is therefore associated with this process a characteristic time, or structural relaxation time, which describes the equilibration of the cluster size and number distribution after a perturbation of the equilibrium conditions. This process can therefore lead to absorption in excess of that predicted by the classical mechanisms of viscosity and conduction.

CHAPTER V

SUMMARY AND CONCLUSIONS

A relatively simple theory to account for the dynamical behavior of liquids has been proposed, using a molecular viewpoint, to obtain general dynamical equations similar to the phenomenological relaxation equations first advanced by Maxwell (Ref. 10). The theory is based on the concept that in a continuously straining liquid distortions from spherical symmetry of the average molecular spacing, and the average random translational energy of the molecules, take place. This leads to the definition of a molecular strain tensor to describe the deviation of the radial distribution function from its equilibrium value, and a translational temperature tensor to describe the directional dependence of the random translational energy of the molecules. If all disturbances are removed from the fluid, the radial and velocity distribution functions eventually revert to spherical symmetry at rates characterized by the relaxation times for each process. The relaxation time for equilibration of translational kinetic energy has been identified with the collision time, while the time required to obtain isotropicity of molecular spacing has been related to the

time required for a molecule to jump into a neighboring vacancy.

A dynamical equation of state has been obtained, using statistical mechanical techniques, by postulating that directionally dependent, quasi equilibrium, velocity and radial distribution functions could be written. The stress tensor has thus been related to the molecular strain and translational temperature tensors by evaluating the partition function obtained from simple cell theory and considering the distortion of the free volume.

The equations obtained from the proposed theory have been solved for the problems of steady shearing flow, the propagation of oscillating shear waves, and the propagation of longitudinal waves.

For steady shear flow the solutions indicate that at slow shear rates the flow is Newtonian, and an expression for the viscosity of a liquid similar to the very successful Macedo-Litovitz equation is obtained. This equation has been applied, with good success, to the pressure and temperature dependence of the viscosity of two lubricating oils.

At high shear rates, the decrease in apparent viscosity with increasing strain rate observed by both Smith and Crook (Refs. 40, 41) in their EHD lubrication experi-

ments, can be described using the present theory. The reduction in apparent viscosity can be attributed to the enhanced jump probability of the molecules caused by the distortion of the radial distribution function from spherical symmetry. Calculations also predict the existence of normal stresses whose relative magnitudes are similar to those obtained for a simple Maxwell fluid.

Under conditions of oscillatory shear, results obtained from the present theory indicate that a liquid behaves like a Newtonian fluid at low frequency and like an elastic solid at high frequency. The relaxation region between these limits is described by precisely the same expression as for a Maxwell fluid with a single relaxation time. Experiments indicate, however, that for most liquids the relaxation region is in general broader than that described by single relaxation time theory. This discrepancy has been attributed to the presence of molecular clusters. The calculated numerical values of the high frequency shear modulus for the two lubricating oils considered in the high shear rate experiments, turn out to be of the same order of magnitude as those measured by Barlow and Lamb (Ref. 55) in oscillatory shear.

The theory which has been proposed also provides a satisfactory qualitative description of the propagation

of longitudinal waves in a liquid. At low frequencies both the sound speed and the absorption are found to have classical values, and at higher frequencies velocity dispersion with a single relaxation time is obtained. The experimentally observed excess absorption in monatomic liquids, indicating a non-zero bulk viscosity, is again attributable to the presence of molecular clusters.

A general feature of all the cases studied so far is that classical results are predicted for low strain rates, and that as the strain rate is increased, the behavior of the liquid becomes viscoelastic. The present theory is, however, superior to the phenomenological viscoelastic theories in that the elastic moduli are all expressed in terms of molecular and thermodynamic properties. Thus from a qualitative viewpoint a good description of the dynamical behavior of liquids is provided. Nevertheless, some discrepancies in the quantitative results exist. These are due to a large extent to the fact that other relaxation processes, such as thermal and structural relaxation, have not been included.

Thermal relaxation effects can be incorporated into the present theory in precisely the same way as they have been added to the classical theory as described by Herzfeld and Litovitz (Ref. 5). This is done by adding

the applicable energy mode to the energy equation and by writing relaxation equations connecting this mode to the other modes between which energy exchange occurs. The results which have been obtained previously by relaxation theory are then also applicable to the present theory.

Structural relaxation is at present not nearly as well understood as thermal relaxation. One promising approach in trying to gain some understanding of this process is to view the liquid as a mixture of molecular clusters of varying density, and defining a distribution function which describes the probability that a molecule is located in a cluster with a particular mean spacing. This method has been used with some success by Kerley (Ref.60) to describe the thermodynamic properties of liquid argon and hydrogen. If it would be possible to relate this distribution function to flow conditions, it should be feasible to write relaxation equations which describe the behavior of the clusters under dynamic conditions, and in such a manner account for the excess absorption and the width of the relaxation region.

Further improvements which could be made to the theory are to use a better approximation to the partition function than that provided by simple cell theory and to obtain a more accurate expression for the collision

frequency in the liquid. Experimentally it would be useful if high shear rate and oscillating shear experiments could be performed on the same liquid, and if thermodynamic data and transport properties for this liquid could be obtained in the high pressure range of the steady shear flow experiments.

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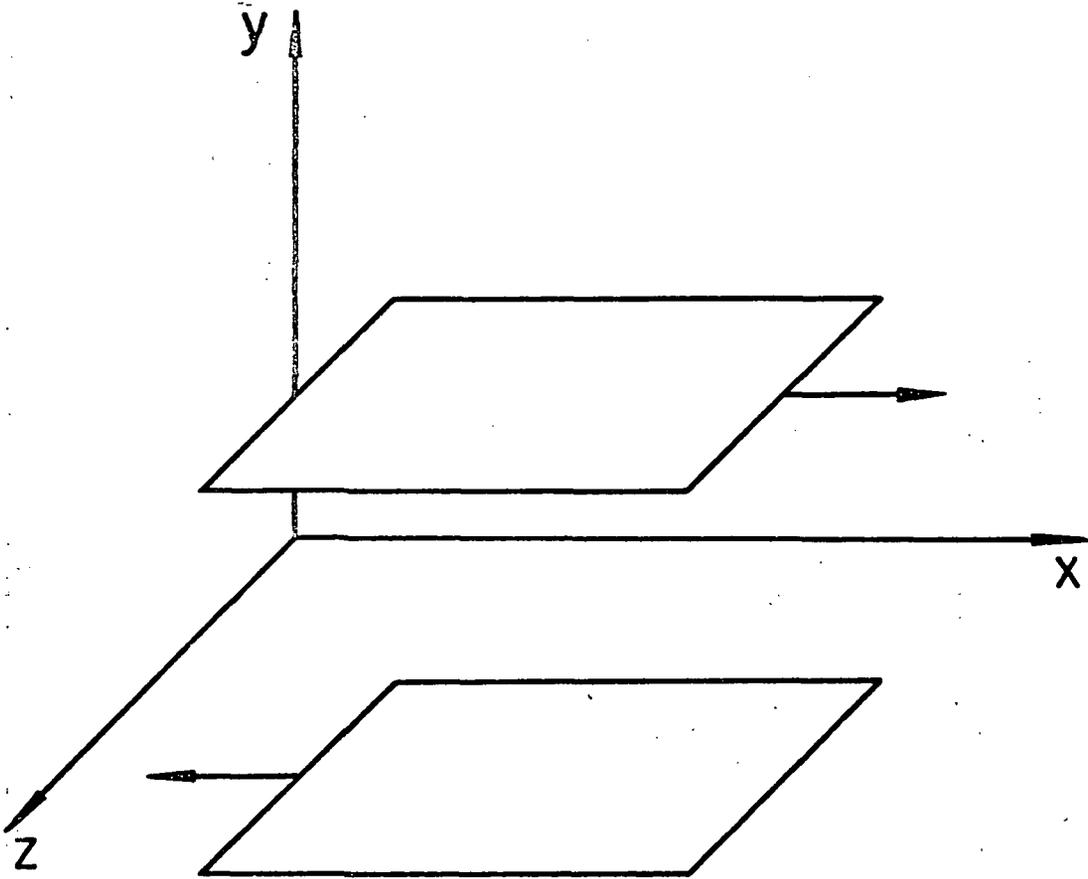


