

Angular Momentum Transport in Quantum Statistical Mechanics*

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Equations of motion are derived for the many-body operators associated with local densities of linear and angular momentum. It is illustrated that the transfer equations for orbital and spin angular momentum are formally identical. Finally, an approximate theory is developed for the elastic tensor of diatomic media or media composed of atoms with intrinsic spin.

EQUATIONS of change for macroscopic variables such as the densities of mass, momentum, and energy are basic to the study of transport processes. In classical statistical mechanics these equations can be derived directly from the Liouville equation and in quantum statistics the Schrödinger equation plays an analogous role. The usual prescription for dealing with the quantum case, that due to Irving and Zwanzig,¹ involves the introduction of Wigner distribution functions (Fourier transforms of the quantum density matrix) and the application of the Weyl correspondence between classical dynamical variables and quantum operators. Although this technique is thoroughly satisfactory for most purposes, its reliance upon the Weyl correspondence does limit its applicability to operators which have classical analogs. In previous papers we have examined the transfer or dissipation of the internal angular momentum originating in rotational motions of polyatomic molecules² and we have also presented a complementary continuum theory³ which was purportedly applicable to any sort of angular momentum, be it orbital or intrinsic. While the equation of change for the density of orbital or rotational angular momentum can and has been derived on the basis of the Irving and Zwanzig method,² this same technique obviously cannot be applied to nuclear or electron spins. The purpose of the present paper is to report a quantum mechanical derivation of the equation of change for spin angular momentum. This derivation, together with that for the Cauchy equation of linear momentum transfer, is accomplished without the introduction of intermediate steps such as those involving Wigner distribution functions and the Weyl operator correspondence. The method we adopt is neither new nor very complicated; it is a simple generalization of that used by Landau in his original derivation of the equations of change for the mass and momentum density operators in the two-fluid theory of helium. Thus, we work in the Heisenberg representation and derive equations of motion for certain many-body operators whose ensemble-averaged expectation values

correspond to variables of importance in the macroscopic description of transport phenomena. A program of this sort has been carried out previously by Mori⁴ for the case of structureless particles and so we shall begin the present communication with a brief study of diatomic fluids (without intrinsic spin) and then proceed directly to an examination of particles with spin.

I. OPERATOR EQUATIONS OF MOTION

For the Hamiltonian of the diatomic fluid we choose the simple form

$$H = \sum_k [(1/2m)P_k^2 + (1/2\mu)\mathbf{p}_k^2 + V(\mathbf{r}_k) + \varphi(\mathbf{r}_k, \mathbf{R}_k) + \frac{1}{2} \sum_{j \neq k} U_{kj}]. \quad (1)$$

Here, \mathbf{R}_k and \mathbf{P}_k denote the position and momentum for the center of mass of the k th molecule, \mathbf{r}_k the internuclear separation, and \mathbf{p}_k the corresponding conjugate momentum. $V(\mathbf{r}_k)$ is the interatomic potential of the molecule and $\varphi(\mathbf{r}_k, \mathbf{R}_k)$ is its potential energy due to interactions with conservative external fields. Finally, $U_{kj} = U(\mathbf{R}_{kj}, \mathbf{r}_k, \mathbf{r}_j)$ is the potential of the (noncentral) intermolecular force between the j th and k th molecules, and $\mathbf{R}_{kj} \equiv \mathbf{R}_k - \mathbf{R}_j$. The Hermitian operator corresponding to mass density at the point \mathbf{R} in three-space is clearly $\rho(\mathbf{R}) = \sum_k m \delta(\mathbf{R}_k - \mathbf{R}) \equiv \sum_k m \delta_k$. Changing to the Heisenberg representation, we obtain the equation of motion:

$$\partial \rho / \partial t = (1/i\hbar)[\rho, H] = (1/2i\hbar) \sum_k [\delta_k, P_k^2], \quad (2)$$

where

$$\begin{aligned} [\delta_k, P_k^2] \psi &= (-i\hbar)^2 \{ \delta_k \nabla_k^2 \psi - \nabla_k^2 (\delta_k \psi) \} \\ &= (-i\hbar)^2 \{ -2 \nabla_k \delta_k \cdot \nabla_k \psi - \psi \nabla_k^2 \delta_k \} \\ &= (-i\hbar)^2 \nabla \cdot [\delta_k \nabla_k \psi + \nabla_k (\delta_k \psi)] \\ &= -i\hbar \nabla \cdot [(\delta_k \mathbf{P}_k + \mathbf{P}_k \delta_k) \psi]. \end{aligned}$$

Here $\nabla_k \equiv \partial / \partial \mathbf{R}_k$ and $\nabla \equiv \partial / \partial \mathbf{R}$. Therefore, ρ satisfies the familiar continuity equation

$$\partial \rho / \partial t + \nabla \cdot \mathbf{J} = 0, \quad (3)$$

where \mathbf{J} , the operator for mass current density, is given by the Hermitian form,

$$\mathbf{J} = \sum_k \frac{1}{2} (\delta_k \mathbf{P}_k + \mathbf{P}_k \delta_k) \equiv \sum_k \mathbf{J}_k. \quad (4)$$

⁴ H. Mori, Phys. Rev. **112**, 1829 (1958).

