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# The Statistical Mechanical Theory of Transport Processes

## I. General Theory

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Outlines are sketched for a general statistical mechanical theory of transport processes; e.g., diffusion, heat transfer, fluid flow, and response to time-dependent external force fields. In the case of gases the theory leads to the Maxwell-Boltzmann integro-differential equation of transport. In the case of liquids and solutions, it leads to a generalized theory of Brownian motion, in which the friction constant is explicitly related to the intermolecular forces acting in the system. Specific applications are postponed for treatment in later articles.

## I. INTRODUCTION AND GENERAL THEORY

### Part A: Introductory Remarks

THE equilibrium theory of statistical mechanics has achieved a satisfactory general formulation at the hands of Gibbs and of later investigators. It provides a systematic interpretation from the molecular standpoint of the equilibrium behavior of thermodynamic systems. Of equal physico-chemical importance are the irreversible processes by which thermodynamic systems attain equilibrium in response to changes in external restraints. In addition to chemical reaction, the most common irreversible processes are the transport processes; diffusion, heat transfer, fluid flow, and response to external forces dependent upon time. Although much has been written on the interpretation of transport processes from the molecular standpoint, no systematic statistical mechanical theory has yet been formulated. In the present article, we shall suggest certain lines of thought on which we believe such a general theory of transport processes might be based. Since we shall formulate the theory within the frame of classical statistical mechanics, we shall not treat chemical reactions, which require the introduction of quantum-mechanical ideas and which are tolerably well described by the transition state theory of Eyring and Polanyi.<sup>1</sup> Quantum-mechanical generalization of the methods to be discussed will be postponed for later treatment.

Since the literature on transport processes is

extensive and varied, we shall give here only a few key references and limit our preliminary remarks to a brief mention of the principal methods which have been used in investigating them. An exact and rigorous theory of transport exists for gases at sufficiently low density to be amenable to binary collision analysis. This theory is based upon the Maxwell-Boltzmann integro-differential equation, the consequences of which have been worked out in detail by Chapman and Enskog.<sup>2</sup> A satisfactory theory also exists for transport in dilute solutions, based upon the theory of Brownian motion, the foundations of which are due to Einstein.<sup>3</sup> The theory has been used very successfully in the treatment of irreversible processes in electrolyte solutions by Debye, Onsager, Falkenhagen, and others.<sup>4</sup> Recently Chandrasekar<sup>5</sup> has written an elegant review of the foundations and methods of the theory of Brownian motion, containing many new results, as well as an extensive bibliography. Although self-consistent, the theory of Brownian motion suffers from the defect that it contains an empirical friction constant related to intermolecular forces and molecular structure in a manner not described by the theory. A semi-phenomenological discussion of the Thomson reciprocal relations in coupled transport processes has been given by Onsager<sup>6</sup> and is recommended

<sup>2</sup> See Chapman and Cowling, *The Mathematical Theory of Non-Uniform Gases* (Cambridge University Press, New York, 1939).

<sup>3</sup> Einstein, *Ann. d. Physik* **17**, 549 (1905); **19**, 371 (1906).

<sup>4</sup> See L. Onsager and R. T. Fuoss, *J. Phys. Chem.* **36**, 2689 (1932).

<sup>5</sup> S. Chandrasekar, *Rev. Mod. Phys.* **15**, 1-89 (1943).

<sup>6</sup> L. Onsager, *Phys. Rev.* **37**, 405 (1931); **38**, 2265 (1931).

<sup>1</sup> See Gladstone, Laidler, and Eyring, *Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941).

for its perspectives on the general aspects of the problem of transport. Finally, there have been developed numerous model theories of transport processes, which are based upon simplified representations of the underlying elementary mechanisms. Significant results along these lines have been obtained in recent years by Eyring<sup>1</sup> and his co-workers using the transition state theory.

In the theoretical developments to be presented here, we shall attempt to integrate many of the ideas latent in the kinetic theory of gases and in the theory of Brownian motion into a systematic formulation. Although the notation is necessarily rather complicated, we have written from the physical rather than the mathematical standpoint. Although many mathematical problems are raised, the solution of which would require special and detailed investigation, none but relatively simple mathematical operations are employed in the development of the theory.

### Part B: Basic Concepts and Definitions

The macroscopic state of a system of molecules is specified by a small number of molar variables, for example temperature, composition, and parameters of external force. Since its dynamical state is incompletely defined by the molar variables, the macroscopic behavior of the system requires interpretation from the standpoint of statistical mechanics, if a description in molecular terms is desired.

On the other hand, a phenomenological description of macroscopic behavior, without reference to the molecular structure of the system, is possible. Equilibrium behavior is described by thermodynamics. When the values of the molar variables are inconsistent with the conditions for thermodynamic equilibrium, transport processes occur, for example diffusion, heat transfer, and fluid flow. The most common transport processes are macroscopically described by the hydrodynamic equations of continuity, motion, and energy transport, supplemented by certain empirically established relations connecting the mass and heat currents and the stress tensor with the gradients of the molar variables or functions of those variables, for example, the chemical potential gradients, temperature gradient, and rate of strain. The supplementary rela-

tions, constituting in their simplest form the laws of diffusion, heat conduction, and viscous fluid flow, contain certain material constants, the coefficients of diffusion, thermal conductivity, and viscosity, which depend upon the local macroscopic state of the system. The differential equations of transport, together with a specification of initial and boundary values of the molar variables, determine the macroscopic state as a function of time and position in the interior of the system.

The principal objectives of the statistical mechanical theory of transport are the formulation of the macroscopic differential equations of transport from the standpoint of molecular dynamics, the investigation of the limits of validity of the empirical laws of diffusion, heat conduction, and viscous flow, and the determination of the coefficients of diffusion, thermal conductivity, and viscosity, from the structure of the system on the molecular scale in terms of the forces acting between the molecules of which it is composed. A second important objective is the molecular interpretation of the linear stimulus-response theory\* (based upon the concept of a relaxation time spectrum), describing departures from thermodynamic equilibrium, produced by time dependent external forces. This aspect of the theory is pertinent to such important problems as those of dielectric and mechanical loss.

As a preliminary step in the formulation of the theory of transport, it is necessary to examine the operation of measurement of a property in a system, the macroscopic state of which is changing with time. Since the dynamical state of a system of many degrees of freedom is incompletely defined by the small number of molar variables characterizing its macroscopic state, the first step in an operation of measurement consists in sampling a system at time  $t$  from an ensemble representing an initial distribution among accessible microscopic dynamical states. Although the initial distribution is arbitrary, we shall generally be concerned with distributions departing but slightly from statistical equilibrium, to be represented by the canonical or

\* See, for example, Kármán and Biot, *Mathematical Methods in Engineering* (McGraw-Hill Book Company Inc., New York, 1940), Chap. X.

microcanonical ensembles of Gibbs, according to convenience. The second step in the operation or measurement consists in recording a time average of the property in question in the sample of the ensemble,\*\* with specified dynamical state at time  $t$ , over an interval of time  $\tau$ , macroscopically short, but microscopically long in a sense presently to be made more precise. If, as is customarily true for systems of many degrees of freedom, the fluctuation of the time averaged property in the ensemble is sufficiently small, the complete operation of measurement yields a value differing by quantities of negligible order from a group average in the ensemble of the time average of the property over a microscopically long but macroscopically short interval  $\tau$ . A third averaging operation is occasionally necessary, if the property in question is a point function in the three-dimensional configuration space of an individual molecule. This is an average over a macroscopically small domain of configuration space having a representative linear dimension large relative to the range of intermolecular force. The latter average is necessary in the formulation of the hydrodynamic equations of motion and energy transport and in the definition of such quantities as the stress tensor and the heat current.

Although we are forced to defer a detailed analysis of the time average and the magnitude of the interval  $\tau$  until after the quantitative aspects of the theory have been developed, a few comments seem desirable at this point. To obtain

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\*\* From the logical point of view, we shall regard the class of macroscopic properties to be defined by the two operations described. That properties experimentally defined by thermodynamic measurements fall into this class, and involve the time as well as group average is fairly obvious. For example, instruments designed for the measurement of a representative property such as the pressure in a fluid in equilibrium automatically record a time average over an interval of the order of magnitude, say, of a second, a millisecond, or perhaps a microsecond. If the area of the surface on which the normal force is recorded is sufficiently small and the time resolution of the instrument sufficiently fine, fluctuations will of course be observed which are independent of the characteristics of the instrument. These fluctuations are, as is well known, responsible for the Brownian motion of colloidal particles. With sufficiently fine resolution, the force acting on unit area, therefore, ceases to be a macroscopic property in the sense in which we have defined this class. Thus, when we speak of pressure in a fluid as a macroscopic property, we mean the normal force per unit area averaged over a macroscopic interval of time of such a magnitude that the recorded average is not sensibly dependent on the magnitude of the interval.

an adequate macroscopic description of the secular variation of the observable properties of a system, it is necessary to select  $\tau$  of sufficient magnitude to smooth out microscopic fluctuations in molecular distribution. For systems of suitable dynamical structure, the macroscopic description will then be independent of  $\tau$ , as long as the periods of secular variation are long relative to  $\tau$ . In the case of gases of such low density that molecular motion can be adequately analyzed in terms of binary collisions, the general theory leads to the Maxwell-Boltzmann integro-differential equation. Here it is obvious that  $\tau$  must be long relative to the duration of a representative collision. In the case of liquids and liquid solutions where the collision analysis fails or becomes unduly complicated, the general theory may be cast in the form of the theory of Brownian motion, but extends this theory by explicitly relating the friction constant to the intermolecular forces acting in a system of molecules. Here it is found that  $\tau$  must be long relative to the interval within which there is appreciable correlation between the total intermolecular force acting on a representative molecule at the beginning and end of that interval.

In classical statistical mechanics the dynamical states of a system of  $N$  molecules constitute a phase space and the ensemble representing a distribution in initial conditions, incompletely specified by the molar variables, is characterized by a probability density  $f^{(N)}(\mathbf{p}, \mathbf{q}; t)$  in phase space,  $\mathbf{p}$  representing the momentum coordinates and  $\mathbf{q}$  the configuration coordinates of the system. In order to simplify our analysis somewhat, we shall suppose that the molecules possess only translatory degrees of freedom. The vector  $\mathbf{p}$  is then defined in  $3N$ -dimensional momentum space and is composed of  $N$  vectors  $\mathbf{p}_1 \cdots \mathbf{p}_N$ , its projections on the 3-momentum spaces of the several molecules. Likewise  $\mathbf{q}$  is a vector in  $3N$ -dimensional configuration space with components  $\mathbf{R}_1, \cdots \mathbf{R}_N$  specifying the positions of the molecular centers of gravity in the 3-configuration spaces of the several molecules. The extension of the results which we shall obtain to molecules possessing internal degrees of freedom, for example rotational, will be obvious providing such internal degrees of freedom

are of the low frequency type in the sense of van Vleck and are therefore amenable to classical statistics to an adequate degree of approximation.

We shall denote by  $\mathbf{X}_i$ , dependent only on the coordinates of that molecule, the external force acting on a molecule  $i$  of the system. If  $\mathbf{X}_i$  is time dependent, we shall suppose that this dependence is secular, that is to say,  $\mathbf{X}_i$  is not sensibly affected by an average over the microscopic interval  $\tau$ . We shall denote by  $\mathbf{F}_i$  the intermolecular force exerted on a specified molecule  $i$  by the other molecules of the system. Although many of our results will be independent of the assumption, we shall further assume that the potential of intermolecular force  $V^{(N)}$  has the form

$$V^{(N)} = \sum_{k < l} V_{kl}(R_{kl}), \quad (1)$$

$$R_{kl} = |\mathbf{R}_l - \mathbf{R}_k|,$$

where  $V_{kl}$  depends only on the distance  $R_{kl}$  of the molecular pair consisting of molecules of types  $k$  and  $l$ . For the potential of Eq. (1), the intermolecular force is expressible in the form,

$$\mathbf{F}_i = \sum_{l=1 \neq i}^N \mathbf{F}_{li},$$

$$\mathbf{F}_{li} = -\nabla_l V_{li} = (\mathbf{R}_{li}/R_{li}) \frac{dV_{li}}{dR_{li}}, \quad (2)$$

$$\mathbf{R}_{li} = \mathbf{R}_l - \mathbf{R}_i.$$

By Liouville's theorem, embodying the equation of continuity in phase space and the laws of mechanics, it is well known that the probability distribution function,  $f^{(N)}(\mathbf{p}, \mathbf{q}; t)$ , satisfies the partial differential equation,

$$L f^{(N)} + i \frac{\partial f^{(N)}}{\partial t} = 0, \quad (3)$$

$$L = i \sum_{l=1}^N \left\{ \frac{\mathbf{p}_l}{m_l} \cdot \nabla_{\mathbf{R}_l} + (\mathbf{X}_l + \mathbf{F}_l) \cdot \nabla_{\mathbf{p}_l} \right\},$$

where  $m_l$  is the mass of molecule  $l$ . By introducing the factor  $i$ , the imaginary unit, the operator  $L$  is made self-adjoint when applied to a suitably restricted class of functions, a property to be used at a later stage of our discussion. Although  $\mathbf{X}_l$  might be defined to include wall forces confining each molecule to a finite region of configuration space, say the interior of a containing vessel, we shall not include these forces in  $\mathbf{X}_l$ ,

but shall take them into account by requiring  $f^{(N)}$  to vanish exterior to a region of volume  $v$  in the configuration space of each molecule, bounded by the walls of the container.

The characteristics of the partial differential Eq. (3) have the equations of motion of the dynamical system.

$$m_l(d\mathbf{R}_l/dt) = \mathbf{p}_l,$$

$$(d\mathbf{p}_l/dt) = \mathbf{X}_l + \mathbf{F}_l, \quad (4)$$

$$(d/dt) = (\partial/\partial t)_{\mathbf{p}_0 \mathbf{q}_0},$$

where  $\mathbf{p}_0$  and  $\mathbf{q}_0$  are the coordinates of the system at an arbitrarily selected initial instant of time. If the ensemble is viewed from the hydrodynamical standpoint  $\mathbf{p}_0$  and  $\mathbf{q}_0$  may also be interpreted as the Lagrange coordinates of an element of the representative fluid in phase space.