Figure 1. Coordinate system for steady shear flow

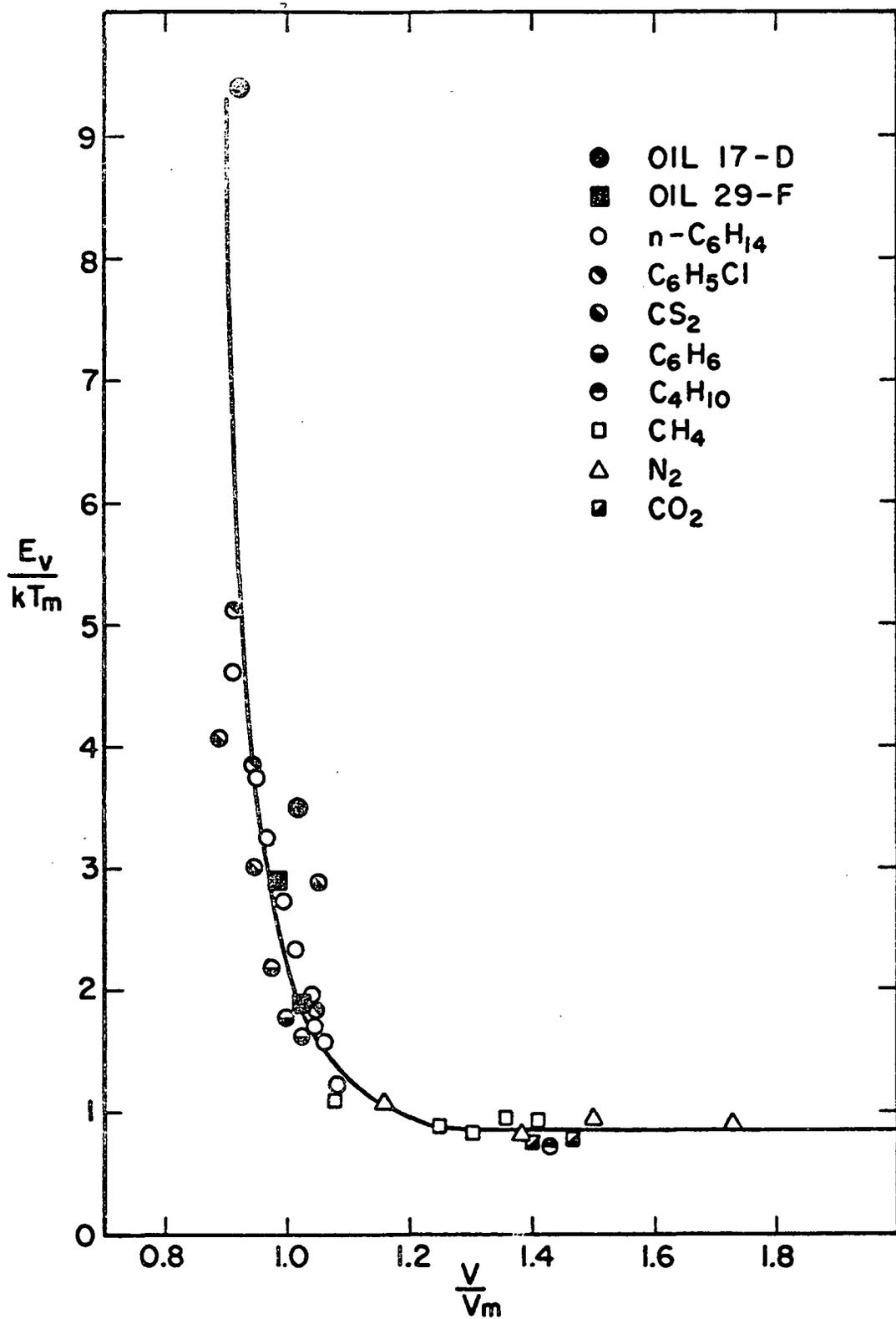


Figure 2. The energy required for a molecular jump as a function of volume

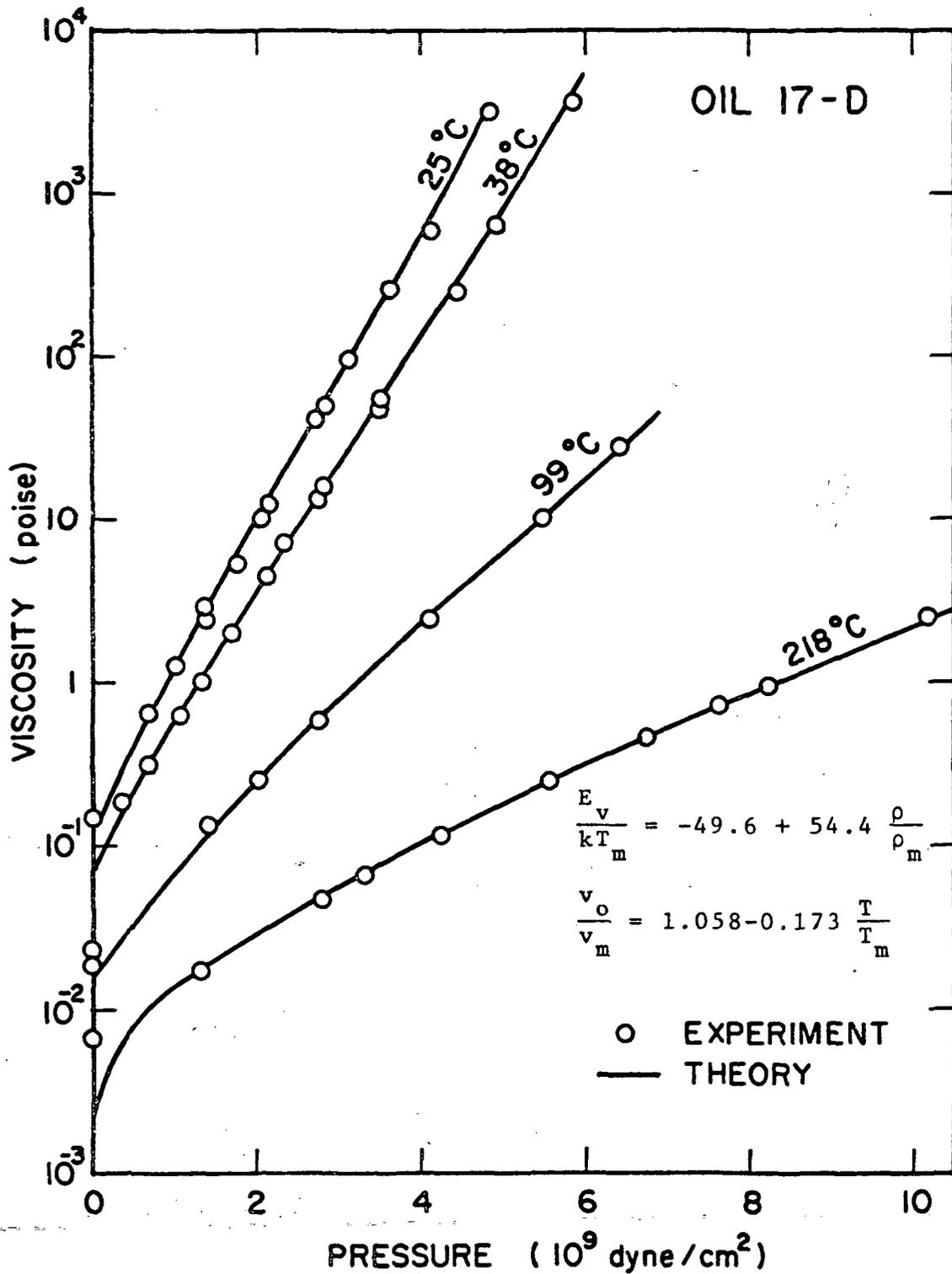


Figure 3. The viscosity of Oil-17D as a function of temperature and pressure

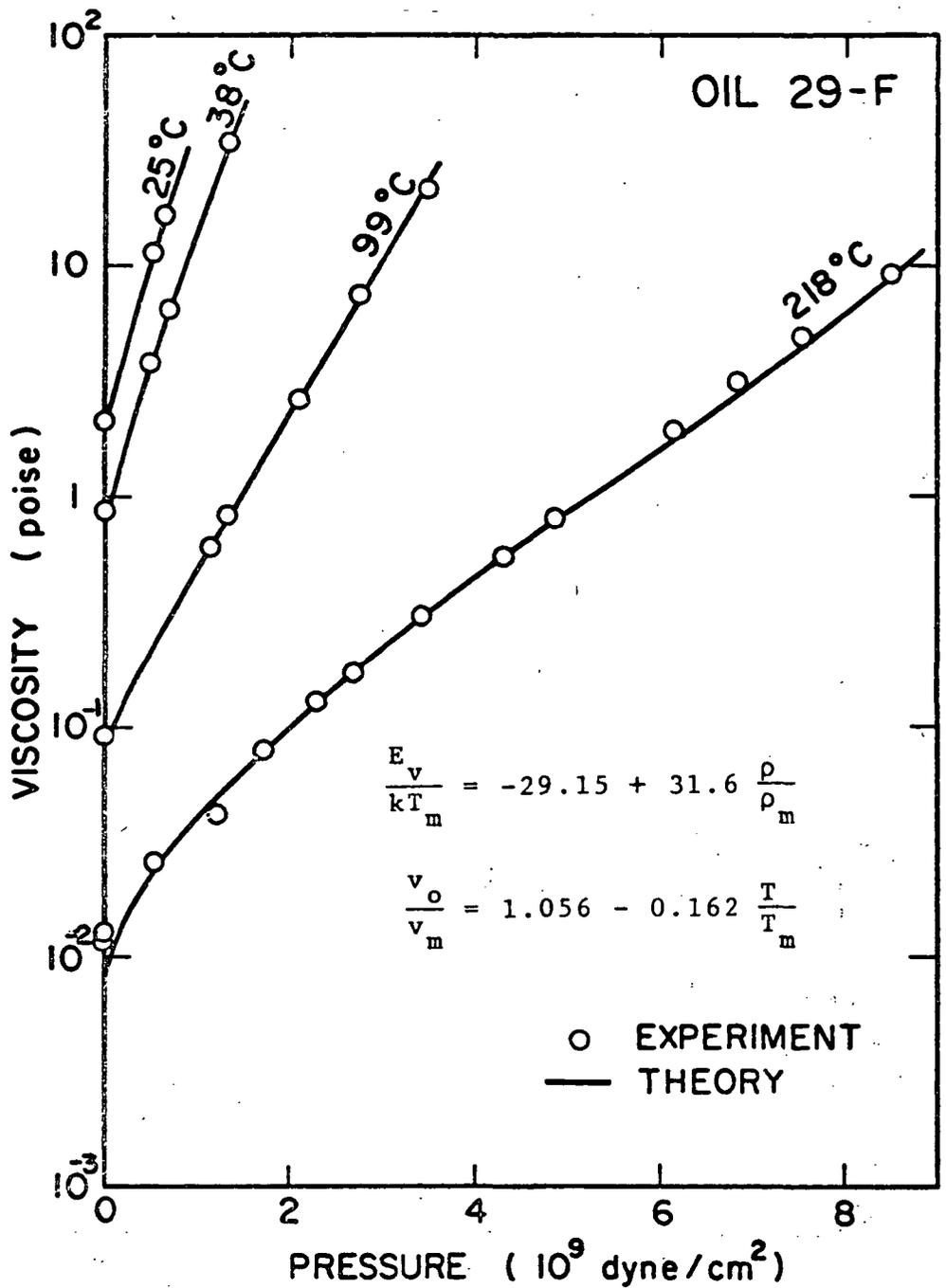


