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A classical virial theorem for open systems

Jan-Åke Schweitz

Department of Materials Science, Institute of Technology, Uppsala University, Box 534, S-751 21 Uppsala, Sweden

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Abstract. A generalized classical virial equation is derived, superior to the equations already existing in three respects:

(i) applicability to assemblies of fluctuating numbers of particles;
(ii) applicability to assemblies subjected to net external action;
(iii) applicability to any arbitrarily selected part of a larger assembly.

It is found that the momentum in- and out-flux densities, caused by particles crossing the limiting surfaces, contribute to the virial. The equation is applied to a homogeneous gas, and the ideal gas law is derived. Invariance criteria are studied, and translations and division into subsystems are discussed. Various internal and external contributions to the virial are discussed and compared for the new and the already existing virial equations.

1. Introduction

The classical virial theorem (Clausius 1870) relates the average kinetic energy of a system of particles to the average action of forces on the same particles. In many cases it is possible to express the average action of forces in terms of the average potential energy, and in these cases the virial theorem governs the balance between kinetic and potential energy in the system. This important theorem has a direct analogy also in quantum mechanics (Fock 1930, Slater 1933).

The applicability of this theorem, however, is subject to several important limitations. It is valid only for a fixed number of particles contained in a limited volume, and the long-time average of the total resultant external force must be zero. In statistical mechanics, a system of this type is represented by a *petit ensemble*.

It is of great interest, however, to apply a similar theorem to systems of fluctuating numbers of particles (for instance electrons in a limited part of a crystal) or to systems subject to non-zero external action (for instance electrons in a field gradient). This type of system, where we have an exchange of particles through the surfaces of the observed volume, is represented by *grand ensembles*.

In the present paper a classical virial theorem, applicable to grand ensembles, is derived. It is found that the momentum in- and out-flux densities, caused by particles crossing the limiting surfaces, contribute to the virial. This is by no means surprising, since an action of force is, by definition, nothing but a flux of momentum. The denomination of the statistical mechanics is accepted here. Thus, the 'petit' virial equation of Clausius is obtained as a special case of the 'grand' equation—derived in this work—when the surface flux is zero.

2. The classical virial equation for a grand ensemble

The virial equation of Clausius can be expressed in the following manner:

$$\left(\sum_{i=1}^{N}(2T_i+\boldsymbol{r}_i\cdot\boldsymbol{F}_i)\right)_{\text{time average}}=0, \tag{1}$$

where the summation runs over a fixed number N of particles contained in a limited volume, and T_i, $\boldsymbol{r}_i$ and $\boldsymbol{F}_i$ are kinetic energy of, location of and force acting on the ith particle, respectively. For the corresponding quantum mechanical expression the condition of limited volume is replaced by a condition of vanishing wavefunctions at large distances.

The petit virial equation (1) is only applicable to a petit ensemble. Here we shall derive the corresponding expression for a grand ensemble, essentially following Clausius' original method.

We study the function

$$M(\tau)=\sum \boldsymbol{r}_i(\tau)\cdot\boldsymbol{p}_i(\tau); \qquad (\boldsymbol{r}_i\in V), \tag{2}$$

where $\boldsymbol{p}_i$ is the momentum of the ith particle located at $\boldsymbol{r}_i$ at the time τ. The summation is only extended over particles contained in the volume V at the time τ. The function $M(\tau)$ may be discontinuous, since the summation only runs over particles instantaneously contained in V; particles may leave or enter the volume, thereby changing the number of terms in the sum. During the period t_p we assume $N(t_p)$ discontinuities to occur at the points of time τ_n $(n=1,2,\ldots,N)$. We define $\tau_0=0$ and $\tau_{N+1}=t_p$.