The solutions of the partial differential Eq. (3) may be expressed in the form,

$$f^{(N)}(\mathbf{p}, \mathbf{q}; t+s) = f^{(N)}(\mathbf{p}_0, \mathbf{q}_0; t),$$

$$\mathbf{p} = \exp(-isL_0)\mathbf{p}_0, \quad (5)$$

$$\mathbf{q} = \exp(-isL_0)\mathbf{q}_0,$$

where the operator  $\exp(-isL_0)$  is defined as follows.\* If  $\varphi(\mathbf{p}, \mathbf{q})$  is a function of  $\mathbf{p}$  and  $\mathbf{q}$  not explicitly dependent on time,

$$\psi(\mathbf{p}_0, \mathbf{q}_0; s) = \exp(-isL_0)\varphi(\mathbf{p}_0, \mathbf{q}_0), \quad (6)$$

is defined as the solution of the partial differential equation

$$i(\partial\psi/\partial s) = L_0\psi,$$

$$\psi(\mathbf{p}_0, \mathbf{q}_0; 0) = \varphi(\mathbf{p}_0, \mathbf{q}_0), \quad (7)$$

which satisfies the initial condition  $\psi_0 = \varphi$ . In domains of phase space free from singularities of  $L_0$ , the formal power series,

$$\exp(-isL_0) = \sum_{n=0}^{\infty} \frac{(-is)^n}{n!} L_0^n, \quad (8)$$

may frequently be employed to obtain useful

\* We note that the operator  $L$  of Eq. (3) is a function

$$L(\mathbf{p}, \mathbf{q}, \nabla_{\mathbf{p}}, \nabla_{\mathbf{q}})$$

of  $\mathbf{p}, \mathbf{q}, \nabla_{\mathbf{p}}$ , and  $\nabla_{\mathbf{q}}$ . By  $L_0$  we mean

$$L(\mathbf{p}_0, \mathbf{q}_0, \nabla_{\mathbf{p}_0}, \nabla_{\mathbf{q}_0})$$

where  $\mathbf{p}_0$  and  $\mathbf{q}_0$  are the Lagrange coordinates of the system at an arbitrary initial instant  $t$  preceding the interval  $s$  under discussion.

results. We note also the property

$$\begin{aligned}\exp(-isL_0)\varphi(\mathbf{p}_0, \mathbf{q}_0) &= \varphi(\mathbf{p}, \mathbf{q}), \\ \mathbf{p} &= \exp(-isL_0)\mathbf{p}_0, \\ \mathbf{q} &= \exp(-isL_0)\mathbf{q}_0.\end{aligned}\quad (9)$$

The mathematical theory of the operator  $\exp(-isL_0)$  may be formulated from a rigorous standpoint by the methods of spectral theory in Hilbert space.<sup>7</sup> In the analysis to follow, we shall find it sufficient to use the formal operator notation without reference to spectral theory. It should be remembered that explicit application of the operator  $\exp(-isL_0)$  requires the construction of the solutions of the equations of motion, Eq. (4), and that the operation is merely a symbolic expression of the finite transformation, associated with the infinitesimal transformation  $L_0$ , implied in the solution of the equations of motion. An additional property, which will presently be used, is embodied in the well-known statement of Liouville's theorem that the transformation determinant or Jacobian for  $\mathbf{p}_0 \rightarrow \mathbf{p}$ ;  $\mathbf{q}_0 \rightarrow \mathbf{q}$  is unity

$$[\partial(\mathbf{p}, \mathbf{q})]/[\partial(\mathbf{p}_0, \mathbf{q}_0)] = 1, \quad (10)$$

which follows from the fact that  $\exp(-isL_0)$  is a contact transformation.

We now proceed to formulate the averaging operations implied in a macroscopic measurement of a property,  $\varphi(\mathbf{p}, \mathbf{q})$  not explicitly dependent on time. The time average over the microscopic interval  $\tau$  will be denoted by  $\alpha_\tau$  and is expressible in the form

$$\alpha_\tau \varphi = \frac{1}{\tau} \int_0^\tau \varphi(\exp(-isL_0)\mathbf{p}_0, \exp(-isL_0)\mathbf{q}_0) ds, \quad (11)$$

where  $\mathbf{p}_0$  and  $\mathbf{q}_0$  are the coordinates of the system at time  $t$ . The average in the ensemble from which the system is sampled for observation will be denoted by  $\alpha_e$  and is expressible in the form

$$\alpha_e \varphi = \int \int \varphi(\mathbf{p}_0, \mathbf{q}_0) f^{(N)}(\mathbf{p}_0, \mathbf{q}_0; t) d\mathbf{p}_0 d\mathbf{q}_0, \quad (12)$$

at time  $t$ , where  $d\mathbf{p}_0$  and  $d\mathbf{q}_0$  denote volume elements in momentum and configuration space.

<sup>7</sup> von Neumann, Proc. Nat. Acad. Sci. **18**, 70 (1932); Koopman and von Neumann, Proc. Nat. Acad. Sci. **18**, 255 (1932).

We identify the observed value  $(\varphi)_{\text{obs}}$  with  $\alpha_e \alpha_\tau \varphi$

$$\begin{aligned}(\varphi)_{\text{obs}} &= \alpha_e \alpha_\tau \varphi, \\ \alpha_e \alpha_\tau \varphi &= \frac{1}{\tau} \int \int \int_0^\tau \varphi[\exp(-isL_0)\mathbf{p}_0, \\ &\quad \exp(-isL_0)\mathbf{q}_0] f^{(N)}(\mathbf{p}_0, \mathbf{q}_0; t) ds d\mathbf{p}_0 d\mathbf{q}_0\end{aligned}\quad (13)$$

in accordance with our earlier analysis of the operation of macroscopic measurement. We now calculate  $\alpha_\tau \alpha_e$  in which the averaging operations have been commuted.

$$\begin{aligned}\alpha_\tau \alpha_e \varphi &= \int \int \varphi(\mathbf{p}_0, \mathbf{q}_0) \\ &\quad \times \bar{f}^{(N)}(\mathbf{p}_0, \mathbf{q}_0; t) d\mathbf{p}_0 d\mathbf{q}_0, \quad (14) \\ \bar{f}^{(N)}(\mathbf{p}_0, \mathbf{q}_0; t) &= \frac{1}{\tau} \int_0^\tau f^{(N)}(\mathbf{p}_0, \mathbf{q}_0; t+s) ds,\end{aligned}$$

where  $\bar{f}^{(N)}$  is the time-smoothed probability density of the ensemble. Returning to Eq. (13), transforming the variables of integration, and using Eqs. (9) and (10), we obtain

$$\alpha_e \alpha_\tau \varphi = \int \int \varphi(\mathbf{p}, \mathbf{q}) f^{(N)}(\mathbf{p}, \mathbf{q}; t) d\mathbf{p} d\mathbf{q}, \quad (15)$$

the right-hand side of which is identical with that of Eq. (14). We have therefore demonstrated that  $\alpha_\tau$  and  $\alpha_e$  commute and we may write,

$$\begin{aligned}(\varphi)_{\text{obs}} &= \alpha_e \alpha_\tau \varphi = \alpha_\tau \alpha_e \varphi, \\ \alpha_e \alpha_\tau - \alpha_\tau \alpha_e &= 0.\end{aligned}\quad (16)$$

In an ensemble representing statistical equilibrium, for example the canonical ensemble of Gibbs, for which the distribution function is

$$f^{(N)} = e^{\beta(A-H)}, \quad (17)$$

where  $H$  is the Hamiltonian function and  $\beta$  is equal to  $1/kT$ , we obtain from Eq. (15), since  $f^{(N)}$  is independent of time,

$$\alpha_e \alpha_\tau \varphi = \alpha_e \varphi, \quad (\varphi)_{\text{obs}} = \alpha_e \varphi. \quad (18)$$

Here the group average of the time average is equal to the group average, and  $(\varphi)_{\text{obs}}$  is equal to the group average, the usual assumption of the equilibrium theory of statistical mechanics. The justification of Eqs. (16) and (18) as representations of a macroscopically observed property of course require a further step, the demonstration that the fluctuation in the ensemble of

$\alpha_\tau \varphi$  is sufficiently small to reduce to a negligible value the expectation of an observation departing from  $\alpha_\epsilon \alpha_\tau \varphi$  by an amount exceeding the precision of measurement.

It might be surmised that Eq. (18) would apply to observations in systems undergoing stationary transport processes, as well as in systems in thermodynamic equilibrium. Such a surmise would not in general be true, since stationary transport processes are stationary in the secular sense but not in the microscopic sense. That is to say,  $\hat{f}^{(N)}$  may be independent of time although  $f^{(N)}$  is not.

For brevity, we shall henceforth use the following notation

$$\begin{aligned}\alpha_\tau \varphi &= \langle \varphi \rangle_\tau, & \alpha_\epsilon \varphi &= \langle \varphi \rangle, \\ \alpha_\epsilon \alpha_\tau \varphi &= \langle \langle \varphi \rangle_\tau \rangle, & (19) \\ \alpha_\tau \alpha_\epsilon \varphi &= \langle \langle \varphi \rangle \rangle_\tau = \langle \varphi \rangle_N,\end{aligned}$$

to represent the results of the several averaging operations. The commutability of  $\alpha_\tau$  and  $\alpha_\epsilon$  has been demonstrated when  $\alpha_\epsilon$  denotes an average over all degrees of freedom of the system. We shall presently find that  $\alpha_\tau$  and  $\alpha_\epsilon$  do not in general commute when  $\alpha_\epsilon$  represents a partial average over some but not all coordinates. This lack of commutability is closely associated with the dissipative mechanism by which, in the drift toward equilibrium, energy is distributed among the degrees of freedom in the system.

If we desire to determine the average value of a function  $\varphi(\mathbf{p}, \mathbf{q})$  depending not on all coordinates in phase space, but only on these of a subset of  $n$  molecules, we may conveniently employ a distribution function of lower order. If we now let  $\mathbf{p}$  and  $\mathbf{q}$  denote the coordinates of the subset  $n$  alone and  $\mathbf{P}$  and  $\mathbf{Q}$  those of the set of  $N-n$  molecules comprising the remainder of the system, the distribution function of order  $n$  is defined in the form

$$\begin{aligned}f^{(n)}(\mathbf{p}, \mathbf{q}; t) &= \int \int f^{(N)}(\mathbf{p}, \mathbf{q}, \mathbf{P}, \mathbf{Q}; t) d\mathbf{P} d\mathbf{Q}, \\ \bar{f}^{(n)}(\mathbf{p}, \mathbf{q}; t) &= \frac{1}{\tau} \int_0^\tau f^{(n)}(\mathbf{p}, \mathbf{q}; t+s) ds.\end{aligned}\quad (20)$$

By Eqs. (15) and (16), we obtain, after integration over those coordinates  $\mathbf{P}$  and  $\mathbf{Q}$  on which

$\varphi(\mathbf{p}, \mathbf{q})$  does not depend,

$$\langle \langle \varphi \rangle \rangle_\tau = \langle \varphi \rangle_N = \int \int \varphi(\mathbf{p}, \mathbf{q}) f^{(n)}(\mathbf{p}, \mathbf{q}; t) d\mathbf{p} d\mathbf{q}. \quad (21)$$

If the system consists of several components, the molecular types represented in the set  $n$  will be represented by subscripts. Thus

$$f_{i \dots l}^{(n)}(\mathbf{p}_1, \dots, \mathbf{p}_n, \mathbf{R}_1, \dots, \mathbf{R}_n; t)$$

denotes a distribution function of order  $n$  in a set comprising  $n$  specified molecules 1,  $\dots$ ,  $n$  of respective types  $i \dots l$ , the coordinates  $(\mathbf{p}, \mathbf{q})$  of which have the components  $\mathbf{p}_1 \dots \mathbf{p}_n, \mathbf{R}_1 \dots \mathbf{R}_n$  in the phase spaces of the individual molecules of the set.

The distribution functions  $f^{(N)}$  and  $f^{(n)}$  are related in the following way

$$\begin{aligned}f^{(N)}(\mathbf{p}, \mathbf{q}, \mathbf{P}, \mathbf{Q}; t) \\ = f^{(n/N)}(\mathbf{p}, \mathbf{q}; \mathbf{P}, \mathbf{Q}; t) f^{(n)}(\mathbf{p}, \mathbf{q}; t),\end{aligned}\quad (22)$$

to a third type of distribution function  $f^{(n/N)}$  defining the relative probability density in the phase space of the set of  $N-n$  molecules, if the set  $n$  is situated at a point  $(\mathbf{p}, \mathbf{q})$  in its phase sub-space.

The distribution function  $\bar{f}_i^{(1)}(\mathbf{R}, \mathbf{p}; t)$  represents the probability density of any specified molecule of type  $i$ , contained in the system, in the 6-dimensional phase space  $(\mathbf{p}, \mathbf{R})$  of that molecule. The microscopic time average of the concentration of molecular species  $i$  at a point  $\mathbf{R}$  in the vessel containing the system is

$$C_i(\mathbf{R}, t) = N_i \int \bar{f}_i^{(1)}(\mathbf{p}, \mathbf{R}; t) d\mathbf{p}, \quad (23)$$

where  $N_i$  is the total number of molecules of type  $i$  in the system. The mass current density of species  $i$  at point  $\mathbf{R}$  is given by

$$\mathbf{j}_i = N_i \int \mathbf{p} \bar{f}_i^{(1)}(\mathbf{p}, \mathbf{R}; t) d\mathbf{p}. \quad (24)$$

The local temperature  $T(\mathbf{R}, t)$  is defined in classical statistical mechanics by the relation

$$\begin{aligned}T(\mathbf{R}, t) &= [\langle \mathbf{p}^2 \rangle_N - \langle \mathbf{p} \rangle_N^2] / 3mk, \\ \langle \mathbf{p}^2 \rangle_N &= (N/C) \int \mathbf{p}^2 \bar{f}^{(1)}(\mathbf{p}, \mathbf{R}; t) d\mathbf{p},\end{aligned}\quad (25)$$

$$\langle \mathbf{p} \rangle_N = (N/C) \int \mathbf{p} \bar{f}^{(1)}(\mathbf{p}, \mathbf{R}; t) d\mathbf{p},$$

where  $k$  is Boltzmann's constant. The temperature is thus determined by  $\bar{f}^{(1)}$ .