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¹ J. H. Irving and R. W. Zwanzig, J. Chem. Phys. **19**, 1173 (1951).

² J. S. Dahler, J. Chem. Phys. **30**, 1447 (1959).

³ J. S. Dahler and L. E. Scriven, Nature **192**, 36 (1961); and (to be published).

In turn, the equation of motion for this operator is

$$\begin{aligned} \partial \mathbf{J} / \partial t &= (1 / i \hbar) [\mathbf{J}, H] \\ &= - [(-i \hbar)^2 / 4 m] \sum_k [(\delta_k \nabla_k + \nabla_k \delta_k), \nabla_k^2] \\ &\quad - \sum_k [(\delta_k \nabla_k + \nabla_k \delta_k), \varphi_k + \frac{1}{2} \sum_{j \neq k} U_{kj}]. \end{aligned} \quad (5)$$

A direct calculation of the commutators reveals that

$$- [(i \hbar)^2 / 4 m] \sum_k [(\delta_k \nabla_k + \nabla_k \delta_k), \nabla_k^2] = - \nabla \cdot \mathfrak{P}_K$$

where the tensor \mathfrak{P}_K is given by

$$\begin{aligned} \mathfrak{P}_K &= (1 / 4 m) \sum_k [\delta_k \mathbf{P}_k \mathbf{P}_k + \mathbf{P}_k \delta_k \mathbf{P}_k \\ &\quad + (\mathbf{P}_k \mathbf{P}_k \delta_k + \mathbf{P}_k \delta_k \mathbf{P}_k)^\dagger] \\ &= (1 / 2 m) \sum_k [\mathbf{J}_k \mathbf{P}_k + (\mathbf{P}_k \mathbf{J}_k)^\dagger]. \end{aligned} \quad (6)$$

Next we observe that

$$\begin{aligned} \frac{1}{2} \sum_k \sum_{j \neq k} [(\delta_k \nabla_k + \nabla_k \delta_k), U_{kj}] \\ = \sum_k \sum_{j \neq k} \delta_k \nabla_k U_{kj} = \frac{1}{2} \sum_k \sum_{j \neq k} \{ \delta_k \nabla_k + \delta_j \nabla_j \} U_{kj} \\ = \frac{1}{2} \sum_k \sum_{j \neq k} (\delta_k - \delta_j) \nabla_k U_{kj} = \nabla \cdot \mathfrak{p}_U, \end{aligned}$$

where \mathfrak{p}_U is the dyadic operator

$$\begin{aligned} \mathfrak{p}_U &= - \frac{1}{2} \sum_k \sum_{j \neq k} \mathbf{R}_{kj} (\partial U_{kj} / \partial \mathbf{R}_{kj}) \\ &\quad \times [1 - (1/2!) \mathbf{R}_{kj} \cdot \nabla + (1/3!) \mathbf{R}_{kj} \mathbf{R}_{kj} \cdot \nabla \nabla + \dots] \delta_k. \end{aligned} \quad (7)$$

To arrive at this last result, we have made use of a Taylor's expansion of the Dirac delta function $\delta_j = \delta(\mathbf{R}_j - \mathbf{R})$. Combining these expressions we obtain for \mathbf{J} the equation of motion

$$\partial \mathbf{J} / \partial t + \nabla \cdot (\mathfrak{P}_K + \mathfrak{p}_U) = \mathbf{F}_e, \quad (8)$$

where

$$\mathbf{F}_e \equiv - \sum_k \delta_k \nabla_k \varphi_k \quad (9)$$

is the operator for the force on the fluid due to external fields. To transform (8) into a more obvious analog of the Cauchy equation for momentum transfer, we now introduce the Hermitian velocity operator \mathbf{u}

$= \frac{1}{2} (\rho^{-1} \mathbf{J} + \mathbf{J} \rho^{-1})$. In terms of this operator $\mathbf{J} = \frac{1}{2} (\rho \mathbf{u} + \mathbf{u} \rho)$, and (8) becomes

$$\begin{aligned} \frac{1}{2} [\rho (\partial \mathbf{u} / \partial t) + \frac{1}{2} (\rho \mathbf{u} + \mathbf{u} \rho) \cdot (\nabla \mathbf{u})] \\ + \frac{1}{2} [(\partial \mathbf{u} / \partial t) \rho + (\nabla \mathbf{u})^\dagger \cdot \frac{1}{2} (\rho \mathbf{u} + \mathbf{u} \rho)] = - \nabla \cdot \mathfrak{p} + \mathbf{F}_e. \end{aligned} \quad (10)$$

