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"Virial Theorem" for the Flow of Energy

R. EISENSCHITZ
Queen Mary College, University of London, London, England

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Expressions are obtained for the flow of energy and momentum in assemblies of densely packed molecules, using a generalized virial theorem. They differ to some extent from expressions put forward by previous authors who had only derived the divergence of the flow vectors. Classical results are shown to be valid also in quantum mechanics.

INTRODUCTION

USES of the virial theorem in modern physics were recently published by Parker[1]; in the present paper, the theorem is applied to the molecular theory of irreversible processes.

Applying the conservation laws of mechanics, Born and Green[2] and Irving and Kirkwood[3] obtained expressions for the divergence of the flow of energy and momentum in fluids; their results remain valid in quantum theory as shown by Irving and Zwanzig.[4]

The same authors also gave expressions for the flow of energy which, however, do not agree with each other. They are, in fact, plausible but arbitrary conjectures, the flow being not uniquely determined by its divergence. Their expressions for the flow of momentum do agree and are in accordance with previous work by Falkenhagen.[5]

As these flow vectors are significant in many contexts, to quote only the flow properties of liquid helium and the sound absorption in dense gases, the subject is considered in the present paper again and from an alternative point of view. Instead of attempting to derive the fluxes by the way of their divergence they are obtained by applying a generalized virial theorem that is due to Rayleigh[6]; he (like Clausius before him) obtained the virial theorem in the form of a relation between time averages. Its validity is then restricted to periodic movement; in quantum mechanics the corresponding theorem applies only to steady pure states. In the present paper, results are freed from these restrictions by obtaining relations between ensemble averages.

PREMISES

The macroscopic properties of an assembly of molecules in a container are assumed to be determined by a probability distribution in phase space which, if not independent of the time, has a stationary projection on two-molecule subspaces.

Forces between molecules are derived from a potential energy depending on the distances between the molecules

$$X=\tfrac{1}{2}\sum_{j}\sum_{k\neq j}\chi_{jk}, \tag{1}$$

where χ_{jk} is the familiar potential energy of interaction between isolated molecules (j, $k=1, 2 \ldots N$). Forces arising from the interaction of molecules with the wall of the container are derived from a potential energy

$$\Omega=\sum_{j}\omega_j, \tag{2}$$

which depends partly on dynamical variables appropriate to the wall, such as the position of the molecules of the container.

Movement of the liquid molecules is determined by equations of motion

$$\begin{aligned} d\mathbf{r}_j/dt&=\mathbf{p}_j/m,\\ d\mathbf{p}_j/dt&=\sum_{k\neq j}\mathbf{f}_{jk}+\mathbf{F}_j, \end{aligned} \tag{3}$$

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[1] E. N. Parker, Phys. Rev. **96**, 1686 (1954).

[2] M. Born and H. S. Green, Proc. Roy. Soc. (London) **A190**, 455 (1947).

[3] J. H. Irving and J. G. Kirkwood, J. Chem. Phys. **18**, 817 (1950).

[4] J. H. Irving and W. Zwanzig, J. Chem. Phys. **19**, 1173 (1951).

[5] H. Falkenhagen, Physik. Z. **32**, 745 (1931).

[6] W. J. Rayleigh, Phil. Mag. **50**, 210 (1900).

where $\mathbf{F}_j$ and $\mathbf{f}_{jk}=-\mathbf{f}_{kj}$ are the forces on the molecule j arising from the potentials X and Ω, respectively, and $\mathbf{r}_j$ is its position; m is the molecular mass.