The distribution function  $\bar{f}^{(2)}$  defines the probability density in the 12-dimensional phase space of a molecular pair. It may be regarded as a function of  $\mathbf{R}_1$  and  $\mathbf{R}_2$  or of  $\mathbf{R}_1$  and  $\mathbf{R}$ , the position  $\mathbf{R}_2 - \mathbf{R}_1$  of molecule 2 of the pair relative to molecule 1. Thus  $\bar{f}_{ii}^{(2)}(\mathbf{p}_1, \mathbf{p}_2, \mathbf{R}_1, \mathbf{R}; t)$  is the distribution function of order 2 for a pair of molecules of types  $i$  and 1, respectively. Its importance in the theory of transport will presently be made clear.

The central problem in the statistical mechanical theory of transport consists in the determination of the sequence of time averaged lower order distribution functions  $\bar{f}^{(n)}(\mathbf{p}, \mathbf{q}; t)$ , of which  $\bar{f}^{(1)}$  and  $\bar{f}^{(2)}$  play a role of particular

importance. When the lower order distribution functions are known, pertinent average values of the properties of the system may be calculated by Eq. (21). In the investigation of mass transport by diffusion and convection, the mass current densities  $\mathbf{j}_i$ , related to the distribution functions  $\bar{f}_i^{(1)}$  by Eq. (24), are of special importance.

In the investigation of fluid flow and the equation of motion of hydrodynamics from the molecular standpoint, the relation between the stress tensor  $\sigma$  and the potentials of intermolecular force is of special importance. For a system of one component composed of  $N$  molecules, with intermolecular forces of the type described by Eq. (1), contained in volume  $v$ , the stress tensor  $\sigma$  at a point  $\mathbf{r}$  in the region  $v$  is found to be

$$\begin{aligned}\sigma &= -\frac{C}{m}[\langle \mathbf{p}\mathbf{p} \rangle_{Av} - \langle \mathbf{p} \rangle_{Av} \langle \mathbf{p} \rangle_{Av}] + \frac{C^2}{2} \int \frac{\mathbf{R}\mathbf{R}}{R} \frac{dV}{dR} \bar{g}^{(2)}(\mathbf{r}, \mathbf{R}; t) d\mathbf{R}, \\ \bar{g}^{(2)}(\mathbf{r}, \mathbf{R}; t) &= \frac{N^2}{C^2} \iint f^{(2)}(\mathbf{p}_1, \mathbf{p}_2, \mathbf{r}, \mathbf{R}; t) d\mathbf{p}_1 d\mathbf{p}_2, \\ C(\mathbf{r}, t) &= N \int \bar{f}^{(1)}(\mathbf{p}, \mathbf{r}) d\mathbf{p}, \\ \langle \mathbf{p}\mathbf{p} \rangle_{Av} &= \frac{N}{C} \int \mathbf{p}\mathbf{p} \bar{f}^{(1)}(\mathbf{p}, \mathbf{r}; t) d\mathbf{p},\end{aligned}\tag{26}$$

where  $V(R)$  is the potential of intermolecular force for a molecular pair,  $m$  is the molecular mass,  $\mathbf{r}$  the position of one molecule of the pair, held fixed in the averaging operation, and  $\mathbf{R}$  is the position  $\mathbf{R}_2 - \mathbf{R}_1$  of the second member of the pair relative to the first. The integral of the second term in  $\sigma$  extends over the relative coordinates of the pair. The stress tensor is thus determined by the distribution functions  $\bar{f}^{(1)}$  and  $\bar{f}^{(2)}$ . The first term arising from momentum transport is identical with that customarily encountered in the kinetic theory of gases, for example in the Chapman-Enskog formulation. The second term, arising from intermolecular forces, becomes of dominant importance in liquids and solids.

In the investigation of heat transfer on the molecular scale, the relation between the heat current density  $\mathbf{j}_q$  and the distribution functions and intermolecular forces is of primary significance. Again in a system of one component, this relation is found to be,

$$\begin{aligned}\mathbf{j}_q &= \frac{C}{2m^2} \langle (\mathbf{p} - \langle \mathbf{p} \rangle_{Av}) (\mathbf{p} - \langle \mathbf{p} \rangle_{Av})^2 \rangle_{Av} - \frac{N^2}{2m} \iiint \{ \mathbf{R}(\mathbf{p}_1 - \langle \mathbf{p} \rangle_{Av}) \cdot \nabla V - V(\mathbf{p}_1 - \langle \mathbf{p} \rangle_{Av}) \} \\ &\quad \times \bar{f}^{(2)}(\mathbf{p}_1, \mathbf{p}_2, \mathbf{r}, \mathbf{R}; t) d\mathbf{p}_1 d\mathbf{p}_2 d\mathbf{R}.\end{aligned}\tag{27}$$

The heat current thus depends upon the distribution functions  $\bar{f}^{(1)}$  and  $\bar{f}^{(2)}$ . The first term, associated with kinetic energy transport, is the familiar term of the kinetic theory of gases. The second term, associated with energy transport by

intermolecular forces, becomes of dominant importance in liquids and solids.

The macroscopic hydrodynamic equations of motion and energy transport will be treated from the molecular standpoint in separate articles on



viscous fluid flow and heat transfer. In these articles, Eqs. (26) and (27) will be derived from fundamental principles and the ordinary laws of viscosity and thermal conduction will be shown to be valid under suitable conditions by expansion of the distribution functions  $\tilde{f}^{(1)}$  and  $\tilde{f}^{(2)}$  in the velocity and temperature gradients. The phenomenon of diffusion will also be treated in detail in a later article.

## II. THE THEORY OF BROWNIAN MOTION

In liquids and other condensed systems, we shall find it convenient to use the concepts of the theory of Brownian motion in the formulation of the partial differential equations describing the behavior of the sequence of distribution functions  $\tilde{f}^{(n)}$ . It is therefore desirable to examine the concepts of this theory from the molecular standpoint before proceeding to the problem of determining the distribution functions.

The theory of Brownian motion, which describes transport processes in dilute solution, is based upon the Langevin equation describing the motion of a molecule in an environment in statistical equilibrium. The Langevin equation has the form,

$$\frac{d\mathbf{p}_i}{dt} + \frac{\zeta_i^0}{m_i} \mathbf{p}_i = \mathbf{X}_i + \mathbf{G}_i, \quad (28)$$

where  $\mathbf{p}_i$  is the momentum of a specified molecule  $i$ ,  $m_i$  its mass,  $\mathbf{X}_i$  the external force acting on it, and  $\mathbf{G}_i$  a fluctuating intermolecular force, the time average of which vanishes over a macroscopically short interval  $\tau$ , and which is uncorrelated in successive intervals of magnitude  $\tau$ . In the dissipative term,  $\zeta_i^0 \mathbf{p}_i / m_i$  the friction con-

stant  $\zeta_i^0$  is a phenomenological constant, recognized to be determined by intermolecular forces, but the precise relationship between  $\zeta_i^0$  and the intermolecular forces in the system has not heretofore been established. Estimates of  $\zeta_i^0$  have therefore been limited to macromolecules dispersed in solvents of low molecular weight, where macroscopic hydrodynamics may reasonably be expected to apply. For a spherical molecule of radius  $a$ , in solvent of viscosity coefficient  $\eta$ , Stokes law yields the estimate  $6\pi\eta a$  for the friction constant  $\zeta_i^0$ .

We shall now attempt to show how the Langevin equation may be obtained from statistical mechanics and how the friction constant is related to the intermolecular forces. If  $\mathbf{p}_i$  is the momentum of a specified molecule  $i$  in a system with completely specified coordinates  $\mathbf{p}_{i0}, \mathbf{R}_{i0}, \mathbf{P}_0, \mathbf{Q}_0$ , the latter being those of the remaining  $N-1$  molecules, at an arbitrary initial instant of time  $t$ , the equation of motion for the molecule in question is

$$\frac{d\mathbf{p}_i}{dt} = \left( \frac{\partial \mathbf{p}_i}{\partial t} \right)_{\mathbf{p}_{i0} \dots \mathbf{Q}_0} = \mathbf{X}_i + \mathbf{F}_i, \quad (29)$$

where  $\mathbf{X}_i$  is the external force and  $\mathbf{F}_i$  the intermolecular force acting on molecule  $i$ .

We now define  $\mathbf{G}_i$  by the relation

$$\mathbf{G}_i = \mathbf{F}_i - {}^i\langle (\mathbf{F}_i)_\tau \rangle, \quad (30)$$

$${}^i\langle (\mathbf{F}_i)_\tau \rangle = {}^i\alpha_\epsilon \alpha_\tau \mathbf{F}_i,$$

where the left superscript  $i$  denotes an average in the ensemble, from which the system is sampled, with fixed initial coordinates  $\mathbf{p}_{i0}$  and  $\mathbf{R}_{i0}$  of molecule  $i$ . By the definitions of Part I, we have

$${}^i\langle (\mathbf{F}_i)_\tau \rangle = \frac{1}{\tau} \int \int \int_0^\tau \mathbf{F}_i(t+s) f_i^{(1/N)}(\mathbf{p}_{i0} \mathbf{R}_{i0} / \mathbf{P}_0, \mathbf{Q}_0; t) ds d\mathbf{P}_0 d\mathbf{Q}_0, \quad (31)$$

where  $\mathbf{F}_i(t+s)$  is used for brevity to denote  $\mathbf{F}_i(\mathbf{R}_i, \mathbf{Q})$  considered as a function of  $\mathbf{R}_{i0}, \mathbf{Q}_0$ , and  $s$ , and  $f_i^{(1/N)}$  is the relative probability density in the ensemble at time  $t$  in the phase space of the  $N-1$  molecules other than  $i$ , if  $i$  has the coordinates  $\mathbf{p}_{i0}$  and  $\mathbf{R}_{i0}$ . We remark that  $\mathbf{G}_i$  has the first property assigned to the fluctuating force in the Langevin equation, that is,

$${}^i\alpha_\epsilon \alpha_\tau \mathbf{G}_i = 0, \quad (32)$$

but in the somewhat extended sense that average in the ensemble of the time average of  $\mathbf{G}_i$  vanishes. This extension is necessary to give precision to the concept of the fluctuating force. The second property, that of no correlation in successive  $\tau$  intervals, will presently be discussed.

We now examine the average force  $\langle \mathbf{F}_i \rangle_\tau$ . If we make the hypothesis that the environment of molecule  $i$  is in statistical equilibrium, or can be regarded to be so to a sufficient degree of approximation, we may write Eq. (30) in the form

$$\begin{aligned} \langle \mathbf{F}_i \rangle_\tau &= \frac{1}{\tau} \int \int \int_0^\tau \mathbf{F}_i(t+s) {}^0f_i^{(1/N)}(\mathbf{p}_{i0}\mathbf{R}_{i0}/\mathbf{P}_0, \mathbf{Q}_0) d\mathbf{s} d\mathbf{P}_0 d\mathbf{Q}_0, \\ {}^0f_i^{(1/N)} &= \left( \frac{\beta}{2\pi m_i} \right)^{\frac{3}{2}} \frac{1}{v} \exp [\beta(A^N - H_0^N) + \beta p_{i0}^2/2m_i + \beta W_i^{(1)}(\mathbf{R}_{i0})], \end{aligned} \quad (33)$$

where  ${}^0f_i^{(1/N)}$  is the relative probability density in the canonical ensemble representing statistical equilibrium and defined by Eq. (22). The potential of the equilibrium average force\* acting on molecule  $i$  is denoted by  $W_i^{(1)}$ . We next consider the average force  $\langle \mathbf{F}_i \rangle_\tau$  in which the order of the averaging operations  $\alpha_\tau$  and  $\alpha_\epsilon$  is interchanged and we find,

$$\langle \mathbf{F}_i \rangle_\tau = \langle \mathbf{F}_i \rangle^0 = \int \int \mathbf{F}_i(\mathbf{R}_{i0}, \mathbf{Q}) {}^0f_i^{(1/N)}(\mathbf{p}_{i0}, \mathbf{R}_{i0}/\mathbf{P}, \mathbf{Q}) d\mathbf{P} d\mathbf{Q}, \quad (34)$$

if  $\langle \mathbf{F}_i \rangle^0$ , the equilibrium intermolecular force has only secular dependence on time so that it is not affected by an average over the microscopic interval  $\tau$ . It will be shown in a later article on diffusion that in the equilibrium ensemble corresponding to specified composition gradients

$$\langle \mathbf{F}_i \rangle^0 = -\nabla \mu_i + kT \nabla \log C_i, \quad (35)$$

where  $\mu_i$  is the chemical potential of a molecule of type  $i$  and  $C_i$  is its concentration. Thus  $\langle \mathbf{F}_i \rangle^0$  will be secular for gradients appreciable only over distances of macroscopic magnitude and will in fact vanish if molecule  $i$  is a solute component of an ideal dilute solution. It also vanishes identically if the hypothesis of thermodynamic equilibrium is strictly fulfilled and there are no external forces  $\mathbf{X}_i$  acting on the system.