Figure 4. The viscosity of Oil 29-F as a function of temperature and pressure

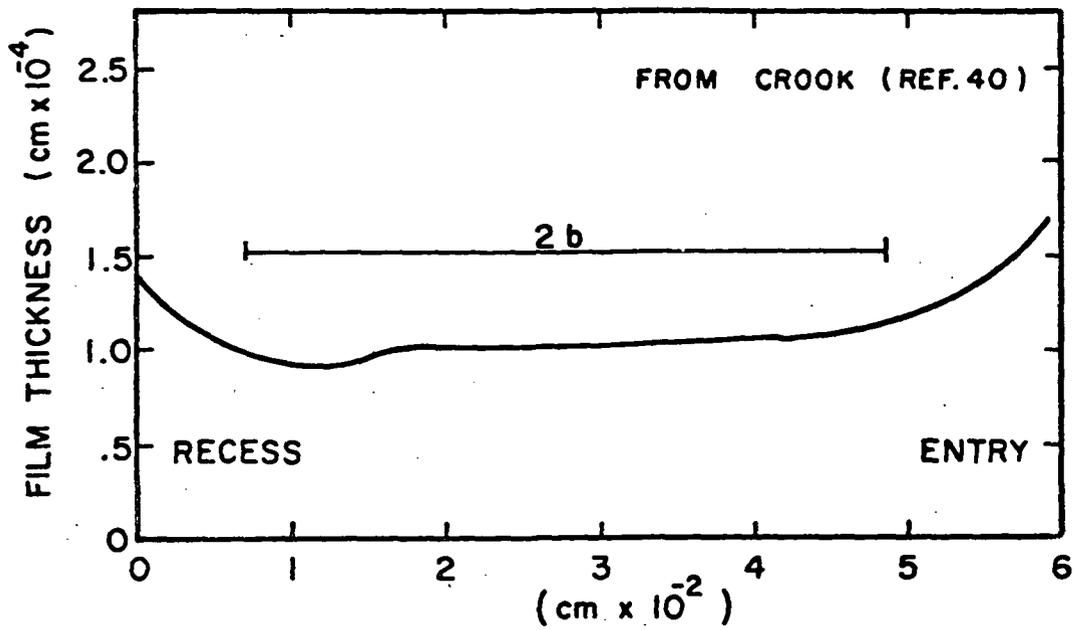


Figure 5. Typical film thickness variation in EHD lubrication

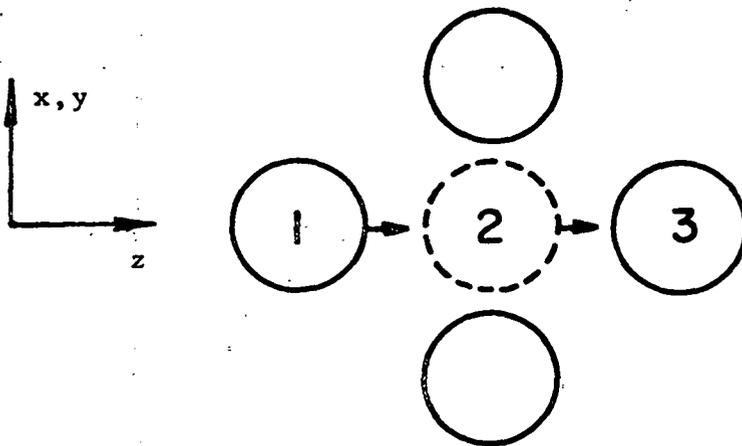


Figure 6. Mechanism of a molecular jump

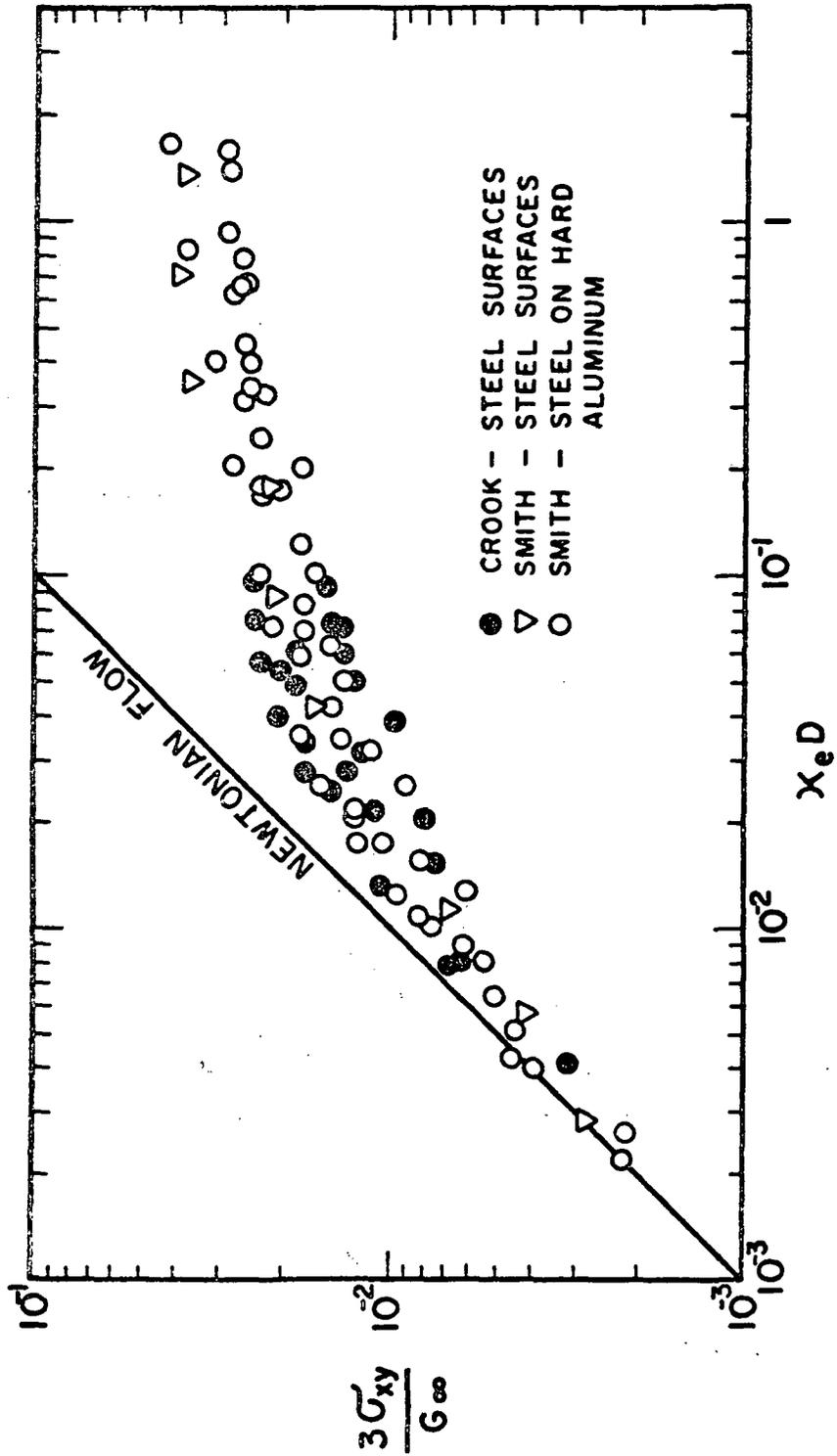


Figure 7. Measured variation of the dimensionless shear stress as a function of the strain rate