Here $\mathfrak{p} = \mathfrak{p}_K + \mathfrak{p}_U$ is the operator whose ensemble-averaged expectation is the fluid pressure tensor. It consists of two parts, \mathfrak{p}_U contributed by momentum transfers from one molecule to another and

$$\begin{aligned} \mathfrak{p}_K &= \mathfrak{P}_K - \frac{1}{2} \{ \mathbf{J} \mathbf{u} + (\mathbf{u} \mathbf{J})^\dagger \} = \frac{1}{2} \{ \sum_k \mathbf{J}_k (\mathbf{P}_k / m) - \mathbf{J} \mathbf{u} \\ &\quad + \{ \frac{1}{2} \sum_k (\mathbf{P}_k / m) \mathbf{J}_k - \mathbf{u} \mathbf{J} \}^\dagger, \end{aligned} \quad (11)$$

the momentum flux associated with the translational diffusion of individual molecular units. With due allowance for the commutation rules of quantum mechanics we see that the operator equation (10) is the precise analog of the classical Cauchy equation,

$$\rho [\partial \mathbf{u} / \partial t + \mathbf{u} \cdot \nabla \mathbf{u}] = - \nabla \cdot \mathfrak{p} + \mathbf{F}_e.$$

We now turn to the derivation of the equation of motion for the internal angular momentum operator $\mathbf{M} = \sum_k \mathbf{r}_k \times \mathbf{p}_k \delta_k = \sum_k \mathbf{M}_k$. From the relationships

$$[\mathbf{r}_k \times \mathbf{p}_k \delta_k, p_k^2 / 2 \mu] = [\mathbf{r}_k \times \mathbf{p}_k \delta_k, V(r_k)] = 0,$$

$$[\mathbf{r}_k \times \mathbf{p}_k \delta_k, \varphi_k] = \delta_k (\mathbf{r}_k \times \mathbf{p}_k) \varphi_k,$$

and

$$\begin{aligned} [\mathbf{r}_k \times \mathbf{p}_k \delta_k, P_k^2 / 2 m] \\ = - (i \hbar / m) \mathbf{r}_k \times \mathbf{p}_k (\nabla \cdot \mathbf{J}_k) = - (i \hbar / m) \nabla \cdot [\mathbf{r}_k \times \mathbf{p}_k \mathbf{J}_k]^\dagger, \end{aligned}$$

it is readily verified that

$$\begin{aligned} \partial \mathbf{M} / \partial t &= - (1 / m) \nabla \cdot \sum_k [\mathbf{r}_k \times \mathbf{p}_k \mathbf{J}_k]^\dagger \\ &\quad - \sum_k \delta_k (\mathbf{r}_k \times \nabla_k' \varphi_k) \\ &\quad + (1 / i \hbar) \sum_k \sum_{j \neq k} [\mathbf{M}_k, U_{kj}]. \end{aligned} \quad (12)$$

Here the abbreviated notation $\nabla_k' \equiv \partial / \partial \mathbf{r}_k$ has been introduced. Next, we consider the operator identity

$$\begin{aligned} (1 / i \hbar) \sum_k \sum_{j \neq k} [\mathbf{M}_k, U_{kj}] &= - \frac{1}{2} \sum_k \sum_{j \neq k} \{ (\delta_k - \delta_j) \mathbf{r}_k \times \nabla_k' U_{kj} + \delta_j (\mathbf{r}_k \times \nabla_k' + \mathbf{r}_j \times \nabla_j') U_{kj} \} \\ &= - \frac{1}{2} \sum_k \sum_{j \neq k} \{ (\delta_k - \delta_j) \mathbf{r}_k \times \nabla_k' U_{kj} - \delta_j (\mathbf{R}_k \times \nabla_k + \mathbf{R}_j \times \nabla_j) U_{kj} \}, \end{aligned} \quad (13)$$

where the last form follows from the first because of our assumption of pair-additive intermolecular forces. Expansion of $(\delta_k - \delta_j)$ in a Taylor series then leads to the result

$$\begin{aligned} (1 / i \hbar) \sum_k \sum_{j \neq k} [\mathbf{M}_k, U_{kj}] \\ = \nabla \cdot \frac{1}{2} \sum_k \sum_{j \neq k} \mathbf{R}_{kj} (\mathbf{r}_k \times \nabla_k' U_{kj}) (1 - \frac{1}{2} \mathbf{R}_{kj} \cdot \nabla + \dots) \delta_k + \frac{1}{2} \sum_k \sum_{j \neq k} \delta_j \mathbf{R}_{kj} \times (\partial U_{kj} / \partial \mathbf{R}_{kj}) \\ \equiv - \nabla \cdot \mathbf{C}_U - \mathbf{U} \times \frac{1}{2} \sum_j \sum_{k \neq j} \mathbf{R}_{kj} (\partial U_{kj} / \partial \mathbf{R}_{kj}) \delta_j \equiv - \nabla \cdot \mathbf{C}_U + \mathbf{U} \times \mathfrak{p}_U, \end{aligned} \quad (14)$$