If  $\alpha_\epsilon$  and  $\alpha_\tau$  were commutable as are  $\alpha_\epsilon$  and  $\alpha_\tau$ ,  $\langle \mathbf{F}_i \rangle_\tau$  would be identical with  $\langle \mathbf{F}_i \rangle^0$ . This, however, is not the case. In order to establish the relation between  $\langle \mathbf{F}_i \rangle_\tau$  and  $\langle \mathbf{F}_i \rangle^0$ , we rewrite Eq. (33) in the following form,

$$\langle \mathbf{F}_i \rangle_\tau = \frac{1}{\tau} \int_0^\tau \int \int \int \int \mathbf{F}_i(t+s) \delta(\mathbf{p}_{i0}' - \mathbf{p}_{i0}) \delta(\mathbf{R}_{i0}' - \mathbf{R}_{i0}) {}^0f_i^{(1/N)}(\mathbf{p}_{i0}', \mathbf{R}_{i0}'/\mathbf{P}_0, \mathbf{Q}_0) d\mathbf{p}_{i0}' d\mathbf{R}_{i0}' d\mathbf{P}_0 d\mathbf{Q}_0 ds, \quad (36)$$

where the order of integration over time and phase space has been interchanged (this is permissible and has nothing to do with the commutation of  $\alpha_\epsilon$  and  $\alpha_\tau$ ), and the integration has extended over all of phase space at time  $t$  by introducing the delta functions  $\delta(\mathbf{p}_{i0}' - \mathbf{p}_{i0})$  and  $\delta(\mathbf{R}_{i0}' - \mathbf{R}_{i0})$ , each the product of three delta functions for each component of the vector arguments. We next note the following properties of the functions appearing in the integrand of Eq. (36).

$$\begin{aligned} {}^0f_i^{(1/N)}(\mathbf{p}_{i0}', \mathbf{R}_{i0}'/\mathbf{P}_0, \mathbf{Q}_0) &= {}^0f_i^{(1/N)}(\mathbf{p}_i', \mathbf{R}_i'/\mathbf{P}, \mathbf{Q}) {}^0f_i^{(1)}(\mathbf{p}_i', \mathbf{R}_i') / {}^0f_i^{(1)}(\mathbf{p}_{i0}', \mathbf{R}_{i0}'), \\ \frac{{}^0f_i^{(1)}(\mathbf{p}_i', \mathbf{R}_i')}{{}^0f_i^{(1)}(\mathbf{p}_{i0}', \mathbf{R}_{i0}')} &= \exp \{ -\beta(p_i'^2 - p_{i0}'^2)/2m_i - \beta[W_i^{(1)}(\mathbf{R}_i') - W_i^{(1)}(\mathbf{R}_{i0}')] \}, \\ &= 1 - \frac{\beta \mathbf{p}_i'}{m_i} \cdot \Delta \mathbf{p}_i' + O[(\Delta \mathbf{p}_i')^2] + O(\Delta \mathbf{R}_i'), \end{aligned} \quad (37)$$

$$\Delta \mathbf{p}_i' = \mathbf{p}_i' - \mathbf{p}_{i0}' = \int_0^t \mathbf{F}_i(t+s') ds' + \mathbf{X}_i s,$$

$$\Delta \mathbf{R}_i' = \mathbf{R}_i' - \mathbf{R}_{i0}' = \int_0^t (\mathbf{p}_i'/m_i) ds'.$$

\* Note: For a discussion of equilibrium average forces and distribution functions, see J. G. Kirkwood, J. Chem. Phys. 3, 300 (1935).

These relations follow at once from Eqs. (17), (20), (22), and (29) and the invariance of  $H^{(N)}$  the complete Hamiltonian of the system under the transformation  $(\mathbf{p}_{i0}', \mathbf{R}_{i0}', \mathbf{P}_0, \mathbf{Q}_0) \rightarrow (\mathbf{p}_i', \mathbf{R}_i', \mathbf{P}, \mathbf{Q})$  by the operator  $\exp(-isL_0)$ . We further note

$$\begin{aligned} \mathbf{F}_i(t+s) &= \mathbf{F}_i(\mathbf{R}_i', \mathbf{Q}), \\ \delta(\mathbf{p}_{i0}' - \mathbf{p}_{i0}) &= \delta(\mathbf{p}_i' - \mathbf{p}_{i0} - \Delta\mathbf{p}_i'), \\ &= \delta(\mathbf{p}_i' - \mathbf{p}_{i0}) + \Delta\mathbf{p}_i' \cdot \nabla_{\mathbf{p}_{i0}} \delta(\mathbf{p}_i' - \mathbf{p}_{i0}) + O[(\Delta\mathbf{p}_i')^2], \\ \delta(\mathbf{R}_{i0}' - \mathbf{R}_{i0}) &= \delta(\mathbf{R}_i' - \mathbf{R}_{i0}) + O(\Delta\mathbf{R}_i'). \end{aligned} \quad (38)$$

The expansions of the delta functions in power series in  $\Delta\mathbf{p}_i'$  and  $\Delta\mathbf{R}_i'$  are formal operations which can be justified by more tedious methods of calculation which circumvent their use. Substitution of the relations of Eqs. (37) and (38) into the integral of Eq. (36) after transformation to the new variables  $\mathbf{p}_i', \mathbf{R}_i', \mathbf{P}, \mathbf{Q}$  yields, after some calculation,

$$\langle \langle \mathbf{F}_i \rangle_\tau \rangle = \langle \mathbf{F}_i \rangle^0 - \zeta_i \cdot \mathbf{p}_{i0}/m_i + kT \nabla_{\mathbf{p}_{i0}} \cdot \zeta_i + O(\tau). \quad (39)$$

$$\zeta_i = \frac{\beta}{\tau} \int_0^\tau \int_0^\tau \int_0^\tau \int_0^\tau \mathbf{F}_i(t+s) \mathbf{F}_i(t+s') {}^0f_i^{(1/N)}(\mathbf{p}_i, \mathbf{R}_i/\mathbf{P}, \mathbf{Q}) ds' ds d\mathbf{P} d\mathbf{Q},$$

where in the expression for  $\zeta_i$ , resulting from the calculation,  $\mathbf{p}_{i0}$  and  $\mathbf{R}_{i0}$  have been replaced by  $\mathbf{p}_i$  and  $\mathbf{R}_i$  and the remainder included in the term  $O(\tau)$ . If the tensor  $\zeta_i$  has a plateau value, not sensibly dependent on  $\tau$ , for a microscopic interval  $\tau$  of sufficient length, in a sense to be discussed presently, the remainder terms arising from the terms  $O[(\Delta\mathbf{p}_i')^2]$  and  $O[\Delta\mathbf{R}_i']$  in the integrand of Eq. (36) may be shown to be of order  $\tau$ . In fluid systems such as liquids and liquid solutions, it is apparent that  $\zeta_i$  must be isotropic.

$$\zeta_i = \zeta_i \mathbf{1},$$

$$\zeta_i(\tau) = \frac{\beta}{3\tau} \int_0^\tau \int_{-s}^0 \int \int \mathbf{F}_i(t+s) \cdot \mathbf{F}_i(t+s+s') {}^0f_i^{(1/N)}(\mathbf{p}_i, \mathbf{R}_i/\mathbf{P}, \mathbf{Q}) d\mathbf{P} d\mathbf{Q} ds' ds, \quad (40)$$

where a permissible change in the order of integration has been made and a change of time variable introduced.

If the structure of the dynamical system is such that in the equilibrium ensemble there exists a microscopic time interval  $\tau_i$ , of sufficient length that the integral

$$\frac{\beta}{3} \int_{-\tau_i}^0 \int \int \mathbf{F}_i(t) \cdot \mathbf{F}_i(t+s') {}^0f_i^{(1/N)}(\mathbf{p}_{i0}, \mathbf{R}_{i0}/\mathbf{P}_0, \mathbf{Q}_0) d\mathbf{P}_0 d\mathbf{Q}_0 ds'$$

possesses a plateau value  $\zeta_i$  given by

$$\zeta_i = \frac{\beta}{3} \int_{-\tau_i}^0 \int \int \mathbf{F}_i(t) \mathbf{F}_i(t+s) {}^0f_i^{(1/N)}(\mathbf{p}_{i0}, \mathbf{R}_{i0}/\mathbf{P}_0, \mathbf{Q}_0) d\mathbf{P}_0 d\mathbf{Q}_0 ds, \quad (41)$$

in the sense that for values of  $s$  greater than  $\tau_i$ , but small on the macroscopic scale, the integral differs in absolute value from  $\zeta_i$  by an amount less than the precision error of a macroscopic measurement of the quantity, then  $\zeta_i(\tau)$  possesses the same plateau value  $\zeta_i$  in the same sense for  $\tau > \tau_i'$  where  $\tau_i/\tau_i' \ll 1$ . This may be expressed more precisely in the form,

$$|\zeta_i(\tau) - \zeta_i| = O(\epsilon); \quad \tau_i' < \tau < \tau^* \quad (42)$$

where  $\epsilon$  is less than the precision error in the macroscopic measurement of  $\zeta_i$  and  $\tau^*$  is a macroscopic interval of time certainly of smaller magnitude than the representative period of the Poincaré cycles of the system. We have intentionally avoided identifying  $\zeta_i(\tau)$ , for sufficiently long  $\tau$ , with its asymptotic value  $\zeta_i(\infty)$ , since the latter value may be shown to vanish for systems confined to a

finite region of configuration space. The apparent paradox encountered here is precisely the paradox between dynamical reversibility and thermodynamic irreversibility. The dissipative processes appearing to operate in thermodynamic systems provide a valid description of macroscopic behavior only if the time over which the properties of the system are averaged in a macroscopic observation is long relative to the periods of microscopic fluctuation but short relative to the periods of Poincaré cycles,\* within which secular changes in state may be spontaneously reversed. It is for these reasons that we are forced to speak of a plateau value for  $\zeta_i(\tau)$  rather than of its asymptotic value at  $\tau \rightarrow \infty$ , in discussing macroscopic transport processes. Whether such a plateau value exists will depend upon the dynamical structure of the system, that is upon the particular form of its Hamiltonian.

We shall investigate the friction constant  $\zeta_i$  in greater detail in Part IV. Anticipating a result to be obtained there, we remark that the integrand of Eq. (41) is found to be an even function of  $s$ .† This allows us to express  $\zeta_i$  in the following form,

$$\zeta_i = \frac{1}{6kT} \int_{-\tau_i}^{+\tau_i} {}^i\langle \mathbf{F}_i \cdot e^{-isL} \mathbf{F}_i \rangle^0 ds, \quad (43)$$

$${}^i\langle \mathbf{F}_i \cdot e^{-isL} \mathbf{F}_i \rangle^0 = \int \int [\mathbf{F}_i(\mathbf{R}_i, \mathbf{Q}_i) \cdot e^{-isL} \mathbf{F}_i(\mathbf{R}_i, \mathbf{Q}_i)] {}^0f_i^{(1/N)}(\mathbf{p}_i, \mathbf{R}_i/P, \mathbf{Q}) d\mathbf{P} d\mathbf{Q}.$$

Although it is apparent that in fluid systems  $\zeta_i$  will not depend upon the position  $\mathbf{R}_{i0}$  of the molecule in configuration space,  $\zeta_i$  may depend upon the momentum  $\mathbf{p}_{i0}$  of the molecule. It will be shown in Part IV that  $\zeta_i$  does not sensibly depend upon momentum, if the mass of molecule  $i$  is large relative to those of the other molecules of the system, for example, when  $i$  is a macromolecule in a solvent of low molecular weight. Also, even when molecule  $i$  has a mass comparable with those of its environment,  $\zeta_i$  may not depend sensibly on momentum in condensed systems such as liquids or liquid solutions. When  $\zeta_i$  does depend upon momentum it is an even function of this variable.

Returning now to Eq. (29), introducing Eqs. (30), (39), and (40) and neglecting the terms of order  $\tau$  in Eq. (39), after selecting  $\tau$  of sufficient magnitude to achieve the plateau value of  $\zeta_i(\tau)$ , we obtain the equation of motion,

$$\frac{d\mathbf{p}_i}{dt} + \zeta_i^0 \mathbf{p}_i / m_i = \mathbf{X}_i + \mathbf{G}_i, \quad \zeta_i^0 = \zeta_i - 2kT \frac{d\zeta_i}{d\mathbf{p}_i^2}, \quad (44)$$

where we have suppressed  ${}^i\langle \mathbf{F}_i \rangle^0$ , shown to vanish for an ideal dilute solution, and have identified  $\mathbf{p}_{i0}$  in Eq. (39) with  $\mathbf{p}_i$ , since the instant of time  $t$ , in the neighborhood of which the average  ${}^i\langle (\mathbf{F}_i)_\tau \rangle$  is made is properly to be taken as identical with the instant  $t$  at which the acceleration  $d\mathbf{p}_i/dt$  is to be calculated. If the plateau value  $\zeta_i$  exists, it is evident that

$${}^i\langle \mathbf{F}_i(t) \cdot \mathbf{F}_i(t+\tau) \rangle^0 = 0, \quad (45)$$

is valid to the same degree of approximation, that is  $\tau$  exceeds the time interval during which there is sensible correlation between the total intermolecular force acting in molecule at instants of time separated by that interval. This implies that, with neglect of terms of order  $\tau$ , there is no correlation between the force  $\mathbf{G}_i$  acting on molecule  $i$  at successive instants  $t$  and  $t+\tau$ .

Equation (44) thus becomes identical with the Langevin equation, if  $\zeta_i$  and therefore  $\zeta_i^0$  is independent of  $\mathbf{p}_i$ . When  $\zeta_i$  depends upon  $\mathbf{p}_i$ , a generalized Langevin equation containing a friction

\* Poincaré has stated the theorem that in a system of particles in which the forces depend only upon the spatial coordinates, a given initial state must recur to any specified degree of accuracy, an infinite number of times if the system is confined to a finite region of phase space. The term Poincaré cycle period is used to designate the time of recurrence of a given state to within a specified degree of accuracy in such "quasi-periodic" motion. For systems of molecules such periods are very long on the macroscopic time scale. It may therefore seem that we have placed undue emphasis on the rather obvious point that  $\tau_i$  should be short relative to such periods. We have done so in order to call attention to the circumstance that the apparently innocent mathematical procedure of letting  $\tau_i \rightarrow \infty$  in evaluating the friction constant leads to serious physical difficulties. For a more detailed discussion of these points, see S. Chandrasekar, *Rev. Mod. Phys.* **15**, 1-89 (1943), Appendix V.