The time derivative of M, in the open time intervals $\tau_n<\tau<\tau_{n+1}$ $(n=0,1,\ldots,N)$, is

$$\dot{M}(\tau)=\sum\left(\frac{\boldsymbol{p}_i^2}{m_i}+\boldsymbol{r}_i\cdot\boldsymbol{F}_i\right)=\sum(2T_i+\boldsymbol{r}_i\cdot\boldsymbol{F}_i). \tag{3}$$

The time average of $\dot{M}$ over all the open intervals $\tau_n<\tau<\tau_{n+1}$ is

$$\begin{aligned}A(t_p)&=\frac{1}{t_p}\sum_0^N\int_{\tau_n^+}^{\tau_{n+1}^-}\dot{M}(t)\,dt=\frac{1}{t_p}\sum_0^N[M(\tau_{n+1}^-)-M(\tau_n^+)]\\&=\frac{1}{t_p}(M(t_p)-M(0))+\frac{1}{t_p}\sum_0^N(M(\tau_n^-)-M(\tau_n^+)),\end{aligned} \tag{4}$$

where $\tau_n^+=\lim_{\epsilon\to0}(\tau_n+\epsilon)$ and $\tau_n^-=\lim_{\epsilon\to0}(\tau_n-\epsilon)$, $\epsilon>0$, and $M(\tau_n^+)$ and $M(\tau_n^-)$ are the corresponding limits of $M(\tau)$.

From equation (2) we conclude that $M(t_p)$ and $M(0)$ must be finite quantities for every choice of t_p. Thus we obtain

$$A_v=\lim_{t_p\to\infty}A(t_p)=\lim_{t_p\to\infty}\frac{1}{t_p}\sum_1^N(M(\tau_n^-)-M(\tau_n^+)). \tag{5}$$

Here, and in the following discussion, the limit $t_p\to\infty$ denotes a period of time, sufficiently long to make $(M(t_p)-M(0))/t_p$ negligible, but nevertheless short compared with a Poincaré recurrence time.

Let us adopt the following notation: the momentum vector of a particle *leaving* the volume V is $\tilde{\boldsymbol{p}}_i$ and the corresponding notation for a particle *entering* V is $\bar{\boldsymbol{p}}_i$. We can

now express equation (5) as

$$A_v = \lim_{t_p \to \infty} \frac{1}{t_p} \left(\sum_1^J \boldsymbol{r}_j \cdot \vec{\boldsymbol{p}}_j - \sum_1^K \boldsymbol{r}_k \cdot \tilde{\boldsymbol{p}}_k \right), \tag{6}$$

where $J(t_p) + K(t_p) = N(t_p)$. The contribution to A_v from a small surface element $\Delta \boldsymbol{S}$ at the point $\boldsymbol{r}$ is

$$\Delta A_v(\boldsymbol{r}) = \lim_{t_p \to \infty} \frac{1}{t_p} \boldsymbol{r} \cdot \left(\sum_1^{\Delta J} \vec{\boldsymbol{p}}_j(\boldsymbol{r}) - \sum_1^{\Delta K} \tilde{\boldsymbol{p}}_k(\boldsymbol{r}) \right) \tag{7}$$

where $\Delta J(t_p, \boldsymbol{r})$ and $\Delta K(t_p, \boldsymbol{r})$ are the total number of particles leaving and entering, respectively, the volume V through the surface element $\Delta \boldsymbol{S}$ at $\boldsymbol{r}$ during the period t_p.

Let us define the *mean flux of momentum* (momentum/time) *out* through $\Delta \boldsymbol{S}$ as

$$\Delta \vec{\boldsymbol{P}}(\boldsymbol{r}) = \lim_{t_p \to \infty} \frac{1}{t_p} \sum_1^{\Delta J} \vec{\boldsymbol{p}}_j(\boldsymbol{r}), \tag{8}$$

and the corresponding expression *in* through $\Delta \boldsymbol{S}$ as

$$\Delta \tilde{\boldsymbol{P}}(\boldsymbol{r}) = \lim_{t_p \to \infty} \frac{1}{t_p} \sum_1^{\Delta K} \tilde{\boldsymbol{p}}_k(\boldsymbol{r}). \tag{9}$$