where

$$\begin{aligned} \mathbf{C}_U &= - \frac{1}{2} \sum_k \sum_{j \neq k} \mathbf{R}_{kj} (\mathbf{r}_k \times \nabla_k' U_{kj}) \\ &\quad \times [1 - (1/2!) \mathbf{R}_{kj} \cdot \nabla + \dots] \delta_k \end{aligned} \quad (15)$$

is the "collisional transfer" contribution to the flux of internal angular momentum. In (14) we have used the symbol \mathbf{U} for the unit dyadic and $\mathbf{U} \times \mathbf{A}$ for the dual of the dyadic \mathbf{A} , i.e., $[\mathbf{U} \times \mathbf{A}]_i = \delta_{ij} \epsilon_{ijk} A_{kl} = \epsilon_{ijk} A_{kj}$.

Combining (14) with (12) we finally obtain the equation of motion,

$$\partial \mathbf{M} / \partial t + \nabla \cdot [\mathbf{u} \mathbf{M} + \mathbf{C}] = \mathbf{U} \times \mathfrak{p} + \mathbf{G}_e, \quad (16)$$

where $\mathbf{C} = \mathbf{C}_K + \mathbf{C}_U$, like $\mathfrak{p} = \mathfrak{p}_K + \mathfrak{p}_U$, is the sum of a intermolecular transfer contribution and a diffusional part

$$\mathbf{C}_K = \sum_k (\mathbf{J}_k / m - \mathbf{u} \delta_k) (\mathbf{r}_k \times \mathbf{p}_k), \quad (17)$$

and where

$$\mathbf{G}_e = -\sum_k \delta_k (\mathbf{r}_k \times \nabla_k' \varphi_k) \quad (18)$$

is the operator for body-torque generated by external fields of force.

Although it is a straightforward exercise to derive equations of change for the total energy density, for the separate densities of translational, rotational, and vibrational energy, and for other quantities of interest such as the electric polarization vector in a fluid of polar molecules, we shall not do so here. Nor shall we present the generalizations of these equations to fluids composed of more complicated chemical species or to fluid mixtures. Instead, we pass directly to the consideration of intrinsic angular momentum and, in particular, to the study of a fluid composed of atoms with spin. For the Hamiltonian of this system we take as typical the operator

$$H = \sum_k [(1/2m)P_k^2 + \mathbf{T}_k \cdot \mathbf{s}_k + \frac{1}{2} \sum_{j \neq k} (\Theta_{kj} : \mathbf{s}_k \mathbf{s}_j + U_{kj})], \quad (19)$$

where \mathbf{P}_k is the atomic linear momentum and \mathbf{s}_k the spin operator for the k th atom. $U_{kj} = U(R_{kj})$ is the spin-independent portion of the interatomic potential energy and Θ_{kj} is the dipole-dipole interaction tensor,

$$\Theta_{kj} = \mu^2 R_{kj}^{-3} (\mathbf{U} - \hat{R}_{kj} \hat{R}_{kj}); \quad \hat{R}_{kj} = \mathbf{R}_{kj} / R_{kj}, \quad (20)$$

with μ equal to "dipole strength." Finally, $\mathbf{T}_k \cdot \mathbf{s}_k$ denotes the energy of interaction of the k th spin with an external field.

The equation of change for the spin density operator, $\mathbf{S} = \sum_k \delta_k \mathbf{s}_k$, is then

$$\begin{aligned} \partial \mathbf{S} / \partial t &= (1/i\hbar) \sum_k [\delta_k \mathbf{s}_k, H] \\ &= -\nabla \cdot \sum_k (\mathbf{J}_k / m) \mathbf{s}_k + \sum_k \delta_k T_k \times \mathbf{s}_k \\ &\quad + \sum_k \sum_{j \neq k} \delta_k (\Theta_{kj} \cdot \mathbf{s}_j) \times \mathbf{s}_k, \end{aligned} \quad (21)$$

where use has been made of the operator identities

$$[\delta_k \mathbf{s}_k, U_{kj}] = 0,$$

$$[\delta_k \mathbf{s}_k, \mathbf{T}_k \cdot \mathbf{s}_k] = \delta_k [\mathbf{s}_k, \mathbf{s}_k] \cdot \mathbf{T}_k = i\hbar \delta_k \mathbf{T}_k \times \mathbf{s}_k,$$

and

$$[\delta_k \mathbf{s}_k, \Theta_{kj} : \mathbf{s}_k \mathbf{s}_j] = \delta_k [\mathbf{s}_k, \mathbf{s}_k] \cdot (\Theta_{kj} \cdot \mathbf{s}_j) = i\hbar \delta_k (\Theta_{kj} \cdot \mathbf{s}_j) \times \mathbf{s}_k.$$