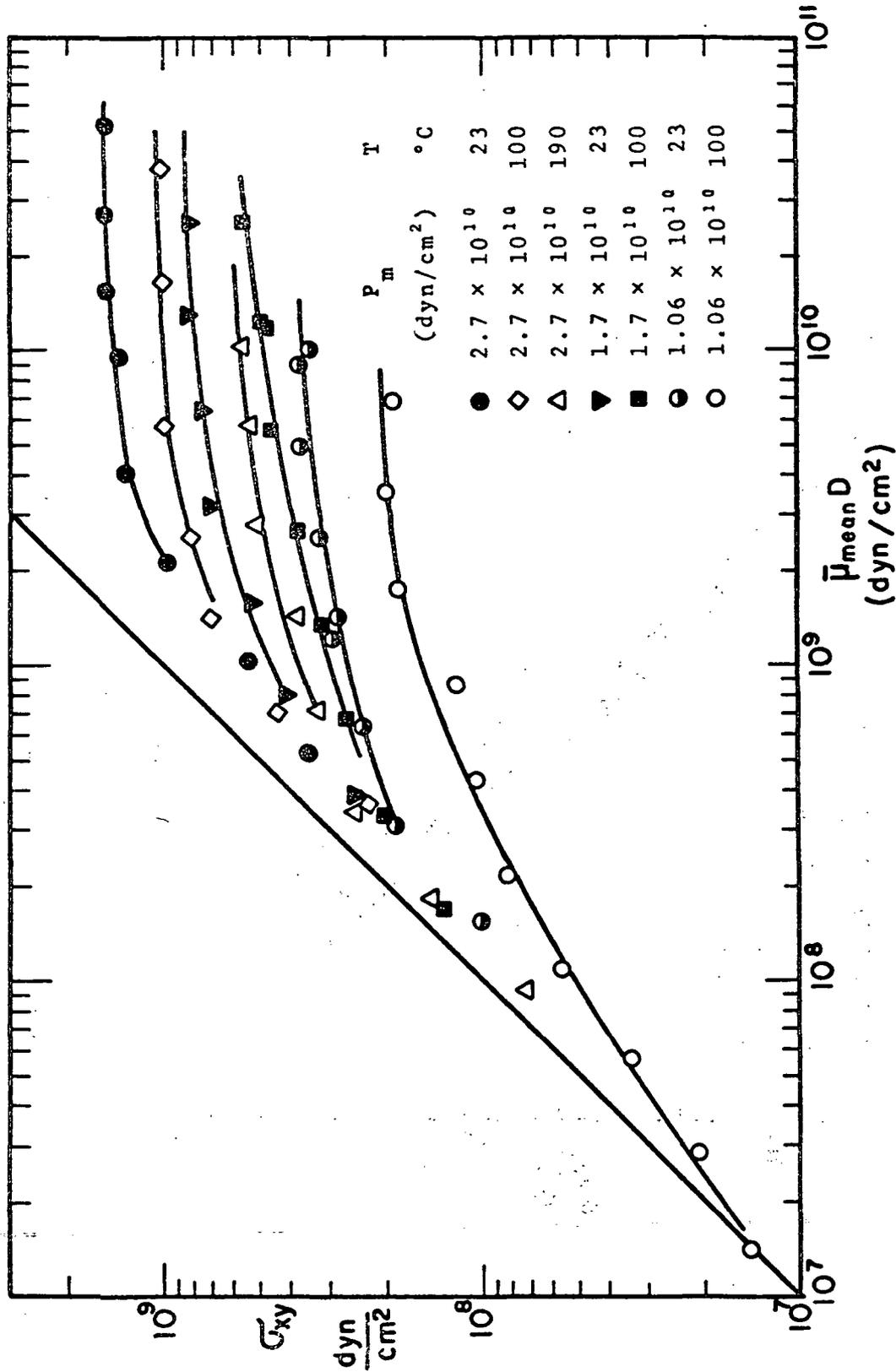


Figure 8. Variation of shear stress as a function of strain rate and load, as obtained by Smith using steel rollers

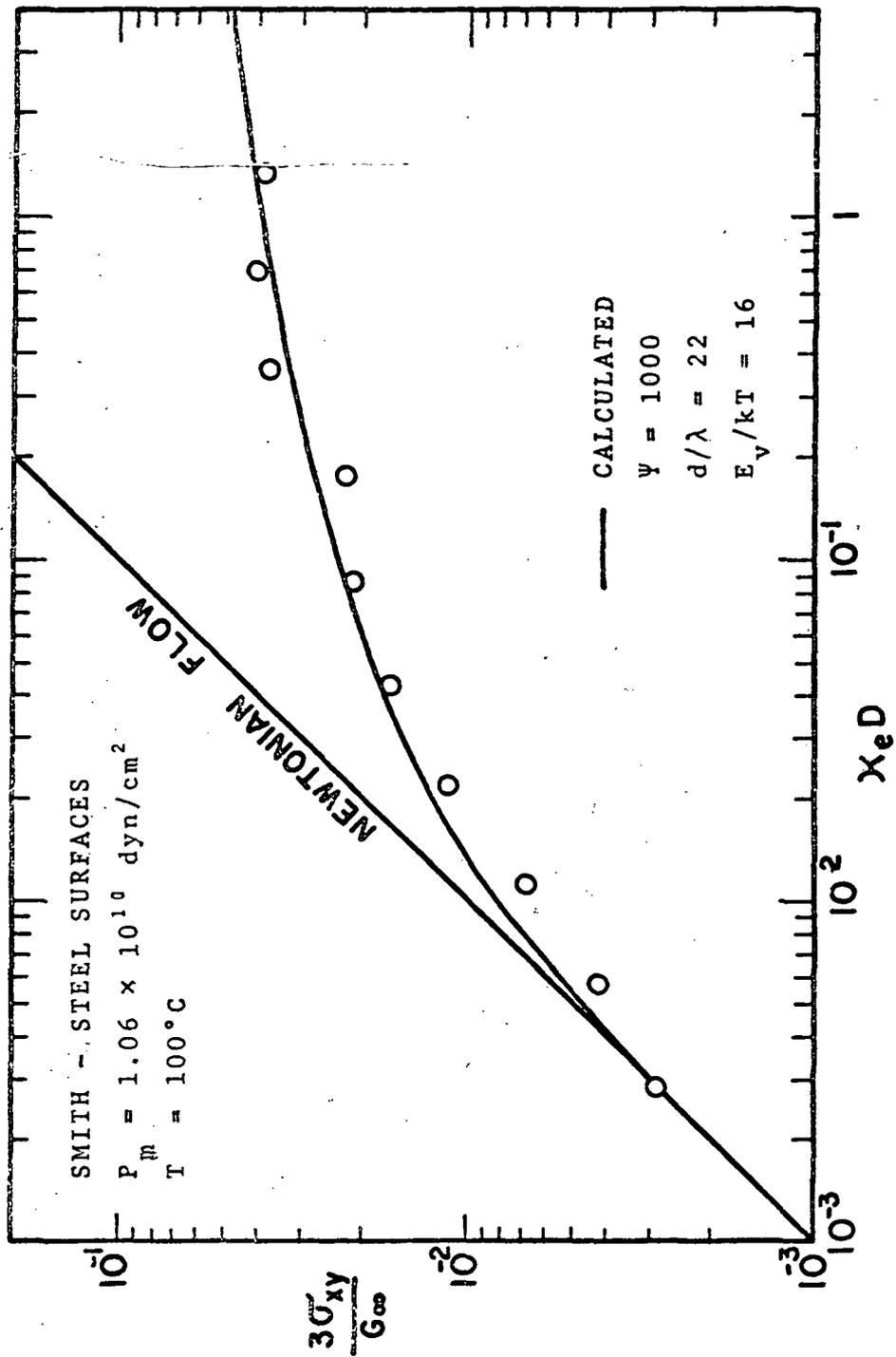


Figure 9. Comparison of measured and calculated shear stress variation as a function of strain rate. Results of Smith using steel rollers.