† This may be regarded as a consequence of the principle of microscopic reversibility.

constant dependent on the velocity of the molecule is obtained. We have by means of our analysis suggested the conditions under which the Langevin equation may be expected to be valid, and, what is more significant, have established a relation, Eq. (41), between the friction constant and the intermolecular forces acting in a system of molecules. Many mathematical points call for further investigation, particularly the specification of the properties of the class of systems for which a plateau value  $\zeta_i$  exists, an investigation of the magnitude of the correlation time  $\tau_i$ , and an examination of the magnitude of the neglected terms of order  $\tau$  in Eq. (39). Some of these points will be discussed in Part IV.

Having established the Langevin equation, the details of the conventional theory of Brownian motion may be developed by the Markoff method or known alternative methods, which we do not need to discuss here

### III. THE DISTRIBUTION FUNCTIONS

We here return to the problem of determining the sequence of distribution functions  $\bar{f}^{(n)}$  from which the average values characterizing macroscopic transport processes are to be calculated. We shall proceed from the Liouville differential equation, Eq. (3), and the definitions, Eq. (20), of the distribution functions  $\bar{f}^{(n)}$ . Our general method leads on the one hand to the Maxwell-Boltzmann integro-differential equation for gases of sufficiently low density to permit analysis by binary collisions, and, on the other hand to a generalized Fokker-Planck equation, by methods closely related to those of the theory of Brownian motion developed in Part II, for liquids and liquid solutions.

The Liouville equation and the definition of the distribution function  $\bar{f}^{(n)}$  are conveniently summarized in the form

$$\sum_{l=1}^N \left\{ \frac{\mathbf{p}_l}{m_l} \cdot \nabla_{\mathbf{R}_l} f^{(N)} + (\mathbf{X}_l + \mathbf{F}_l) \cdot \nabla_{\mathbf{p}_l} f^{(N)} \right\} + \frac{\partial f^{(N)}}{\partial t} = 0,$$

$$f^{(n)}(\mathbf{p}, \mathbf{q}; t) = \int \int f^{(N)}(\mathbf{p}, \mathbf{q}, \mathbf{P}, \mathbf{Q}; t) d\mathbf{P} d\mathbf{Q},$$

$$\bar{f}^{(n)}(\mathbf{p}, \mathbf{q}; t) = \frac{1}{\tau} \int_0^\tau f^{(n)}(\mathbf{p}, \mathbf{q}; t+s) ds,$$
(46)

where, as before,  $\mathbf{p}$  and  $\mathbf{q}$  denote the coordinates of the set of molecules  $n$  and  $\mathbf{P}$  and  $\mathbf{Q}$  those of the set  $N-n$ , constituting the other molecules of system. In our preliminary remarks, we shall repress subscripts indicating the molecule types comprised in the set  $n$ . Integrating the Liouville equation over the partial phase space  $(\mathbf{P}, \mathbf{Q})$ , and restricting our analysis to distributions  $\bar{f}^{(N)}$  for which the surface integrals of the currents vanish on the boundary of the phase space accessible to the system, we obtain with use of Green's theorem,

$$\frac{\partial \bar{f}^{(n)}}{\partial t} + \frac{\mathbf{p}}{m} \cdot \nabla_{\mathbf{q}} \bar{f}^{(n)} + \mathbf{X} \cdot \nabla_{\mathbf{p}} \bar{f}^{(n)} = \nabla_{\mathbf{p}} \cdot \boldsymbol{\Omega}^{(n)},$$

$$\boldsymbol{\Omega}^{(n)} = -\frac{1}{\tau} \int_0^\tau \int \mathbf{F}(\mathbf{q}, \mathbf{Q}) f^{(N)}(\mathbf{p}, \mathbf{q}, \mathbf{P}, \mathbf{Q}; t+s) d\mathbf{P} d\mathbf{Q} ds,$$
(47)

where  $\mathbf{X}$  denotes the total external and  $\mathbf{F}$  the total intermolecular force, regarded as vectors in the  $n$ -configuration space of set  $n$ , and  $\mathbf{p}/m$  represents a vector in the  $n$ -momentum space with projections  $\mathbf{p}_1/m_1 \cdots \mathbf{p}_n/m_n$  on the 3-spaces of the several molecules of the set. If the intermolecular force has the form, Eq. (2), we may express the mean currents due to intermolecular forces as

$$\boldsymbol{\Omega}^{(n)} = - \sum_{i,k=1}^n \mathbf{F}_{ki} \bar{f}^{(n)} + \sum_{i=1}^n \sum_{l=n+1}^N \boldsymbol{\Omega}_{li}^{(n)},$$

$$\boldsymbol{\Omega}_{li}^{(n)} = - \int \int \mathbf{F}_{li}(R_{li}) f^{(n+1)}(\mathbf{p}, \mathbf{q}, \mathbf{p}_l, \mathbf{R}_l; t) d\mathbf{p}_l d\mathbf{R}_l,$$
(48)

where  $\mathbf{F}_{ki}$  and  $\Omega_{li}^{(n)}$  are to be treated as vectors in the 3-configuration space of molecule  $i$  of the set  $n$  (not as vectors in a common 3-space). Eqs. (47) and (48) provide a system of integro-differential equations for the sequence of distribution functions  $f^{(n)}$ , in which the dissipative mechanism affecting their behavior is concealed in time-averaged function of highest order  $f^{(N)}$ . It is therefore necessary to transform the terms  $\Omega_{li}^{(n)}$  with the aid of solutions, Eq. (5) of the Liouville equation for  $f^{(N)}$  in order to obtain useful results.

To avoid undue complication, we shall now specialize the analysis to the distribution function  $f_i^{(1)}$ , the distribution function of order one for a molecule of type  $i$ . The extension of the method to distribution functions of higher order will be obvious. Eq. (47) now reduces to

$$\frac{\partial \bar{f}_i^{(1)}}{\partial t} + \frac{\mathbf{p}_i}{m_i} \cdot \nabla_{\mathbf{R}_i} \bar{f}_i^{(1)} + \mathbf{X}_i \cdot \nabla_{\mathbf{p}_i} \bar{f}_i^{(1)} = \nabla_{\mathbf{p}_i} \cdot \Omega_i^{(1)},$$

$$\Omega_i^{(1)} = \sum_{l=1}^r N_l \Omega_{li}^{(1)}, \quad (49)$$

$$\Omega_{li}^{(1)} = -\frac{1}{\tau} \int_0^\tau \int \cdots \int \mathbf{F}_{li}(R_{il}) f^{(N)}(\mathbf{p}_i, \mathbf{R}_i, \mathbf{p}_l, \mathbf{R}_l, \mathbf{P}, \mathbf{Q}; t+s) d\mathbf{P} d\mathbf{Q} d\mathbf{p}_l d\mathbf{R}_l ds,$$

where  $\mathbf{P}$  and  $\mathbf{Q}$  here denote the coordinates of all molecules except those of a specified pair of molecules  $i$  and  $l$  of types  $i$  and  $l$  respectively (subscripts on coordinates denote specified molecules; on functions  $\Omega_{li}$ ,  $\mathbf{F}_{li}$ , etc., they denote molecular types). Using Eqs. (5) and (22) we may write

$$f^{(N)}(\mathbf{p}_i, \mathbf{R}_i, \mathbf{p}_l, \mathbf{R}_l, \mathbf{P}, \mathbf{Q}; t+s) = f^{(N)}(\mathbf{p}_{i0}, \mathbf{R}_{i0}, \mathbf{p}_{l0}, \mathbf{R}_{l0}, \mathbf{P}_0, \mathbf{Q}_0; t),$$

$$f^{(N)}(\mathbf{p}_{i0}, \mathbf{R}_{i0}, \mathbf{p}_{l0}, \mathbf{R}_{l0}, \mathbf{P}_0, \mathbf{Q}_0; t) = f_{il}^{(2/N)}(\mathbf{p}_{i0}, \mathbf{R}_{i0}, \mathbf{p}_{l0}, \mathbf{R}_{l0}, \mathbf{P}_0, \mathbf{Q}_0; t) f_{il}^{(2)}(\mathbf{p}_{i0}, \mathbf{R}_{i0}, \mathbf{p}_{l0}, \mathbf{R}_{l0}; t), \quad (50)$$

$$f_{il}^{(2)}(\mathbf{p}_{i0}, \mathbf{R}_{i0}, \mathbf{p}_{l0}, \mathbf{R}_{l0}; t) = \varphi_{il}^{(2)}(\mathbf{p}_{i0}, \mathbf{R}_{i0}, \mathbf{p}_{l0}, \mathbf{R}_{l0}; t) f_i^{(1)}(\mathbf{p}_{i0}, \mathbf{R}_{i0}; t) f_l^{(1)}(\mathbf{p}_{l0}, \mathbf{R}_{l0}; t),$$

where  $f_{il}^{(2/N)}$  is the relative probability density in the partial phase space  $(\mathbf{P}, \mathbf{Q})$  when a pair of molecules of type  $i$  and  $l$  have specified coordinates. The correlation function  $\varphi_{il}^{(2)}$  is defined by the last of Eq. (50). In the last of Eq. (49) defining  $\Omega_{li}^{(1)}$  we extend the integration over all of phase space with the use of delta functions, transform the variables of integration from  $\mathbf{p}_i \cdots \mathbf{Q}$  to  $\mathbf{p}_{i0} \cdots \mathbf{Q}_0$ , and introduce the relations of Eq. (50). We then obtain

$$\Omega_{li}^{(1)} = \int \cdots \int \mathbf{K}_{li}(\mathbf{p}_{i0} \cdots \mathbf{R}_{l0}; t) f_l^{(1)}(\mathbf{p}_{l0}, \mathbf{R}_{l0}; t) f_i^{(1)}(\mathbf{p}_{i0}, \mathbf{R}_{i0}; t) d\mathbf{p}_{l0} d\mathbf{R}_{l0} d\mathbf{p}_{i0} d\mathbf{R}_{i0},$$

$$\mathbf{K}_{li} = -\frac{1}{\tau} \int_0^\tau \int \int \mathbf{F}_{li}(t+s) \delta(\mathbf{p}_{i0} + \Delta \mathbf{p}_i - \mathbf{p}_i) \delta(\mathbf{R}_{i0} + \Delta \mathbf{R}_i - \mathbf{R}_i) \varphi_{il}^{(2)}(\mathbf{p}_{i0} \cdots \mathbf{R}_{l0}; t)$$

$$\times f^{(2/N)}(\mathbf{p}_{i0}, \mathbf{R}_{i0}, \mathbf{p}_{l0}, \mathbf{R}_{l0}/\mathbf{P}_0, \mathbf{Q}_0; t) d\mathbf{P}_0 d\mathbf{Q}_0 ds, \quad (51)$$

$$\mathbf{F}_{li}(t+s) = \mathbf{F}_{li}(R_{il}) = \mathbf{F}_{li}(\mathbf{p}_{i0} \cdots \mathbf{Q}_0; s), \quad \Delta \mathbf{p}_i = \int_0^s \mathbf{F}_i ds' + \mathbf{X}_i s; \quad \Delta \mathbf{R}_i = \int_0^s \mathbf{p}_i/m_i ds'.$$

An integral of the type of  $\mathbf{K}_{li}$  vanishes for sufficiently large  $\tau$  if, in place of  $\varphi_{il}^{(2)}$ , the integrand contains a factor which is a short range function of the distance between molecules  $i$  and  $l$ , diminishing say with distance in the same order as  $\mathbf{F}_{li}$ . If we use the identity

$$\varphi_{il}^{(2)} = \exp(-\beta W_{il}^{(2)}) [1 + (\varphi_{il}^{(2)} \exp(\beta W_{il}^{(2)}) - 1)], \quad (52)$$

where  $W_{il}^{(2)}$  is equilibrium potential of mean force acting on the pair  $il$  and restrict our analysis to distributions for which  $(\varphi_{il}^{(2)} \exp(\beta W_{il}^{(2)}) - 1)$  is a short range function of the intermolecular distance, we may express  $\mathbf{K}_{li}$  in the form

$$\mathbf{K}_{li} = -\frac{1}{\tau} \int_0^\tau \int \int \mathbf{F}_{li}(t+s) \delta(\mathbf{p}_{i0} + \Delta \mathbf{p}_i - \mathbf{p}_i) \delta(\mathbf{R}_{i0} + \Delta \mathbf{R}_i - \mathbf{R}_i) \exp(-\beta W_{il}^{(2)})$$

$$\times f_{il}^{(2/N)}(\mathbf{p}_{i0}, \mathbf{R}_{i0}, \mathbf{p}_{l0}, \mathbf{R}_{l0}/\mathbf{P}_0, \mathbf{Q}_0; t) d\mathbf{P}_0 d\mathbf{Q}_0 ds, \quad (53)$$

where the factor  $\exp(-\beta W_{il}^{(2)})$ , although convenient for later use, is arbitrary to the extent that it might be replaced by unity or any function differing from unity by short range terms.

An analytical development of the Maxwell-Boltzmann integro-differential equation may be based on Eq. (53) and the assumption of binary molecular collisions, namely that for configurations in which  $\mathbf{F}_{li}$  differs from zero,  $d(\Delta \mathbf{p}_i)/dt = \mathbf{F}_{li}$ . Since the derivation is somewhat complicated, we shall postpone it for special treatment in a later article. The derivation is worth while, since it clarifies certain important points left obscure by the usual physical argument used to establish the Maxwell-Boltzmann equation.