The change in time of the "wall variables" is not specified in detail. It is postulated that certain averages of functions of these variables are stationary and can be expressed in terms of macroscopic quantities. In particular, the average of the forces $\mathbf{F}_j$ is supposed to balance external forces applied at the surface in form of stresses also the average work done by these forces is assumed to be equal to the energy as supplied from external sources through the unity of surface area per unity of time (denoted by $-W$). In quantitative terms

$$\langle \textstyle\sum_j \mathbf{F}_j\,\delta(\mathbf{r}_j-\mathbf{r})\rangle=-\mathbf{n}\cdot\mathbf{P}dS, \tag{4}$$

$$(1/m)\langle \textstyle\sum_j \mathbf{F}_j\cdot\mathbf{p}_j\,\delta(\mathbf{r}_j-\mathbf{r})\rangle=-\mathbf{n}\cdot\mathbf{Q}dS, \tag{5}$$

where δ is the delta function, $\mathbf{P}$ the stress tensor, dS and $\mathbf{n}$ the surface element and $-$normal, $\mathbf{Q}$ the flow of energy ($W=\mathbf{n}\cdot\mathbf{Q}$) and $\mathbf{r}$ the position vector in 3-dimensional space. It follows that

$$\langle \textstyle\sum_j \mathbf{r}_j\mathbf{F}_j\rangle=-\displaystyle\int \mathbf{rn}\cdot\mathbf{Q}dS, \tag{6}$$

$$(1/m)\langle \textstyle\sum_j \mathbf{r}_j\mathbf{F}_j\cdot\mathbf{p}_j\rangle=-\displaystyle\int \mathbf{rn}\cdot\mathbf{Q}dS. \tag{7}$$

The surface integrals are evaluated by means of the Gaussian theorem

$$\int \mathbf{rn}\cdot\mathbf{j}dS=\int \mathbf{j}dV,$$

where $\mathbf{j}$ is a vector or tensor subject to the condition $\operatorname{div}\mathbf{j}=0$ and V is the volume. If $\mathbf{P}$ and $\mathbf{Q}$ are constant it follows that

$$\int \mathbf{rn}\cdot\mathbf{P}dS=V\mathbf{P}, \tag{8}$$

$$\int \mathbf{rn}\cdot\mathbf{Q}dS=V\mathbf{Q}. \tag{9}$$

The above assumptions regarding the forces between the molecules and the wall must be valid unless the stress is balanced by any alternative forces or if the work done by these forces is maintained by an energy supply alternative to that which is taken into account.

Let $A, B\ldots$ be functions of the dynamical variables in the form of a sum, each term of which depends on the coordinates and momenta of not more than two molecules. Then, defining dA/dt in accordance with Eqs. (3), on account of the assumption of stationary conditions:

$$\langle dA/dt\rangle=\langle dB/dt\rangle=\cdots=0. \tag{10}$$

By choosing appropriate expressions for $A, B\ldots$ relations between physically important ensemble averages are obtained.

FLOW OF MOMENTUM

Let

$$A=\textstyle\sum_j \mathbf{r}_j\mathbf{p}_j, \tag{11}$$

so that

$$dA/dt=\sum_j\Big[(\mathbf{p}_j\mathbf{p}_j/m)+\mathbf{r}_j\mathbf{F}_j+\sum_{k\neq j}\mathbf{r}_j\mathbf{f}_{jk}\Big]. \tag{12}$$

The last term may be written as

$$\tfrac{1}{2}\sum_j\sum_{k\neq j}\mathbf{f}_{jk}(\mathbf{r}_j-\mathbf{r}_k).$$

The average of the second term is, for constant $\mathbf{P}$, according to Eq. (8), equal to $-V\mathbf{P}$. By averaging Eq. (12) over the ensemble of systems it follows that

$$\mathbf{P}=(N/Vm)\langle\mathbf{p}_j\mathbf{p}_j\rangle+(N^2/2V)\langle(\mathbf{r}_j-\mathbf{r}_k)\mathbf{f}_{jk}\rangle, \tag{13}$$

where N is the total number of molecules and the subscripts j, k refer to a representative pair. Equation (13) agrees with the results obtained by previous authors.