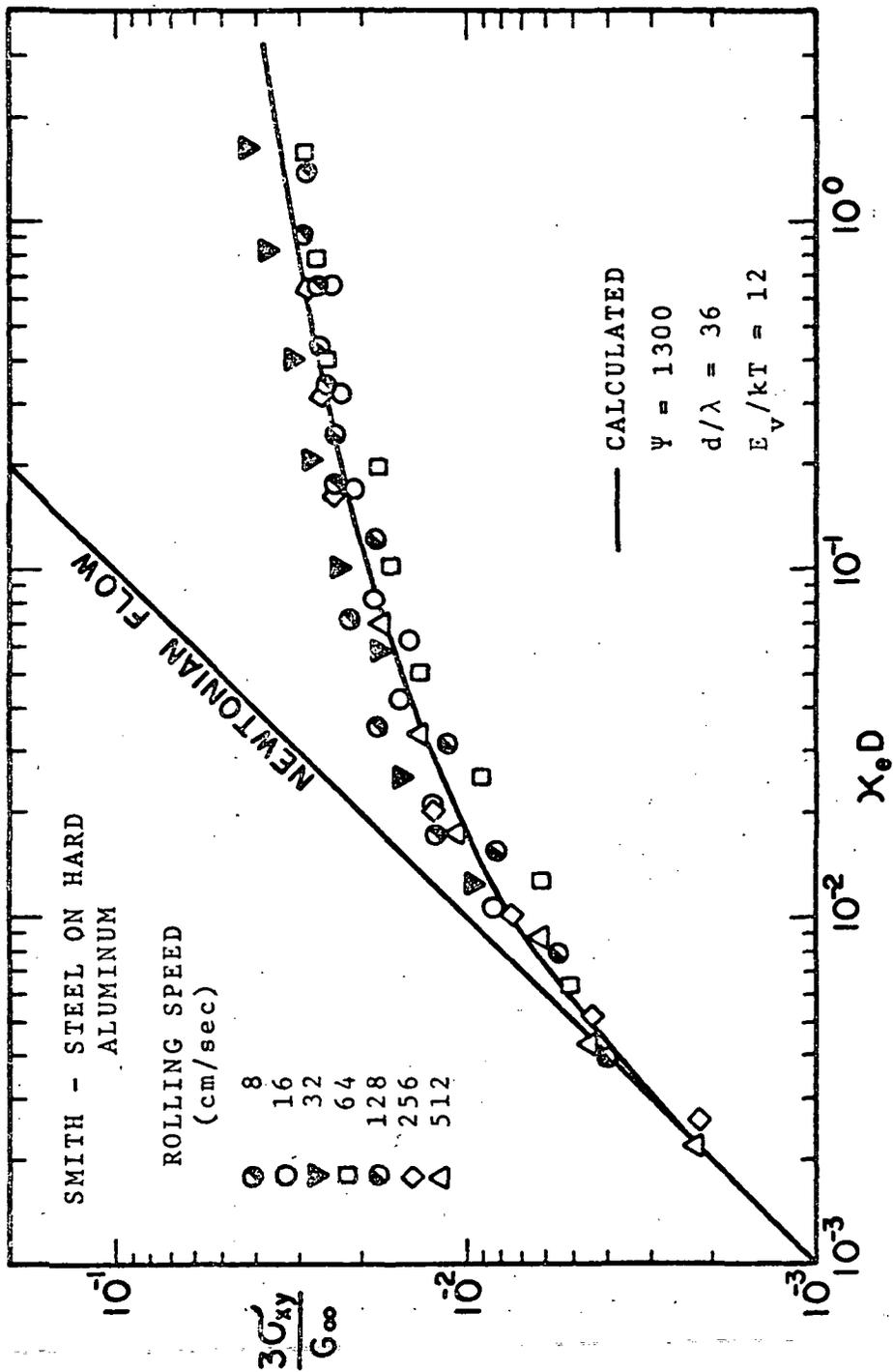


Figure 10. Comparison of measured and calculated shear stress variation as a function of strain rate. Results of Smith using steel on hard aluminum

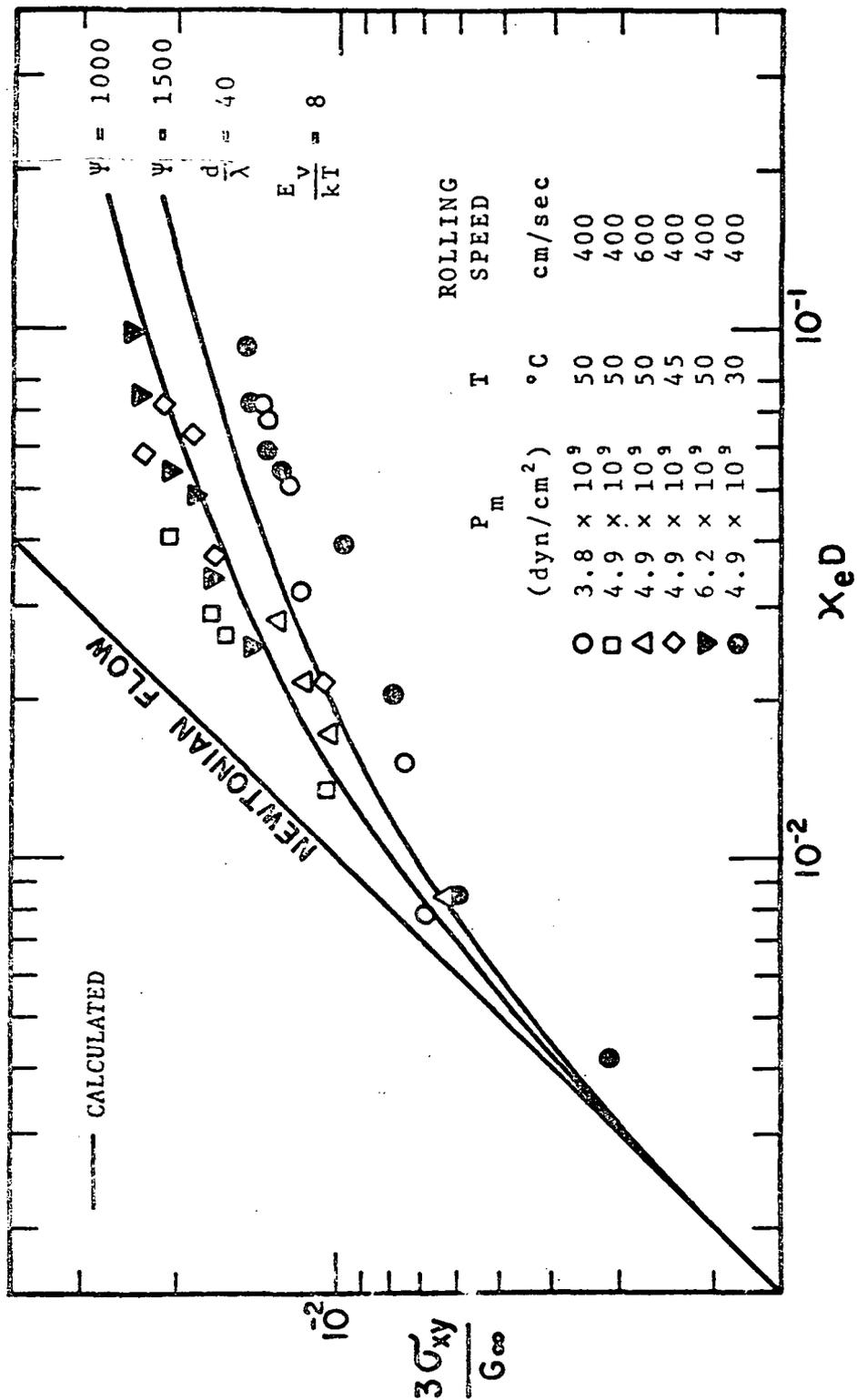


Figure 11. Comparison of measured and calculated shear stress variation as a function of strain rate. Results of Crook.