We shall here employ the methods of the theory of Brownian motion to evaluate  $\mathbf{K}_{li}$ , writing

$$\mathbf{K}_{li} = \mathbf{K}_{li}^0 + \Delta \mathbf{K}_{li},$$

$$\mathbf{K}_{li}^0 = \frac{1}{\tau} \int_0^\tau \int \int \mathbf{F}_{li}(t+s) \delta(\mathbf{p}_{i0} + \Delta \mathbf{p}_i - \mathbf{p}_i) \delta(\mathbf{R}_{i0} + \Delta \mathbf{R}_i - \mathbf{R}_i) \exp[-\beta W_{il}^{(2)}(R_{il})] \times {}^0 f_{il}^{(2/N)}(\mathbf{p}_{i0}, \mathbf{R}_{i0}, \mathbf{p}_{l0}, \mathbf{R}_{l0}/\mathbf{P}_0, \mathbf{Q}_0) d\mathbf{P}_0 d\mathbf{Q}_0 ds, \quad (54)$$

$${}^0 f_{il}^{(2/N)} = \left( \frac{\beta^2}{(2\pi)^2 m_i m_l} \right)^{\frac{1}{2}} \frac{1}{v^2} \exp \{ \beta [A^N - H_0^N + \mathbf{p}_{i0}^2/2m_i + \mathbf{p}_{l0}^2/2m_l + W_{il}^{(2)}(R_{il0})] \},$$

where  ${}^0 f_{il}^{(2/N)}$  is the equilibrium distribution function in the phase space of the molecules constituting the environment of the molecular pair  $il$ , and  $\Delta \mathbf{K}_{li}$  is the contribution to  $\mathbf{K}_{li}$  arising from the departure of  $f_{il}^{(2/N)}$  from the equilibrium distribution  ${}^0 f_{il}^{(2/N)}$ . Introducing the following relations,

$$\exp[-\beta W_{il}^{(2)}(R_{il0})] {}^0 f_{il}^{(2/N)}(\mathbf{p}_{i0}, \mathbf{R}_{i0}, \mathbf{p}_{l0}, \mathbf{R}_{l0}/\mathbf{P}_0, \mathbf{Q}_0) = \exp[-\beta W_{il}^{(2)}(R_{il})] {}^0 f_{il}^{(2/N)}(\mathbf{p}_i, \mathbf{R}_i, \mathbf{p}_l, \mathbf{R}_l/\mathbf{P}, \mathbf{Q}) \times \left\{ 1 - \frac{\beta \mathbf{p}_{i0}}{m_i} \cdot \Delta \mathbf{p}_i - \frac{\beta \mathbf{p}_{l0}}{m_l} \cdot \Delta \mathbf{p}_l + \dots \right\}, \quad (55)$$

$$\delta(\mathbf{p}_{i0} + \Delta \mathbf{p}_i - \mathbf{p}_i) = \delta(\mathbf{p}_{i0} - \mathbf{p}_i) - \Delta \mathbf{p}_i \cdot \nabla_{\mathbf{p}_i} \delta(\mathbf{p}_{i0} - \mathbf{p}_i) + \dots,$$

$$\delta(\mathbf{R}_{i0} + \Delta \mathbf{R}_i - \mathbf{R}_i) = \delta(\mathbf{R}_{i0} - \mathbf{R}_i) + \dots,$$

based upon the invariance of  $H^N$  under the transformation  $(\mathbf{p}_{i0} \dots \mathbf{Q}_0)$  to  $(\mathbf{p}_i \dots \mathbf{Q})$ , and expansion of the delta functions, we finally obtain for  $\Omega_{li}^{(1)}$ ,

$$\Omega_{li}^{(1)} = {}^0 \Omega_{li}^{(1)} + \Delta \Omega_{li}^{(1)},$$

$${}^0 \Omega_{li}^{(1)} = -(\langle \mathbf{F}_{li} \rangle^0 + \zeta_i^l \mathbf{v}_i^*) f_i^{(1)}(\mathbf{p}_i, \mathbf{R}_i; t) + \zeta_i^l \{ \mathbf{p}_i/m_i + kT \nabla_{\mathbf{p}_i} \} f_i^{(1)}(\mathbf{p}_i, \mathbf{R}_i; t) + O(\tau),$$

$$\zeta_i^l = \frac{1}{6kT} \int_{-\tau_i}^{+\tau_i} \langle \mathbf{F}_{li} \cdot e^{-isL} \mathbf{F}_l \rangle^0 ds, \quad \langle \mathbf{F}_{li} \rangle^0 = \frac{1}{v} \int \mathbf{F}_{li} \exp(-\beta W_{il}^{(2)}) d\mathbf{R}_l,$$

$$\mathbf{v}_i^* = (N_l/C_l) \int (\mathbf{p}_l/m_l) \chi_{il} f_l^{(1)}(\mathbf{p}_l, \mathbf{R}_l; t) d\mathbf{R}_l d\mathbf{p}_l,$$

$$\chi_{il} = \frac{\exp(-\beta W_{il}^{(2)})}{6kT \zeta_i^l} \int_{-\tau_i}^{+\tau_i} \langle \mathbf{F}_{li} \cdot e^{-isL} \mathbf{F}_l \rangle^0 ds, \quad (56)$$

where the methods of Part II have been used to simplify the plateau values of the partial friction constant  $\zeta_i^l$ , and departures of  $f_l^{(1)}$  from  ${}^0 f_l^{(1)}$  have been ignored in the expressions for  $\zeta_i^l$  and  $\langle \mathbf{F}_{li} \rangle^0$ , since we are interested here in obtaining relations valid only to the first order in parameters determining departures from equilibrium. Since the gradient of  $f_l^{(1)}(\mathbf{p}_l, \mathbf{R}_l; t)$  in configuration space is supposed to be appreciable only over distances of macroscopic magnitude, and since  $\chi_{il}$  is a short range function of the intermolecular distance  $R_{il}$ , we may write  $f_l^{(1)}(\mathbf{p}_l, \mathbf{R}_l; t)$  in the integral defining

$\mathbf{v}_i^*$ . If  $\chi_{il}$  is independent of  $\mathbf{p}_l$ , the integral  $\int \chi_{il} d\mathbf{R}_l$  is unity and the velocity  $\mathbf{v}_i^*$  reduces after time smoothing to the mean particle velocity,  $\mathbf{v}_l$ , of the molecular species  $l$  at point  $\mathbf{R}_i$ ,

$$\mathbf{v}_l(\mathbf{R}_i, t) = (N_l/C_l) \int (\mathbf{p}_l/m_l) f_l^{(1)}(\mathbf{p}_l, \mathbf{R}_i; t) d\mathbf{p}_l. \quad (57)$$

The term  $\Delta\mathbf{Q}_{li}^{(1)}$  represents the contribution to  $\mathbf{Q}_{li}^{(1)}$  arising from the departure of the molecules of the environment of the pair  $il$  from statistical equilibrium. For convenience in notation, it will be convenient to define a supplementary force  $\mathbf{F}_{li}^+$  by the relation

$$\Delta\mathbf{Q}_{li}^{(1)} = \mathbf{F}_{li}^+ f_i^{(1)}. \quad (58)$$

The calculation of  $\mathbf{F}_{li}^+$  of course requires a knowledge of distribution functions of higher order than  $f^{(1)}$ . If we had calculated  $\mathbf{Q}_{li}^{(1)}$  under the assumption, not that the pair environment was in equilibrium, but in a lower order of approximation, that the environment of molecule  $i$  alone was in equilibrium, we would have obtained all terms in Eq. (56) except those involving the  $\mathbf{v}_i^*$ .

Introducing Eqs. (56) and (58) into Eq. (49), and neglecting terms of order  $\tau$ , and performing a second time average over the interval  $\tau$  on the terms of Eq. (56), which will not affect terms already smoothed and possessing only secular time dependence, we obtain the following partial differential equation for  $\bar{f}_i^{(1)}$ ,

$$\begin{aligned} \frac{\partial \bar{f}_i^{(1)}}{\partial t} + \frac{\mathbf{p}_i}{m_i} \cdot \nabla_{\mathbf{R}_i} \bar{f}_i^{(1)} + \nabla_{\mathbf{p}_i} \cdot (\mathbf{F}_i^* + \mathbf{X}_i) \bar{f}_i^{(1)} &= \nabla_{\mathbf{p}_i} \cdot \zeta_i \left\{ \frac{\mathbf{p}_i}{m_i} \bar{f}_i^{(1)} + kT \nabla_{\mathbf{p}_i} \bar{f}_i^{(1)} \right\}, \\ \mathbf{F}_i^* &= {}^i\langle \mathbf{F}_i \rangle^0 + \sum_{l=1}^v N_l \zeta_l {}^i\mathbf{v}_l^* + \mathbf{F}_i^+, \\ {}^i\langle \mathbf{F}_i \rangle^0 &= \sum_{l=1}^v N_l {}^i\langle \mathbf{F}_{li} \rangle^0 = -\nabla \mu_i + kT \nabla \log C_i, \quad \mathbf{F}_i^+ = \sum_{l=1}^v N_l \mathbf{F}_{li}^+, \\ \zeta_i &= \sum_{l=1}^v N_l \zeta_i^l = \frac{1}{6kT} \int_{-\tau_i}^{+\tau_i} {}^i\langle \mathbf{F}_i \cdot e^{-isL} \mathbf{F}_i \rangle^0 ds, \end{aligned} \quad (59)$$

where, of course,  $\mathbf{F}_i^+$  requires further analysis for its calculation. Equation (59) differs from the generalized Fokker-Planck equation of Chandrasekar<sup>8</sup> in the appearance of the force  $\mathbf{F}_i^*$  and in the fact that we have related the friction constant to the intermolecular forces in an explicit manner. If the equation is formulated under the assumption that molecule  $i$  is a solute component of an ideal dilute solution with an environment in statistical equilibrium,  $\mathbf{F}_i^*$  vanishes. In order to relate  $\zeta_i$  to intermolecular forces, it is necessary to employ statistical mechanics to construct the Brownian motion kernel of Chandrasekar's Eq. (241). This is, in effect, what we have attempted here, although we have made the Liouville equation our starting point rather than the formal integral equation, Chandrasekar (241).

The second group of terms, involving the  $\mathbf{v}_i^*$ , are of importance in the theory of diffusion. They give rise to macroscopic interactions by means of which a chemical potential gradient of one component of a solution may cause transport of another component. These questions will be treated in detail in a later article on diffusion.

The method employed in the formulation of Eq. (59) for the distribution function  $\bar{f}_i^{(1)}$  may be applied to distribution functions of higher order  $\bar{f}_i^{(n)}$ , if the number of degrees of freedom of the set  $n$  is small relative to the total number of degrees of freedom of the entire system. Otherwise, it appears that the plateau values of the friction tensors will not in general exist. With slightly more tedious algebraic details, the method yields for the distribution function  $\bar{f}_{i \dots k}^{(n)}(\mathbf{p}, \mathbf{q}; t)$  in a set of  $n$

<sup>8</sup> S. Chandrasekar, Rev. Mod. Phys. **15**, 1-89 (1943), Eq. (249).



molecules of types  $i \cdots k$ , respectively,

$$\begin{aligned}
 \frac{\partial \tilde{f}_{i \cdots k}^{(n)}}{\partial t} + \frac{\mathbf{p}}{m} \cdot \nabla_{\mathbf{q}} \tilde{f}_{i \cdots k}^{(n)} + \nabla_{\mathbf{p}} \cdot (\mathbf{F}_{i \cdots k}^* + \mathbf{X}_{i \cdots k}) \tilde{f}_{i \cdots k}^{(n)} &= \nabla_{\mathbf{p}} \cdot \zeta_{i \cdots k}^{(n)} \left\{ \frac{\mathbf{p}}{m} \tilde{f}_{i \cdots k}^{(n)} + kT \nabla_{\mathbf{p}} \tilde{f}_{i \cdots k}^{(n)} \right\}, \\
 \mathbf{F}_{i \cdots k}^* &= i \cdots k \langle \mathbf{F}_{i \cdots k} \rangle^0 + \sum_{l=1}^N N_l \int \zeta_{l i \cdots k} \frac{\mathbf{p}_l}{m_l} \tilde{f}_l^{(1)}(\mathbf{p}_l, \mathbf{R}_l; t) d\mathbf{R}_l d\mathbf{p}_l + \mathbf{F}_{i \cdots k}^+, \\
 \zeta_{l i \cdots k} &= \frac{1}{2kT} \left\{ \sum_{\alpha=1}^n \int_{-\tau_{i \cdots k}}^{+\tau_{i \cdots k}} i \cdots k l \langle \mathbf{F}_{\alpha l} e^{-isL\mathbf{F}_l} \rangle^0 ds \right\} \exp(-\beta W_{i \cdots k l}^{(n+1)}), \\
 \zeta_{i \cdots k}^{(n)} &= \frac{1}{2kT} \sum_{\alpha=1}^n \int_{-\tau_{i \cdots k}}^{+\tau_{i \cdots k}} i \cdots k \langle \mathbf{F}_{\alpha'} e^{-isL\mathbf{F}_{\alpha'}} \rangle^0 ds, \\
 \mathbf{F}_{\alpha'} &= \sum_{l=n+1}^N \mathbf{F}_{l\alpha}, \quad i \cdots k \langle \mathbf{F}_{i \cdots k} \rangle^0 = -\nabla_{\mathbf{q}} W_{i \cdots k}^{(n)},
 \end{aligned} \tag{60}$$

where  $W_{i \cdots k}^{(n)}$  is the equilibrium potential of average force in the set  $n$ , and  $\mathbf{F}_{i \cdots k}^+$  is the average force due to the departure from equilibrium of the environment of the set of  $n+1$  molecules of types  $i \cdots k$  and  $l$ . The friction tensor  $\zeta_{i \cdots k}^{(n)}$  is not in general isotropic in the momentum space of the set  $n$  as was  $\zeta_i^{(1)}$ , which we denoted simply by  $\zeta_i$ , for fluid systems. Since  $i \cdots k \langle \mathbf{F}_{i \cdots k} \rangle^0$  may have gradients in configuration space which are appreciable over distances of molecular magnitude, Eq. (60) requires for its validity the additional conditions, not necessary in the case of  $\tilde{f}_i^{(1)}$ , that the correlation time  $\tau_{i \cdots k}$ , be sufficiently short that the changes in configuration of the set  $n$ , with representative velocities in the neighborhood of the equilibrium mean thermal velocities, are negligible in the interval  $\tau_{i \cdots k}$ , in comparison with the range of intermolecular force. Although this question requires more careful examination, we remark here that the condition is probably fulfilled to an adequate degree of approximation in condensed systems such as liquids and liquid solutions.

In a series of later articles treating specific transport processes, diffusion, heat conduction, and viscous fluid flow, we plan to suggest an approximation based upon the neglect of  $\mathbf{F}_{ik}^+$  for pairs, namely the average force arising from the departure of the environment of sets of three molecules from equilibrium.