In order to demonstrate the close relationship between the equation of motion for the rotational angular momentum \mathbf{M} and that for the spin angular momentum \mathbf{S} , we momentarily fix our attention upon a system of only two atoms. In the absence of external fields, the Hamiltonian for this special system will be given by $H_{jk} = (P_j^2 + P_k^2) / 2m + \Theta_{jk} : \mathbf{s}_j \mathbf{s}_k + U_{jk}$ and the operators for the angular momenta of the two by $\mathfrak{R}_k = \mathbf{R}_k \times \mathbf{P}_k + \mathbf{s}_k$ and $\mathfrak{R}_j = \mathbf{R}_j \times \mathbf{P}_j + \mathbf{s}_j$. Then, from the equation of motion

$$\begin{aligned} d\mathfrak{R}_k / dt &= (1/i\hbar) [\mathfrak{R}_k, H_{jk}] = -\mathbf{R}_k \times \nabla_k (\Theta_{kj} : \mathbf{s}_k \mathbf{s}_j) \\ &\quad + (\Theta_{kj} \cdot \mathbf{s}_j) \times \mathbf{s}_k \end{aligned}$$

and the conservation condition $d(\mathfrak{R}_j + \mathfrak{R}_k) / dt = (i\hbar)^{-1}$

$\times [\mathfrak{R}_j + \mathfrak{R}_k, H_{jk}] = 0$, it follows that

$$\begin{aligned} (\Theta_{kj} \cdot \mathbf{s}_j) \times \mathbf{s}_k + (\Theta_{kj} \cdot \mathbf{s}_k) \times \mathbf{s}_j - \mathbf{R}_{kj} \\ \times (\partial / \partial \mathbf{R}_{kj}) (\Theta_{kj} : \mathbf{s}_k \mathbf{s}_j) = 0. \end{aligned} \quad (22)$$

This relationship and its analog

$$(\mathbf{r}_k \times \nabla_k' + \mathbf{r}_j \times \nabla_j' + \mathbf{R}_{kj} \times \partial / \partial \mathbf{R}_{kj}) U_{kj} = 0,$$

which was used in obtaining the result (13) for diatomic molecules, may be viewed as statements of angular momentum conservation for isolated pairs of interacting bodies which possess internal angular momentum. An alternative interpretation of (22) follows from the observation that $(\Theta_{kj} \cdot \mathbf{s}_j) \times \mathbf{s}_k$ is the operator for the torque which acts upon the k th spin due to its interaction with the j th. Therefore, we see from (22) that if the torques which two isolated spins exert upon one another are not precisely equal and oppositely directed, a compensating torque will act about the line of centers of their "supporting particles."

By symmetrizing the last term of (21) and introducing the relationship (22) we find that

$$\sum_k \sum_{j \neq k} \delta_k (\Theta_{kj} \cdot \mathbf{s}_j) \times \mathbf{s}_k \doteq -\nabla \cdot \mathbf{C}_U + \mathbf{U} \times \mathfrak{p}_U, \quad (23)$$

where the physical interpretations of the tensors

$$\begin{aligned} \mathfrak{p}_U &= -\frac{1}{2} \sum_k \sum_{j \neq k} \mathbf{R}_{kj} (\partial / \partial \mathbf{R}_{kj}) (U_{kj} + \Theta_{kj} : \mathbf{s}_k \mathbf{s}_j) \\ &\quad \times [1 - (1/2!) \mathbf{R}_{kj} \cdot \nabla + \dots] \delta_k \end{aligned} \quad (24.1)$$

and

$$\begin{aligned} \mathbf{C}_U &= -\frac{1}{2} \sum_k \sum_{j \neq k} \mathbf{R}_{kj} \mathbf{s}_k \times (\Theta_{kj} \cdot \mathbf{s}_j) \\ &\quad \times [1 - (1/2!) \mathbf{R}_{kj} \cdot \nabla + \dots] \delta_k \end{aligned} \quad (24.2)$$

are precisely the same as for their analogs which appeared earlier in our study of diatomic molecules. Here, the internal rotational angular momentum has simply been replaced by intrinsic spin angular momentum. From (21) and (23)

$$\partial \mathbf{S} / \partial t + \nabla \cdot [\mathbf{uS} + \mathbf{C}] = \mathbf{U} \times \mathfrak{p}_U + \mathbf{G}_e, \quad (25)$$

where

$$\mathbf{C} = \mathbf{C}_k + \mathbf{C}_U, \quad (26.1)$$

$$\mathbf{C}_k = \sum_k (\mathbf{J}_k / m - \mathbf{u} \delta_k) \mathbf{s}_k, \quad (26.2)$$

and

$$\mathbf{G}_e = -\sum_k \delta_k \mathbf{s}_k \times \mathbf{T}_k. \quad (26.3)$$