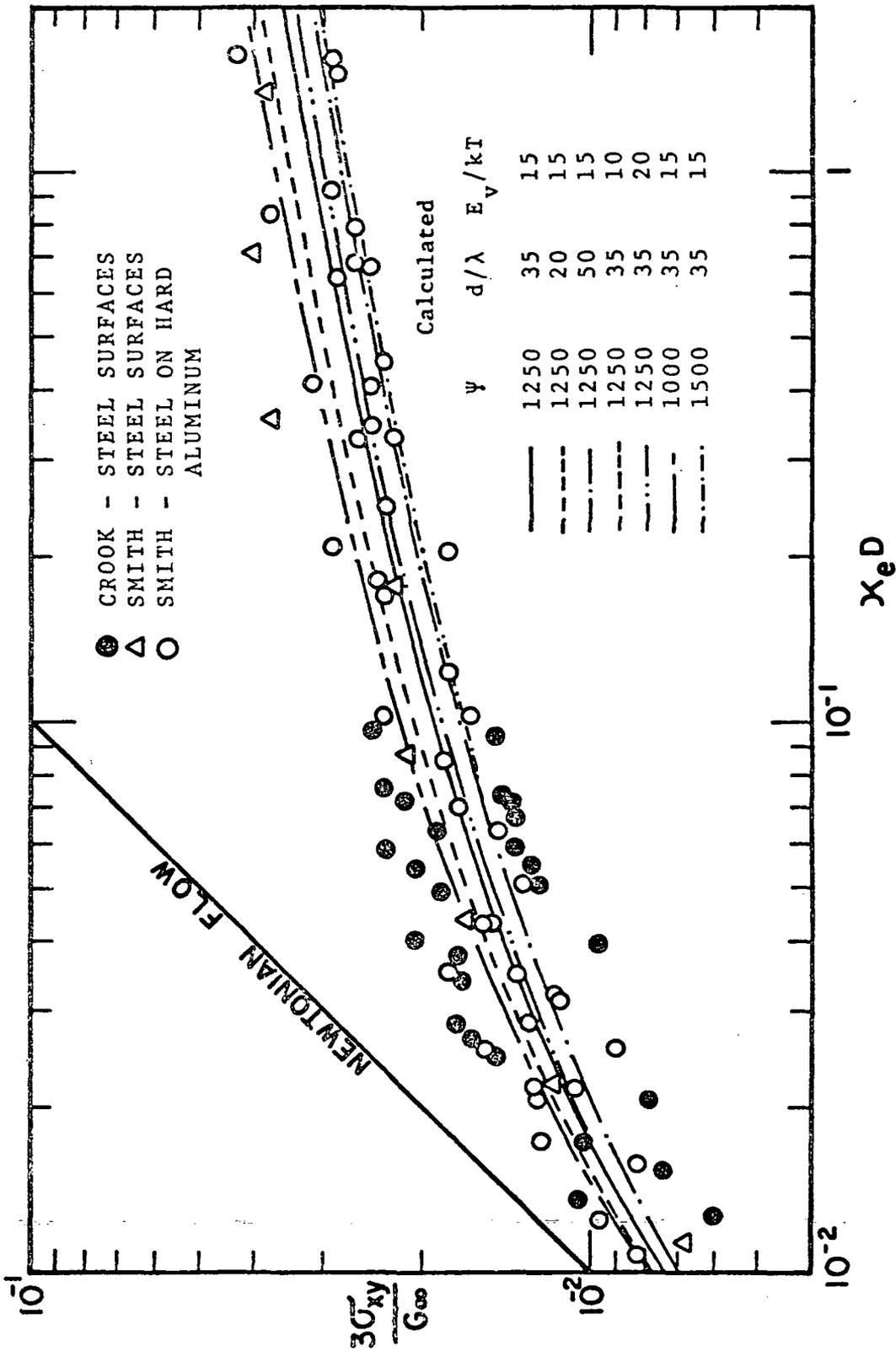


Figure 12. The effects of varying parameters on the calculated shear stress as a function of strain rate