FLOW OF ENERGY

Let

$$B=(1/2m)\textstyle\sum_j p_j^2\mathbf{r}_j, \tag{14}$$

so that

$$dB/dt=\sum_j\Big[(p_j^2\mathbf{p}_j/2m^2)+(\mathbf{r}_j\mathbf{p}_j\cdot\mathbf{F}_j/m)+(1/m)\sum_{k\neq j}\mathbf{r}_j\mathbf{p}_j\cdot\mathbf{f}_{jk}\Big]. \tag{15}$$

The last term may be written as

$$(1/2m)\sum_j\sum_{k\neq j}(\mathbf{r}_j\mathbf{p}_j-\mathbf{r}_k\mathbf{p}_k)\cdot\mathbf{f}_{jk}$$

or

$$\sum_j\sum_{k\neq j}(1/4m)[(\mathbf{r}_j+\mathbf{r}_k)(\mathbf{p}_j-\mathbf{p}_k)+(\mathbf{r}_j-\mathbf{r}_k)(\mathbf{p}_j+\mathbf{p}_k)]\cdot\mathbf{f}_{jk}.$$

The average of the second term is, for constant $\mathbf{Q}$, according to Eq. (9), equal to $-V\mathbf{Q}$.

By averaging Eq. (15) over the ensemble of systems it follows that

$$\begin{aligned}Q=(N/2Vm^2)\langle p_j^2\mathbf{p}_j\rangle&+(N^2/4Vm)\langle[(\mathbf{r}_j+\mathbf{r}_k)(\mathbf{p}_j-\mathbf{p}_k)\\&+(\mathbf{r}_j-\mathbf{r}_k)(\mathbf{p}_j+\mathbf{p}_k)]\cdot\mathbf{f}_{jk}\rangle,\end{aligned} \tag{15a}$$

where the subscripts j and k refer to a representative pair of molecules. This expression will be transformed in order to make it comparable with the expressions obtained by previous authors. Let

$$C=\sum_j\sum_{k\neq j}(\mathbf{r}_j+\mathbf{r}_k)\chi_{jk}. \tag{16}$$

As

$$\begin{aligned}m\,d\chi_{jk}/dt&=(\partial\chi_{jk}/\partial\mathbf{r}_j)\cdot\mathbf{p}_j+(\partial\chi_{jk}/\partial\mathbf{r}_k)\cdot\mathbf{p}_k\\&=-\mathbf{f}_{jk}\cdot(\mathbf{p}_j-\mathbf{p}_k),\end{aligned}$$

it follows that

$$dC/dt=(1/m)\sum_j\sum_{k\neq j}[\chi_{jk}(\mathbf{p}_j+\mathbf{p}_k)-(\mathbf{r}_j+\mathbf{r}_k)\mathbf{f}_{jk}\cdot(\mathbf{p}_j-\mathbf{p}_k)]. \quad (17)$$

By taking the average of Eq. (17) over the ensemble of systems, the relation

$$\langle(\mathbf{r}_j+\mathbf{r}_k)\mathbf{f}_{jk}\cdot(\mathbf{p}_j-\mathbf{p}_k)\rangle=\langle\chi_{jk}(\mathbf{p}_j+\mathbf{p}_k)\rangle$$

is obtained; the subscripts j and k refer to a representative pair of molecules. This relation is used for transforming the second term of Eq. (15a). Hence,

$$\mathbf{Q}=(N/2Vm^2)\langle p_j^2\mathbf{p}_j\rangle+(N^2/4Vm)\langle[\chi_{jk}+(\mathbf{r}_j-\mathbf{r}_k)\mathbf{f}_{jk}\cdot](\mathbf{p}_j+\mathbf{p}_k)\rangle. \quad (18)$$

Formulas given by previous authors do not fully agree with Eq. (18). Born and Green[2] [in their Eqs. (2.17) and (4.15)] give an expression in which the term depending on χ_{jk} in (18) is missing. Irving and Kirkwood[3] (in their Eqs. (6.21) and (6.24)) give an expression in which the factor $(\mathbf{p}_j+\mathbf{p}_k)$ of Eq. (18) is replaced by $2\mathbf{p}_j$ which is equal to $(\mathbf{p}_j+\mathbf{p}_k)+(\mathbf{p}_j-\mathbf{p}_k)$. Unless the terms by which the various expressions for $\mathbf{Q}$ differ make no appreciable contribution to the statistical average, the flow of energy, in particular the heat flow in a steady temperature gradient, should be derived from (18) rather than from the older equations.