The formal equivalence of (25) to the equation of motion for rotational angular momentum is obvious. With the choice of $\mathbf{T}_j = -\gamma \mathfrak{H}(t)$, where $\mathfrak{H}(t)$ is the magnetic field strength, $\mathbf{G}_e = -\gamma \mathfrak{H}(t) \times \mathbf{S}$ and so (25) can be recognized as a generalization of the Bloch spin equation⁵ which is applicable to nonuniform distributions of spin density. According to (25), the transfer of spin density from one portion of a medium to another can be accomplished not only by the diffusional mechanism implicit within \mathbf{C}_K and the collisional transfer processes of \mathbf{C}_U , but also by virtue of the "lattice-

⁵ F. Bloch, Phys. Rev. **105**, 1206 (1957).

strain" effect which has given rise to the term

$$\mathbf{U} \times \mathbf{p}_U = \frac{1}{2} \sum_k \sum_{j \neq k} \Theta_{kj} \times (\mathbf{s}_k \mathbf{s}_j + \mathbf{s}_j \mathbf{s}_k) \delta_k.$$

If the pressure tensor $\mathbf{p} = \mathbf{p}_K + \mathbf{p}_U$ were symmetrical, then $\mathbf{U} \times \mathbf{p}_U = \mathbf{U} \times \mathbf{p}$ would be identically zero. However, this will be the case only if the ensemble average for the expectation of $\mathbf{s}_k \mathbf{s}_j$ is isotropic, i.e., proportional to the unit dyadic. In crystals this is a situation which one might well expect to be the exception rather than the rule.

Collisional transfer is invariably found to provide the dominant mechanism for the transport of energy and linear momentum through condensed phases. Therefore, we can expect that the transfer of spin which accompanies diffusion, the \mathbf{C}_K flux drawn upon in spin-echo measurements of diffusion coefficients,⁶ actually represents only a very small fraction (probably no more than 5 or 10%) of the total spin flux.

II. NONDISSIPATIVE PORTION OF THE STRESS TENSOR

It has already been mentioned that the stress tensors for diatomic media and for media composed of particles with spin will not generally be symmetrical. Thus, in the case of a diatomic *fluid* it can be shown that

$$\mathbf{p} = (\rho - \phi \nabla \cdot \mathbf{u}) \mathbf{U} - 2\eta \mathbf{S} - \zeta \mathbf{U} \times (\text{curl} \mathbf{u} - 2\omega_0), \quad (27)$$

where $\mathbf{S} = \frac{1}{2} [\nabla \mathbf{u} + (\nabla \mathbf{u})^\dagger - \frac{1}{3} \mathbf{U} \nabla \cdot \mathbf{u}]$ is the traceless rate of shear tensor and where the coefficients ρ , ϕ , η , and ζ may be expressed in terms of Kubo-type correlation integrals.⁷ Although the detailed formulas for these coefficients will not be repeated here, it does bear mentioning that ζ , the scalar multiplier for the anti-symmetrical part of \mathbf{p} , is simply the autocorrelation function of $\mathbf{R}_{ij} \times \partial U_{ij} / \partial \mathbf{R}_{ij}$. Therefore, as we would expect on intuitive grounds, ζ will be different from zero only if the intermolecular forces are noncentral.

In stiffer media, dissipative effects associated with the viscosity coefficients ϕ , η , and ζ are often of less interest and importance than effects related to the system's elastic response to an imposed stress. A completely general theory would account for the complicated superposition of these effects and so for the resulting viscoelastic properties of the media. Here we shall be much less ambitious and only attempt to estimate the elastic portion of the stress tensor for a diatomic

medium. In order to simplify our task, it will be assumed that distortions of the molecular velocity distributions which accompany a deformation of the medium are of negligible importance. Therefore, our attention is focused solely upon the configurational state of the system. Results obtained in this way should be satisfactory for describing the local elastic response of a solid as well as for the stress-induced displacement of a fluid which immediately precedes the onset of flow, i.e., the elastic deformation which is usually masked by dissipative viscous flow. Since the "kinetic portion" of the pressure tensor is of negligible importance in condensed phases, we are primarily interested in the "collisional transfer" term. The ensemble-averaged expectation value for this term is given by