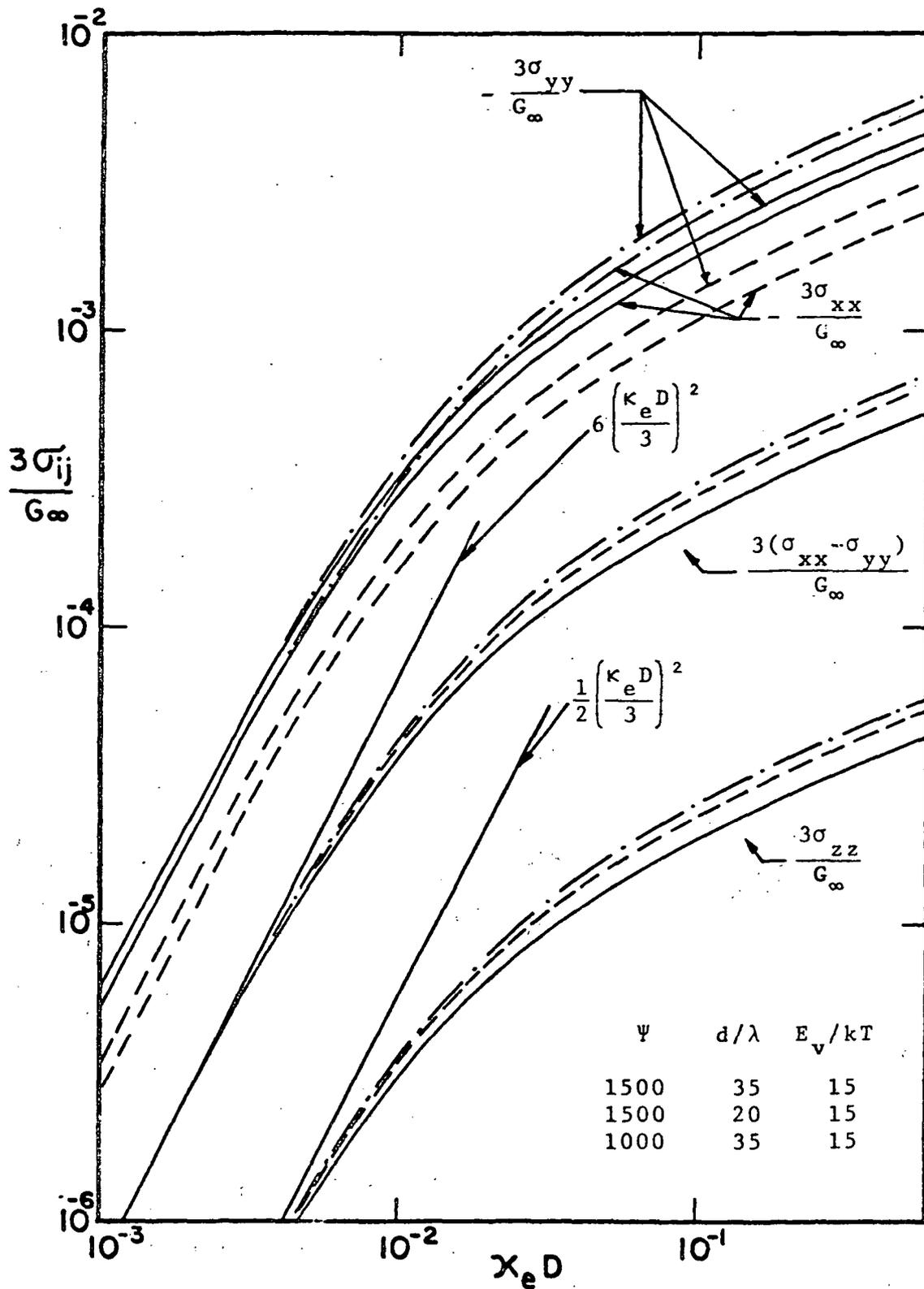


Figure 13. Calculated normal stresses in steady shear

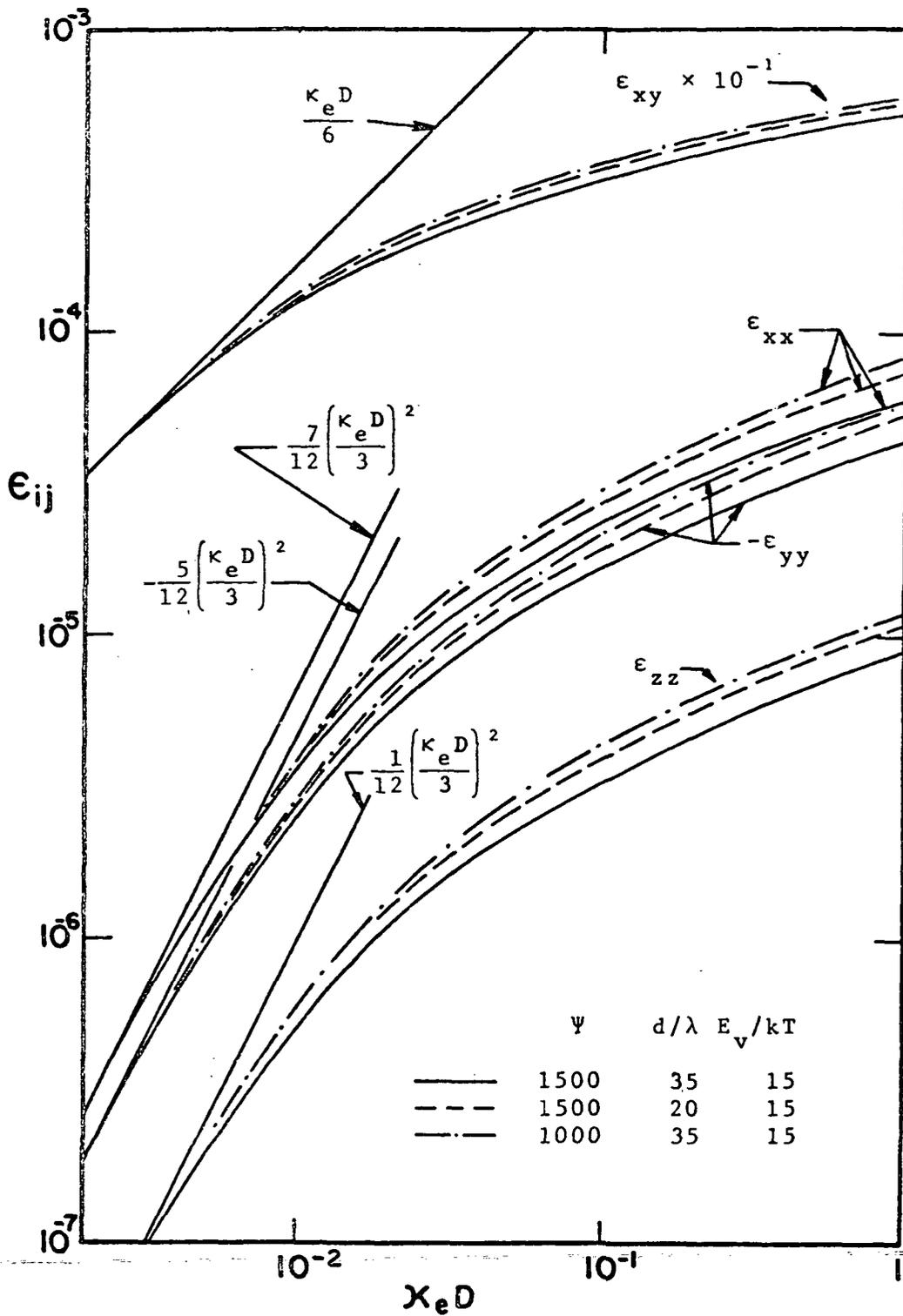


Figure 14. Calculated variations of molecular strain in steady shear as a function of the strain rate

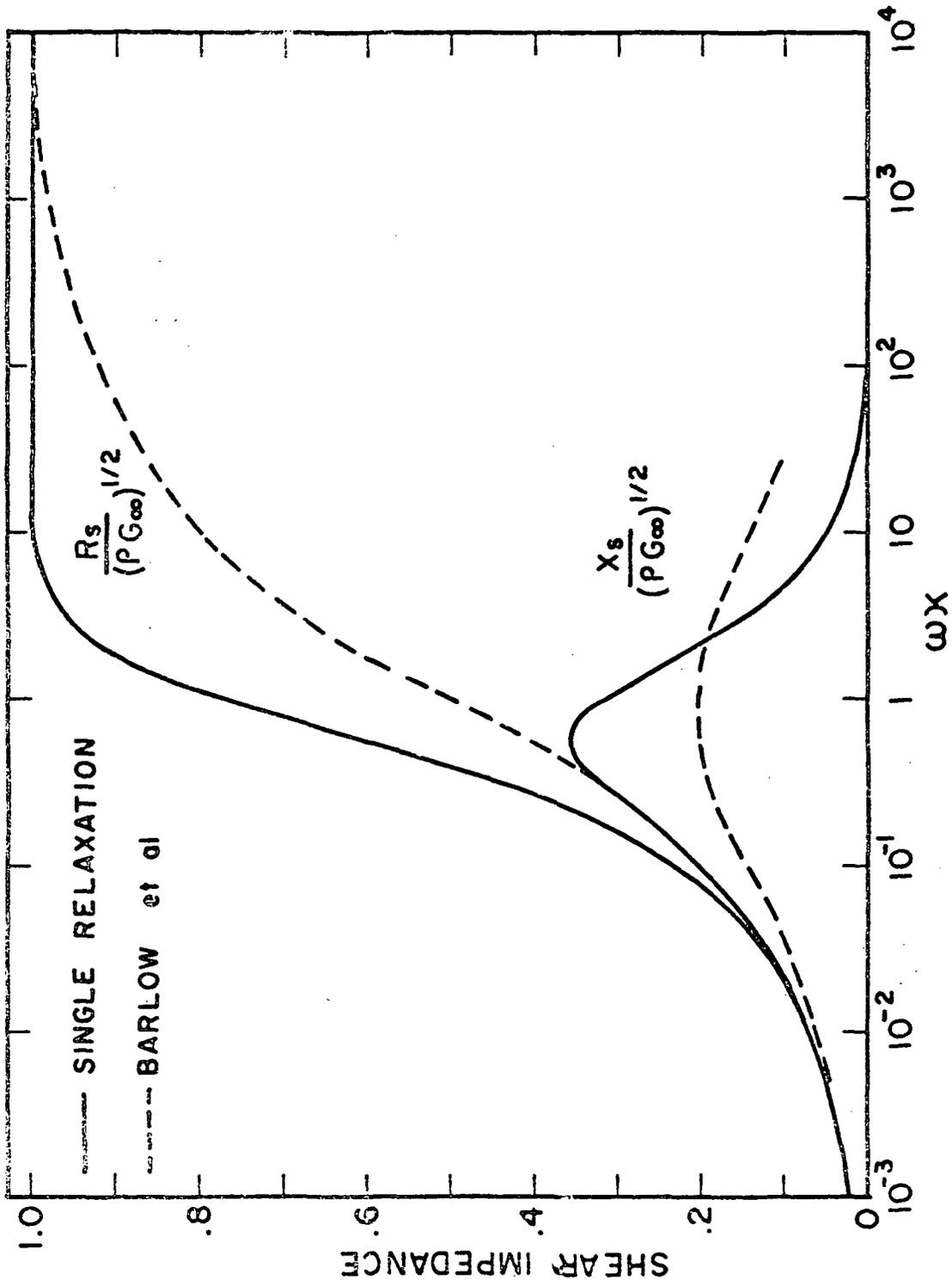


Figure 15. Real and imaginary components of the shear impedance in oscillatory shear

TABLE I

EXPERIMENT	P_m dyne/cm ² $\times 10^9$	P_k dyne/cm ² $\times 10^9$	T °C	$\frac{d}{\lambda}$	G_∞ dyne/cm ² $\times 10^{10}$	$\frac{\mu_{max}}{\mu_{mean}}$	$\frac{E_v}{kT}$
Smith - Steel surfaces	10.6	2.7	100	22	1.4	2.8	16
Smith - Steel on hard aluminum	6.15	3.2	23	36	6.0	3.0	12
Crook - Steel surfaces	3.8	2.2	50	35	4.0	2.5	8
	4.9	2.6	50	40	5.5	2.6	8
	4.9	2.6	45	42	5.7	2.6	8
	6.2	3.0	50	47	7.5	2.8	8
	4.9	2.7	30	46	6.6	2.6	8

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