#### IV. THE FRICTION CONSTANT

The statistical mechanical theory of transport processes which we have outlined leads to a generalized theory of Brownian motion for small sets of  $n$  molecules forming a part of a large system of  $N$  molecules. The most significant result of the theory is the relation which it provides between the friction constant, entering into the Langevin equation and into the differential equations for the distribution functions of lower order, and the intermolecular forces acting in the system. We shall attempt here to transform the expression for the friction constant  $\zeta_i$  into a form suitable for its calculation from the potential of intermolecular force. The method which we shall propose is to be regarded as tentative and the possibility that it may in the future have to be superseded by more refined methods should be kept in mind.

We repeat the expression, Eq. (43), for the friction constant  $\zeta_i$ , introducing the canonical distribution for  ${}^0f_i^{(1/N)}$

$$\begin{aligned}
 \zeta_i &= \frac{1}{6kT} \int_{-\tau_i}^{+\tau_i} i \langle \mathbf{F}_i \cdot e^{-isL\mathbf{F}_i} \rangle^0 ds, \\
 i \langle \mathbf{F}_i \cdot e^{-isL\mathbf{F}_i} \rangle^0 &= \int \int \{ \mathbf{F}_i \cdot e^{-isL\mathbf{F}_i} \} ({}^0f_i^{(1)})^{-1} e^{\beta(A-H)} d\mathbf{P} d\mathbf{Q}, \\
 {}^0f_i^{(1)} &= \left( \frac{\beta}{2\pi m_i} \right)^{\frac{1}{2}} \frac{1}{v} \exp[-\beta p_i^2/2m_i - \beta W_i^{(1)}], \\
 L &= i \sum_{l=1}^N \left\{ \frac{\mathbf{p}_l}{m_l} \cdot \nabla_{\mathbf{R}_l} + \mathbf{F}_l \cdot \nabla_{\mathbf{p}_l} \right\},
 \end{aligned} \tag{61}$$

where in the expression for the operator  $L$ , as also in the Hamiltonian  $H$ , we omit terms arising from the external forces  $\mathbf{X}_i$ , since the latter will contribute at most terms of the second order to the distribution functions, the external forces being assumed small, of the first order, in systems to which the theory is applicable. We recall that the friction constant may be a function  $\zeta_i(\mathbf{R}_i, \mathbf{p}_i)$  of the coordinates of molecule  $i$ , although in fluid systems we would expect no sensible dependence on  $\mathbf{R}_i$ . It will be found to be convenient to introduce a friction constant  $\langle \zeta_i \rangle_{Av}$ , the mean value of  $\zeta$  in the phase space of molecule  $i$ .

$$\begin{aligned} \langle \zeta_i \rangle_{Av} &= \int \int \zeta_i(\mathbf{p}_i, \mathbf{R}_i) f_i^{(1)}(\mathbf{p}_i, \mathbf{R}_i) d\mathbf{p}_i d\mathbf{R}_i \\ &= \frac{1}{6kT} \int_{-\tau_i}^{\tau_i} \langle \mathbf{F}_i \cdot e^{-isL} \mathbf{F}_i \rangle^0 ds, \end{aligned} \quad (62)$$

$$\langle \mathbf{F}_i \cdot e^{-isL} \mathbf{F}_i \rangle^0 = \int \cdots \int \{ \mathbf{F}_i \cdot e^{-isL} \mathbf{F}_i \} e^{\beta(A-H)} d\mathbf{p}_1 \cdots d\mathbf{R}_N.$$

If  $\zeta_i$  is independent of  $\mathbf{p}_i$  as well as  $\mathbf{R}_i$ , it is of course identical with  $\langle \zeta_i \rangle_{Av}$ .

If we assume that the correlation  $\langle \mathbf{F}_i \exp(-isL) \mathbf{F}_i \rangle^0$  between the intermolecular forces acting on molecule  $i$  at instants of time separated by the interval  $s$  is a monotone decreasing function of time in the neighborhood of  $s=0$ , it is reasonable to try to represent the decay by a Gaussian factor determined by the second moment of the operator  $L$ . If we denote by  $\mu_n^{(i)}$  the  $n$ 'th moment of the operator  $L$ , defined as follows

$$\begin{aligned} \mu_n^{(i)} &= \frac{1}{\Delta F_i} \int \cdots \int \{ \mathbf{F}_i \cdot L^n \mathbf{F}_i \} e^{\beta(A-H)} d\mathbf{p}_1 \cdots d\mathbf{R}_N, \\ \Delta F_i &= \langle F_i^2 \rangle^0 = \int \cdots \int F_i^2 e^{\beta(A-H)} d\mathbf{p}_1 \cdots d\mathbf{R}_N, \\ \omega_i^2 &= \mu_2^{(i)}, \end{aligned} \quad (63)$$

where  $L^n$  denotes  $n$  successive applications of the operator  $L$ , we find that the  $\mu_n^{(i)}$  are positive for even  $n$  and vanish for odd  $n$ . Using the formal power series, Eq. (8), for the operator  $\exp(-isL)$  in the integrand of Eq. (62) defining  $\langle \mathbf{F}_i \cdot e^{-isL} \mathbf{F}_i \rangle^0$  and factoring the function  $\exp(-\omega_i^2 s^2/2)$  from the resulting power series,  $\omega_i^2$  being used in place of  $\mu_2^{(i)}$ , the second moment, we obtain,

$$\begin{aligned} \langle \mathbf{F}_i \cdot e^{-isL} \mathbf{F}_i \rangle^0 &= \Delta F_i \exp(-\omega_i^2 s^2/2) \sum_{n=0}^{\infty} \frac{\kappa_n^{(i)} (\omega_i^2 s^2)^n}{(2n)!}, \\ \kappa_n^{(i)} &= \sum_{r=0}^n \frac{(2n)! (-1)^r}{(2r)! (n-r)! 2^{n-r}} \frac{\mu_{2r}^{(i)}}{\mu_2^{(i)r}}. \end{aligned} \quad (64)$$

Substitution of the series (64) into the time integral of Eq. (62) yields the plateau value,

$$\langle \zeta_i \rangle_{Av} = \frac{(2\pi)^{1/2} \Delta F_i}{6kT\omega_i} \left\{ 1 + \sum_{n=2}^{\infty} \frac{\kappa_n^{(i)}}{2^n n!} \right\}, \quad (65)$$

with the neglect of terms of  $O[\exp(-\omega_i^2 \tau_i^2/2)]$ . Assuming the formal procedure leading to Eq. (65) to be valid, we are able to specify more precisely the magnitude of the microscopic time interval  $\tau_i$ , over which the integral defining the friction constant  $\langle \zeta_i \rangle_{Av}$  must be extended in order to attain the plateau value. The correlation time is of the order of  $1/\omega_i$  and  $\tau_i$  must evidently be large relative to  $1/\omega_i$ .

We shall not here attempt to give a mathematical justification of the formal procedure leading to Eq. (65), but tentatively accept the result as plausible for systems of molecules with intermolecular

forces of known types. Properly, the class of dynamical systems, for which the procedure is valid, should be characterized by suitable restrictions on their Hamiltonians. We should probably be prepared to find that, in cases of interest, the series of Eq. (65) is an asymptotic series and not a convergent series.

The variance or fluctuation of intermolecular force  $\Delta F_i$  may, for intermolecular forces of the type of Eq. (2), be expressed as follows

$$\Delta F_i = \sum_{l=1}^v N_l \langle F_{il}^2 \rangle^0 + \sum_{l=1}^v \sum_{l'=1}^v N_l N_{l'} \langle \mathbf{F}_{il} \cdot \mathbf{F}_{l'i} \rangle^0, \quad (66)$$

where  $\mathbf{F}_{il}$  is the force exerted on a molecule of type  $i$  by a molecule of type  $l$ . In the absence of long range forces, for example Coulomb forces acting between ions in solution, the average values of Eq. (66) may be transformed with the aid of Green's theorem to give,

$$\Delta F_i = kT \sum_{l=1}^v c_l \Delta_{il}, \quad \Delta_{il} = N \int \nabla^2 V_{il}(R) \exp(-\beta W_{il}^{(2)}) dv, \quad (67)$$

where  $W_{il}^{(2)}$  is equilibrium potential of average force between a pair of type  $il$ ,  $V_{il}$  the potential of intermolecular force between the pair, and the integral is to be extended over all values of their relative coordinates;  $N$  is here Avogadro's number and  $c_l$  is the concentration of component  $l$  in moles per unit volume. The function  $\exp(-\beta W_{il}^{(2)})$  is the radial distribution function for a pair  $il$  in the equilibrium ensemble.

The characteristic frequency  $\omega_i^2$  may be expressed in the following form,

$$\omega_i^2 = \frac{1}{\Delta F_i} [\langle L^* \mathbf{F}_i \cdot L \mathbf{F}_i \rangle^0], \quad (68)$$

by virtue of the fact that  $L$  is self-adjoint. Integration over momentum space leads to the result

$$\omega_i^2 = \frac{kT}{\Delta F_i} \sum_{l=1}^N (1/m_l) \langle (\nabla_l \mathbf{F}_i) : (\nabla_l \mathbf{F}_i) \rangle^0 \quad (69)$$

where  $(\nabla_l \mathbf{F}_i) : (\nabla_l \mathbf{F}_i)$  denotes the inner product of the dyadic  $\nabla_l \mathbf{F}_i$ , equal to the sum of the squares of its nine components. For intermolecular forces of the type of Eq. (2), a further reduction is possible, in the absence of long range Coulomb forces,

$$\begin{aligned} \omega_i^2 &= \frac{kT}{\Delta F_i} \left\{ \sum_{l=1}^v \left( \frac{1}{M_l} + \frac{1}{M_i} \right) C_l I_l^i + \frac{1}{M_i} \sum_{l=1}^v \sum_{l'=1}^v C_l C_{l'} I_{ll'}^i \right\}, \\ I_l^i &= N^2 \int \left\{ \left( \frac{d^2 V_{il}}{dR^2} \right)^2 + \frac{2}{R^2} \left( \frac{dV_{il}}{dR} \right)^2 \right\} \exp(-\beta W_{il}^{(2)}) dv, \\ I_{ll'}^i &= N^3 \int \int \left\{ \cos^2 \gamma \frac{d^2 V_{il}}{dR^2} \frac{d^2 V_{il'}}{dR'^2} + \sin^2 \gamma \left[ \frac{1}{R} \frac{dV_{il}}{dR} \frac{d^2 V_{il'}}{dR'^2} + \frac{1}{R'} \frac{d^2 V_{il}}{dR^2} \frac{dV_{il'}}{dR'} \right] \right. \\ &\quad \left. + \frac{3 - \cos^2 \gamma}{RR'} \frac{dV_{il}}{dR} \frac{dV_{il'}}{dR'} \right\} \exp(-\beta W_{ill'}^{(3)}) dv' dv, \\ \cos \gamma &= (\mathbf{R}' \cdot \mathbf{R}) / R'R, \end{aligned} \quad (70)$$

where  $M_i$  and  $M_l$  are the molecular weights of components  $i$  and  $l$  respectively, and  $V_{il}(R)$  and  $V_{il'}(R')$  are the potentials of the force between pairs of types  $il$  and  $il'$ , respectively. The potential  $W_{ill'}^{(3)}$  is the equilibrium potential of average force acting on molecules  $l'$  and  $l$  situated at points  $R'$  and  $R$  from the fixed molecule  $i$ . The average values in configuration space have been simplified for fluid systems in which  $W_i^{(1)}$  the equilibrium potential of mean force on any molecule  $i$  is zero.

Returning to the friction constant  $\zeta_i$ , which may depend upon  $\mathbf{p}_i$  and thus differ from  $\langle \zeta_i \rangle_{Av}$ , we make the hypothesis that the time decay of the mean value  $\langle \mathbf{F}_i \cdot e^{-isL} \mathbf{F}_i \rangle^0$  is also of the order of  $\exp(-\omega_i^2 s^2/2)$  with the  $\omega_i^2$  of Eqs. (68)–(70). Using the power series, Eq. (8) for  $\exp(-isL)$  in Eq. (61), again factoring  $\exp(-\omega_i^2 s^2/2)$ , and integrating with respect to time, we obtain the plateau value,

$$\zeta_i = \frac{(2\pi)^{1/2} \Delta F_i}{6kT\omega_i} \left\{ 1 + \sum_{n=1}^{\infty} \frac{\kappa_n^{(i)}}{2^n n!} \right\}, \quad \kappa_n^{(i)} = \sum_{r=0}^n \frac{(2n)!(-1)^r}{(2r)!(n-r)! 2^{n-r}} \frac{\mu_{2r}^{(i)}}{\mu_2^{(i)r}}, \quad (71)$$

$$\mu_{2r}^{(i)} = (1/\Delta F_i) \langle \mathbf{F}_i \cdot L^{2r} \mathbf{F}_i \rangle^0,$$

where  $\kappa_1^{(i)}$  depends upon  $\mathbf{p}_i$  and does not vanish as did  $\kappa_1^{(i)}$ . The moments  $\mu_n^{(i)}$  depend upon  $\mathbf{p}_i$  and therefore differ from the  $\mu_n^{(i)}$ . The coefficients  $\kappa_n^{(i)}$  and  $\mu_n^{(i)}$  can be expressed in terms of semi-invariants, frequently used in statistics, instead of directly in terms of the moments, if desired.