$$\begin{aligned} \mathbf{p}_U &= -\frac{1}{2} \sum_{j \neq i} \langle \mathbf{R}_{ij} (\partial U_{ij} / \partial \mathbf{R}_{ij}) \delta(\mathbf{R}_i - \mathbf{R}_j) \rangle \\ &\doteq -\frac{1}{2} \int \cdots \int \mathbf{R}_{21} (\partial U_{12} / \partial \mathbf{R}_{21}) \\ &\quad \times n^{(2)}(\mathbf{R}, \mathbf{R}_{21}, \mathbf{r}_1, \mathbf{r}_2) d\mathbf{R}_{21} d\mathbf{r}_1 d\mathbf{r}_2, \quad (28) \end{aligned}$$

where $n^{(2)}(\mathbf{R}, \mathbf{R}_{21}, \mathbf{r}_1, \mathbf{r}_2)$ is the projection of the ensemble distribution function upon pair configuration space. At equilibrium, $n^{(2)}$ can in principle be calculated by the methods of equilibrium statistical mechanics or, alternately, $n^{(2)}$ could be extracted directly from diffraction data which yield information about the relative locations and orientations of the molecules.

In response to an externally imposed stress, the centers of mass of molecules 1 and 2 will shift from their equilibrium locations by the amounts $\boldsymbol{\varepsilon}_1 = \boldsymbol{\varepsilon}(\mathbf{R}_1)$ and $\boldsymbol{\varepsilon}_2 = \boldsymbol{\varepsilon}(\mathbf{R}_2) = \boldsymbol{\varepsilon}_1 + \mathbf{R}_{21} \cdot \nabla_1 \boldsymbol{\varepsilon}_1$, respectively. Furthermore, the orientations of the two will shift in the amounts $\mathbf{r}'_1 - \mathbf{r}_1 = \boldsymbol{\theta}_1 \times \mathbf{r}_1$ and $\mathbf{r}'_2 - \mathbf{r}_2 = \boldsymbol{\theta}_2 \times \mathbf{r}_2 = \boldsymbol{\theta}_1 \times \mathbf{r}_2 + \mathbf{R}_{21} \cdot (\nabla_1 \boldsymbol{\theta}_1) \times \mathbf{r}_2$, where $\boldsymbol{\theta}_i$ is the angular displacement of the i th internuclear axis. Compressional distortions of the individual molecules have not been included here since they are judged to be of minor importance in diatomic media. However, in media composed of large squashy molecules, stress-induced distortions of shape and size certainly can be significant. Since the orientational displacements are generated by orthogonal transformations, the Jacobian of the transformation from the primed to the unprimed variables is just equal to $1 + \nabla \cdot \boldsymbol{\varepsilon}$. Therefore, the change of \mathbf{p}_U associated with the deformation is given by

$$\begin{aligned} \Delta \mathbf{p}_U &= \mathbf{p}_{U'} - \mathbf{p}_U = -\frac{1}{2} \left\{ \int \cdots \int \mathbf{R}_{21}' (\partial U_{21}' / \partial \mathbf{R}_{21}') n^{(2)'} d\mathbf{R}_{21}' d\mathbf{r}_1' d\mathbf{r}_2' - \int \cdots \int \mathbf{R}_{21} (\partial U_{21} / \partial \mathbf{R}_{21}) n^{(2)} d\mathbf{R}_{21} d\mathbf{r}_1 d\mathbf{r}_2 \right\} \\ &= -\frac{1}{2} \int \cdots \int \{ \mathbf{R}_{21}' (\partial U_{21}' / \partial \mathbf{R}_{21}') (1 + \nabla \cdot \boldsymbol{\varepsilon}) - \mathbf{R}_{21} (\partial U_{21} / \partial \mathbf{R}_{21}) \} n^{(2)} d\mathbf{R}_{21} d\mathbf{r}_1 d\mathbf{r}_2, \quad (29) \end{aligned}$$

⁶ For example see A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, New York, 1961).

⁷ J. S. Dahler (to be published). More explicit representations for these coefficients are given by N. F. Sather and J. S. Dahler, *Phys. Fluids* 5, 754 (1962).

where

$$\begin{aligned} \mathbf{F}_{21}' &\equiv \partial U_{21}' / \partial \mathbf{R}_{21}' = \mathbf{F}_{21} + (\mathbf{R}_{21}' - \mathbf{R}_{21}) \cdot (\partial \mathbf{F}_{21} / \partial \mathbf{R}_{21}) + (\mathbf{r}_1' - \mathbf{r}_1) \cdot (\partial \mathbf{F}_{21} / \partial \mathbf{r}_1) + (\mathbf{r}_2' - \mathbf{r}_2) \cdot (\partial \mathbf{F}_{21} / \partial \mathbf{r}_2) + \cdots \\ &= \mathbf{F}_{21} + \mathbf{R}_{21} \cdot (\nabla \xi) \cdot (\partial \mathbf{F}_{21} / \partial \mathbf{R}_{21}) + \{\boldsymbol{\theta}_1 \cdot \mathbf{r}_1 \times \partial / \partial \mathbf{r}_1 + \boldsymbol{\theta}_2 \cdot \mathbf{r}_2 \times \partial / \partial \mathbf{r}_2\} \mathbf{F}_{21} + \cdots \\ &= \mathbf{F}_{21} + \mathbf{R}_{21} \cdot (\nabla \xi) \cdot (\partial \mathbf{F}_{21} / \partial \mathbf{R}_{21}) - (\partial / \partial \mathbf{R}_{21}) (\boldsymbol{\theta}_1 \cdot \mathbf{R}_{21} \times \mathbf{F}_{21}) + \cdots \end{aligned} \quad (30)$$