QUANTUM THEORY

Macroscopic properties of the assembly are now determined by a probability distribution for the occurrence of pure states in a mixture. The states are chosen in such a way that they are steady with respect to N-2 molecules. The distribution, in general time dependent, is in the present case assumed to permit averaging with respect to the states of N-2 molecules and to yield an average that is independent of the time.

Equations (3) and (10) remain valid, differentiations with respect to the time being expressed in terms of the appropriate Poisson bracket, such as $(i/\hbar)(H\mathbf{r}_k-\mathbf{r}_kH)$ for $d\mathbf{r}_k/dt$. The Hamilton function H is defined as

$$H=\sum_j p_j^2/2m+\Omega+\mathrm{X}.$$

Equations (4) and (5) must not be used explicitly since they apply to a molecule that is localized at some point near the wall. Equations (6) and (7) which are in classical theory consequences of (4) and (5) should now be valid on their own merit expressing the balance of forces and energy; Eq. (7) will, however, have to be made symmetric with respect to commutations and, accordingly replaced by

$$(1/2m)\langle\sum_j(\mathbf{r}_j\mathbf{F}_j\cdot\mathbf{p}_j+\mathbf{p}_j\cdot\mathbf{F}_j\mathbf{r}_j)\rangle=-\int\mathbf{rn}\cdot\mathbf{Q}dS. \quad (19)$$

The functions A, B are defined also in a symmetric way

$$A=\tfrac{1}{2}\sum_j(\mathbf{r}_j\mathbf{p}_j+\mathbf{p}_j\mathbf{r}_j), \quad (20)$$

$$B=(1/2m)\sum_j(\mathbf{r}_jp_j^2+p_j^2\mathbf{r}_j), \quad (21a)$$

or, alternatively,

$$B=(1/2m)\sum_j(\mathbf{p}_j\cdot-\mathbf{r}_j-\cdot\mathbf{p}_j), \quad (21b)$$

the dots and hyphens signifying scalar multiplication of the first and third factor.

In calculating dA/dt, etc., the following commutation rules are used:

$$uG(x)-G(x)u=(\hbar/i)(dG/dx),$$

$$G(u)x-xG(u)=(\hbar/i)(dG/du),$$

$$u^2G(x)-G(x)u^2=(\hbar/i)[(dG/dx)u+u(dG/dx)].$$

Here x and u denote a Cartesian coordinate and the conjugate component of momentum. $G(x)$ and $G(u)$ are functions of these variables.

By averaging the time derivatives dA/dt, dB/dt, dC/dt over the ensemble of systems expressions for $\mathbf{P}$ and $\mathbf{Q}$ are found which are identical with those presented in Eqs. (13) and (18), respectively. These expressions do not contain any noncommuting factors. Equation (13) applies equally to normal and tangential stress components. Equation (18) is arrived at whether B is defined according to (21a) or according to (21b). The noncommuting factors in B do not give rise to any ambiguity. Averages that are indicated in (13) or (18) can be evaluated by the method of Irving and Zwanzig[4] or by means of the density matrix.

CONCLUSION

Results obtained in this paper do not depend on any arbitrary assumption. They apply to steady conditions; application to time dependent processes is possible if the left-hand sides of Eqs. (12), (15), and (17) are taken into account. In periodic processes, such as the absorption of sound, a time average of the ensemble averages may be taken; if this reduces the mean time derivatives (dA/dt, dB/dt, dC/dt) to zero, Eqs. (13) and (18) remain valid in their present form.