Assuming that moments of  $L$  higher than the second can be neglected and calculating the pertinent average values, we obtain the following approximation to the friction constant  $\zeta_i$ .

$$\zeta_i = \frac{(2\pi)^{1/2} \Delta F_i}{6kT\omega_i} [1 - \alpha_i(1 - \beta p_i^2/3m_i)], \quad \alpha_i = \frac{(kT)^2}{2M_i \Delta F_i \omega_i^2} \sum_{l=1}^v C_l \alpha_l^i, \quad (72)$$

$$\alpha_l^i = N^2 \int (\nabla^4 V_{il}) \exp(-\beta W_{il}^{(2)}) dv,$$

where  $\Delta F_i$  and  $\omega_i$  are given by Eqs. (67) and (70). Green's theorem has again been used in calculating  $\alpha_i$  under the restriction of short range intermolecular forces. We surmise and will later investigate by explicit calculation that in condensed systems such as liquids and liquid solutions, where the second group of terms of Eq. (70) involving the  $I_{il}^i$  make the dominant contribution to  $\omega_i^2$ , that  $\alpha_i$  will be sufficiently small to neglect the dependence of  $\zeta_i$  on  $p_i$  for values of  $p_i$  in the neighborhood of its equilibrium root mean square. In this case our approximation to the friction constant becomes

$$\zeta_i = \frac{(2\pi)^{1/2} \Delta F_i}{6kT\omega_i}. \quad (73)$$

If molecule  $i$  is a macromolecule of high molecular weight  $M_i$  in a solvent of low molecular weight, we shall expect  $\zeta_i$  to be effectively independent of  $p_i$ , since  $\omega_i$  by Eq. (70) becomes independent of  $M_i$  and thus  $\alpha_i$  diminishes with  $M_i$ , vanishing with the ratio of  $M_s/M_i$ , where  $M_s$  is the solvent molecular weight.

For a macromolecule in a solvent of low molecular weight we conclude from Eq. (73) and the asymptotic independence of  $\omega_i$  on  $M_i$  that  $\zeta_i$  will be also independent of  $M_i$ , depending only on the mass of the solvent molecules. The relation between Eq. (73) and the hydrodynamic

estimate of  $\zeta_i$  by Stokes law for macromolecules is connected with the boundary condition of no slip at an interface with a rigid surface, which is used in the hydrodynamics of viscous fluids. The resistance  $\zeta_i \mathbf{p}_i/m_i$  experienced by a macroscopic sphere  $i$ , when determined by our method with the  $\zeta_i$  of Eqs. (61) and (73) is due to a surface layer of molecules of solvent of thickness of the order of the range of intermolecular forces. If the hypothesis of no slip in this layer is made, the resistance  $\zeta_i \mathbf{p}_i/m_i$  experienced by sphere will be equal to the hydrodynamic resistance  $6\pi\eta R \mathbf{p}_i$  exerted by the fluid on the surface layer. This argument might be made the basis for a molecular theory of the viscosity coefficient  $\eta$ , but it turns out not to be the most convenient or consequential approach to this problem.

A few further remarks concerning the dependence of the friction constant  $\zeta_i$  on the mass of molecule  $i$  are of interest. Only when the mass of molecule  $i$  is large relative to those of the molecules of its environment will  $\zeta_i$  be independent of  $M_i$ . In fact from Eqs. (70) and (73), one observes that if the mass of  $i$  is very small relative to those of its environment,  $\zeta_i$  is proportional to  $M_i^{1/2}$ . This circumstance suggests, contrary to the conclusion to be drawn from the hydrodynamic estimate of  $\zeta_i$  based on Stoke's law, that isotope separations by thermal dif-

fusion or electrolysis might be practicable in liquids and liquid solutions, provided the solvent consists of molecules of mass not small relative to the masses of the molecules to be separated.

We remark that we have not proved the existence of a plateau value of the friction constant for systems of molecules interacting with intermolecular forces of the usual type. We have only outlined a method for estimating  $\zeta_i$ , which appears feasible, if the plateau value exists. It is therefore of interest to examine two cases, the crystal with harmonic lattice vibrations and the gas with binary collisions, for which the integral Eq. (61), defining  $\zeta_i$ , can be evaluated directly.

Although we shall not here reproduce the details of the analysis, we remark that the friction constant appears to have no plateau value for the crystal with harmonic lattice vibrations. This is evidently due to the fact that the motion is multiply periodically. We do not conclude from this that no dissipative mechanism exists whereby a molecule moving in the lattice can exchange energy with the harmonic lattice vibrational modes, but only that anharmonic terms must be considered in describing the dissipative mechanism. Nor does this necessarily imply that Eqs. (67), (70), and (71), although they involve derivatives of the potentials of intermolecular force no higher than the second, do not provide an adequate approximation to the friction constant in crystals (of course, in crystals  $\zeta_i$  is a function of  $\mathbf{R}_i$  and requires a supplementary average over a domain of linear dimensions large relative to the lattice parameters before use in macroscopic transport theory). That is to say, the anharmonic terms may assure the approach to a plateau value, by affecting the wings of the force correlation, without sensibly affecting its value.

Although transport in gases of low density is most accurately described by the Maxwell-Boltzmann integro-differential equation, the theory developed here is applicable to a certain degree of approximation. Using binary collision analysis, we find that  $\zeta_i$  does indeed have a plateau value for values of  $\tau_i$ , long relative to the representative duration of a molecular collision. For simplicity, we give the result for a system of one component, easily generalized to

an arbitrary number of components.

$$\begin{aligned}\zeta &= \frac{N}{6\nu kT} \int \int \Phi(\mathbf{R}_0, \alpha, \epsilon) \left( \frac{dV}{dR_0} \right) \\ &\quad \times \exp(-\beta V - \beta p_{20}^2/2m) d\mathbf{R}_0 dp_{20}, \\ \Phi &= \frac{m}{2\alpha} \int_0^{\vartheta^*} \cos(\vartheta - \vartheta_0) R^2 \frac{dV}{dR} d\vartheta, \\ \alpha &= |\mathbf{R}_0 \times \mathbf{p}_{12}^0|; \\ \vartheta^* &= 2 \int_b^\infty \frac{(\alpha/r^2) dr}{[m(\epsilon - V(r) - \alpha^2/mr^2)]^{1/2}}, \\ \epsilon &= p_{12}^{02}/m + V(R_0),\end{aligned}\tag{74}$$

where  $b$  is largest positive root of

$$\epsilon - V(b) - \alpha^2/mb^2 = 0,$$

and  $\mathbf{p}_{12}^0$  and  $\mathbf{R}_0$  are the relative momentum and position of a molecular pair,  $m$  the molecular mass, and  $V$  the potential of intermolecular force. In the integral defining  $\Phi$ ,  $R$  is to be evaluated as a function of  $\vartheta$ , from the equation of the orbit,

$$\begin{aligned}\vartheta &= \int_R^\infty \frac{(\alpha/r^2) dr}{[m(\epsilon - V - \alpha^2/mr^2)]^{1/2}}; \quad 0 \leq \vartheta \leq \vartheta^*/2, \\ \vartheta &= \vartheta^* - \int_R^\infty \frac{(\alpha/r^2) dr}{[m(\epsilon - V - \alpha^2/mr^2)]^{1/2}}; \\ &\quad \vartheta^*/2 < \vartheta \leq \vartheta^*\end{aligned}\tag{75}$$

for a binary collision. A comparison of  $\zeta$  evaluated by Eqs. (74) and (75) with the approximation, Eq. (71), would be desirable. However, it should be kept in mind in making such a comparison that the peak approximation, upon which Eq. (71) is based is without doubt much better in liquids and liquid solutions than in gases.

We close our survey of the general theory by a remark about  $\zeta_i(\infty)$ , the asymptotic value of  $\zeta_i(\tau)$  for  $\zeta \rightarrow \infty$ . In the case of gases, we would find that  $\zeta_i(\infty)$  is vanishing or undeterminate, if we were so unwise as to let  $\tau_i \rightarrow \infty$ , since after a time of the order of the period of a Poincaré cycle, the contribution, Eq. (73), to  $\zeta$  would be cancelled by that from a collision in which the orbit was traversed in the reverse sense. Using spectral theory (see Appendix I), we have convinced ourselves that in a system of molecules

with arbitrary central forces, the only invariants of which are energy, total linear momentum, and total angular momentum,  $\zeta_i(\infty)$  always vanishes. As we have already pointed out, this circumstance is related to the failure of thermodynamic dissipative mechanisms over very long periods comparable with those of Poincaré cycles.

Applications of the general theory, which we have presented here, to special transport processes will follow in later articles.

In conclusion, we wish to express our thanks to Professor Joseph E. Mayer for his kindness in reading this article in manuscript and for providing much illuminating criticism.

#### APPENDIX: REMARKS ON THE MATHEMATICAL THEORY OF THE OPERATOR $\exp(-isL)$

Although we shall not attempt an exhaustive justification of our manipulations of the operator  $\exp(-isL)$ , we wish to call attention to the basic mathematical theory<sup>9</sup> underlying the use of this operator. We first consider the eigenvalue problem

$$L\psi_\lambda = \lambda\psi_\lambda, \quad (\text{A1})$$

where the domain of the operator  $L$  is restricted to functions  $g(p, q)$  in phase space which form a Hilbert space. Since  $L$  is self adjoint, the eigenvalues  $\lambda$  are real. The inner product  $(f, g)$  of two such functions is defined as

$$(f, g) = \int \int f^* g dp dq, \quad (\text{A2})$$

where if  $f, g$  are vectors in phase space  $f^*g$  in the integrand is to be replaced by  $\mathbf{f}^* \cdot \mathbf{g}$ . If  $E(\lambda)$ , the canonical resolution of the identity appropriate to  $L$ , is defined as the operator which projects any function  $g$  on the linear manifold in Hilbert space spanned by the eigenfunctions of  $L$  corresponding to eigenvalues less than  $\lambda$ , the operator  $\exp(-isL)$  may be represented by the Stieltjes integral,

$$e^{-isL} = \int_{-\infty}^{+\infty} e^{-i\lambda s} dE(\lambda). \quad (\text{A3})$$

<sup>9</sup> See von Neumann, Proc. Nat. Acad. Sci. 18 (1932). Also *Quantenmechanik* (Verlagsbuchhandlung Julius Springer, Berlin, 1932); Stone, *Linear Transformations in Hilbert Space* (American Mathematical Society Publication, 1932).

Using Eq. (A3) in Eq. (62) defining the mean friction constant  $\langle \zeta_i \rangle_{Av}$ , we have

$$\begin{aligned} \langle \zeta_i \rangle_{Av} &= \frac{1}{6kT} \int_{-\tau_i}^{+\tau_i} \int_{-\infty}^{+\infty} e^{-i\lambda s} dz_i(\lambda) ds, \\ z_i(\lambda) &= (E(\lambda)\mathbf{A}_i, \mathbf{A}_i), \\ \mathbf{A}_i &= \exp[\beta(A-H)/2]\mathbf{F}_i, \end{aligned} \quad (\text{A4})$$

where the invariance of  $H$  under  $\exp(-isL)$  has been used to symmetrize the expression. The fluctuation of intermolecular force is evidently given by

$$\Delta F_i = \int_{-\infty}^{+\infty} dz_i(\lambda) = (\mathbf{A}_i, \mathbf{A}_i), \quad (\text{A5})$$

and the moments of  $L$ , with respect to  $Z(\lambda)$ , of Eq. (63) are expressible in the form,

$$\mu_n^{(i)} = \frac{1}{\Delta F_i} \int_{-\infty}^{+\infty} \lambda^n dz_i(\lambda). \quad (\text{A6})$$

The justification of the peak approximation,

$$\langle \zeta_i \rangle_{Av} = \frac{(2\pi)^{1/2} \Delta F_i}{6kT\omega_i}, \quad \omega_i^2 = \mu_2^{(i)}, \quad (\text{A7})$$

employed in Part IV to represent  $\langle \zeta_i \rangle_{Av}$ , therefore must rest upon a study of the structure of the projection operator  $E(\lambda)$  for the special dynamical system in question, and a verification that the integral,

$$\int_{-\infty}^{+\infty} e^{-i\lambda s} dz_i(\lambda),$$

is adequately approximated by

$$\Delta F_i \exp(-\omega_i^2 s^2/2)$$

in the neighborhood of  $s=0$  and for subsequent intervals of time of microscopic duration (small relative to the representative interval of macroscopic observation).

A brief discussion of the asymptotic value  $\langle \zeta_i \rangle_{Av}(\infty)$  for  $\tau_i \rightarrow \infty$  is of some interest here. Let us suppose that the spectrum of  $L$  is continuous in the neighborhood of  $\lambda=0$ , and that the operator  $E_0'$  defined by

$$E_0' = \lim_{\lambda \rightarrow 0} \frac{E(\lambda) - E(-\lambda)}{2\lambda} \quad (\text{A8})$$

exists. Then, commuting the order of integra-

tions in Eq. (A4) and letting  $\tau_i \rightarrow \infty$ , we get

$$\zeta_i(\infty) = \frac{\pi}{6kT} (E_0' \mathbf{A}_i, E_0' \mathbf{A}_i), \quad (\text{A9})$$

where  $E_0'$  is the operator projecting a function in Hilbert space on the linear manifold spanned by the eigenfunctions of  $L$  per unit  $\lambda$ -interval in the vicinity of  $\lambda=0$ . The functions spanning this manifold are functions of the invariants of  $L$ , that is the constants of the motion. For arbitrary central intermolecular forces, with energy, total linear momentum, and total angular momentum the only invariants, explicit calculation shows that  $\langle \zeta_i \rangle_{Av}(\infty)$  vanishes, a fact to which attention has already been called.

Other uses of the spectral resolution of  $L$  may be mentioned. For example, the solution  $\varphi(\mathbf{p}, \mathbf{q}; t)$

of the inhomogeneous equation,

$$L\varphi + i\frac{\partial\varphi}{\partial t} = A(\mathbf{p}, \mathbf{q}; t), \quad (\text{A10})$$

$$\varphi(\mathbf{p}, \mathbf{q}; 0) = \varphi_0(\mathbf{p}, \mathbf{q}),$$

may be expressed in the form

$$\varphi(\mathbf{p}, \mathbf{q}; t) = \int_{-\infty}^{+\infty} e^{-i\lambda t} d(E(\lambda)\varphi_0) \\ + \int_0^t \int_{-\infty}^{+\infty} e^{-i\lambda(t-s)} d(E(\lambda)A) ds \quad (\text{A11})$$

which is useful in the treatment of time dependent external forces under certain circumstances.\*

\* This method is being studied by Dr. F. W. Boggs in connection with the general theory of dielectric loss.