In order to obtain the last line of (30), we have made use of the "torque-balance" condition on the pair potential which was discussed previously in connection with Eq. (22). Neglecting higher order terms in the distortions we then obtain from (29) and (30), the result

$$\begin{aligned} \Delta \mathbf{p}_U &= -\frac{1}{2} \int \cdots \int \left[\mathbf{R}_{21} \mathbf{R}_{21} \cdot (\nabla \xi) \cdot \left(\frac{\partial \mathbf{F}_{21}}{\partial \mathbf{R}_{21}} \right) + \mathbf{R}_{21} \cdot (\nabla \xi) \mathbf{F}_{21} - \mathbf{R}_{21} \frac{\partial}{\partial \mathbf{R}_{21}} (\boldsymbol{\theta}_1 \cdot \mathbf{R}_{21} \times \mathbf{F}_{21}) \right] n^{(2)} d\mathbf{R}_{21} d\mathbf{r}_1 d\mathbf{r}_2 \\ &\equiv -\frac{1}{2} (\nabla \xi)^\dagger : \left[\int \cdots \int \left\{ \mathbf{R}_{21} \frac{\partial}{\partial \mathbf{R}_{21}} (\mathbf{R}_{21} \mathbf{F}_{21}) + \mathbf{U} \mathbf{R}_{21} \mathbf{F}_{21} \right\} n^{(2)} d\mathbf{R}_{21} d\mathbf{r}_1 d\mathbf{r}_2 \right] \\ &\quad + \frac{1}{2} \left[\int \cdots \int \left\{ \mathbf{R}_{21} \frac{\partial}{\partial \mathbf{R}_{21}} (\mathbf{R}_{21} \mathbf{F}_{21}) \right\} n^{(2)} d\mathbf{R}_{21} d\mathbf{r}_1 d\mathbf{r}_2 \right] : (\mathbf{U} \times \boldsymbol{\theta}_1). \end{aligned} \quad (31)$$

To determine the form of this elastic equation of state which is appropriate for a particular diatomic crystal we must have additional information concerning the symmetry of $n^{(2)}$. Since a detailed study of the elastic tensor is beyond the scope of the present paper, only the case of an isotropic distribution will be considered here. This special choice for $n^{(2)}$, which is applicable at least approximately to liquids and to amorphous solids, leads from (31) to the formula

$$\begin{aligned} \Delta \mathbf{p}_U &= -\Gamma_1 [\nabla \xi + (\nabla \xi)^\dagger - \frac{1}{3} \mathbf{U} \nabla \cdot \xi] \\ &\quad - \Gamma_2 \mathbf{U} \nabla \cdot \xi - \Gamma_3 \mathbf{U} \times (\text{curl} \xi - 2\boldsymbol{\theta}), \end{aligned} \quad (32)$$

where the coefficients Γ_1 , Γ_2 , and Γ_3 are easily expressed in terms of pair-space averages of the scalars $\mathbf{R}_{21} \cdot \mathbf{F}_{21}$, $\mathbf{R}_{21} \mathbf{R}_{21} : \partial \mathbf{F}_{21} / \partial \mathbf{R}_{21}$, and $R_{21}^2 (\partial / \partial \mathbf{R}_{21}) \cdot \mathbf{F}_{21}$. Γ_3 is found to vanish identically in the case of central interactions. Although the result (32) is of less interest than the more

general equation of state (31), it does clearly illustrate the close formal analogy which exists between the viscous and elastic equations of state.

In the event that the diatomic molecules are polar, $\boldsymbol{\theta}$ can be identified with the angular displacement of the local electrical polarization. The equation of change for this polarization has been derived in reference 3. The coupling between $\boldsymbol{\theta}$ and $\text{curl} \xi$ indicated by (31) and/or (32) illustrates how variations of this polarization induced by an alternating field can give rise to mechanical distortions of the crystal. And, as we have mentioned earlier, the antisymmetrical portion of the stress tensor is a contributor to the torque which transfers internal angular momentum from one portion of the medium to another. Finally, it is clear that the general character of the elastic equation of state derived here for diatomic molecules is also applicable to the case of atoms with spin.