Now let us define the *mean flux density of momentum* (momentum/time and area) out of and into the volume as

$$\vec{\boldsymbol{p}}(\boldsymbol{r}) = \lim_{\Delta S \to 0} \frac{\Delta \vec{\boldsymbol{P}}(\boldsymbol{r})}{\Delta S}, \tag{10}$$

$$\tilde{\boldsymbol{p}}(\boldsymbol{r}) = \lim_{\Delta S \to 0} \frac{\Delta \tilde{\boldsymbol{P}}(\boldsymbol{r})}{\Delta S}. \tag{11}$$

Substitution in equation (7) gives

$$\Delta A_v = \boldsymbol{r} \cdot (\vec{\boldsymbol{p}}(\boldsymbol{r}) - \tilde{\boldsymbol{p}}(\boldsymbol{r}))\ \Delta S. \tag{12}$$

To get the total A_v we integrate over the surface S of the volume

$$A_v = \oint_S \boldsymbol{r} \cdot (\vec{\boldsymbol{p}}(\boldsymbol{r}) - \tilde{\boldsymbol{p}}(\boldsymbol{r}))\, \mathrm{d}S. \tag{13}$$

Since A_v is a time average of $\dot{M}$ we obtain from equation (3):

$$\left(\sum_{r_i \in V} (2T_i + \boldsymbol{r}_i \cdot \boldsymbol{F}_i) \right)_{av} + \oint_S \boldsymbol{r} \cdot (\tilde{\boldsymbol{p}}(\boldsymbol{r}) - \vec{\boldsymbol{p}}(\boldsymbol{r}))\, \mathrm{d}S = 0 \tag{14}$$

which is the *virial equation for a grand ensemble.* It is important to observe that the flux densities $\tilde{\boldsymbol{p}}$ and $\vec{\boldsymbol{p}}$ are not only functions of $\boldsymbol{r}$ but also depend on the orientation of the surface S at $\boldsymbol{r}$.

At this stage it is convenient to introduce some new notation. The virial sum of the petit virial equation is denoted

$$Z_P = \sum \boldsymbol{r}_i \cdot \boldsymbol{F}_i. \tag{15}$$

In the following, Z_P is called the 'petit virial'. The last term of equation (14) is denoted

$$Z_S = \oint_S \boldsymbol{r} \cdot (\tilde{\boldsymbol{p}}(\boldsymbol{r}) - \vec{\boldsymbol{p}}(\boldsymbol{r}))\, \mathrm{d}S, \tag{16}$$

and is in the following called 'surface flux virial'. The sum Z of Z_P and Z_S is called the 'grand virial':

$$Z = Z_P + Z_S. \tag{17}$$

Thus, we may write the grand virial equation as

$$2T + Z = 0, \tag{18}$$

or

$$2T + Z_P + Z_S = 0, \tag{19}$$

where $T = \Sigma T_i$ ($\boldsymbol{r}_i \in V$) and time averages are tacitly implied.

3. Application to homogeneous gas

Consider a gas obeying the grand virial equation (14) and postulate a uniform and isotropic distribution of momentum. This implies that $\vec{\boldsymbol{p}} = -\vec{\boldsymbol{p}}$ and $\vec{\boldsymbol{p}} \parallel \mathrm{d}\boldsymbol{S}$ for any choice of surface element $\mathrm{d}\boldsymbol{S}$, and that $|\vec{\boldsymbol{p}}|$ is a constant for the whole of the particular specimen of gas. For the surface flux virial (16) the condition $\vec{\boldsymbol{p}} = -\vec{\boldsymbol{p}}$ yields

$$Z_S = 2 \oint_S \boldsymbol{r} \cdot \vec{\boldsymbol{p}}(\boldsymbol{r})\, \mathrm{d}S. \tag{20}$$

$-\vec{\boldsymbol{p}} \parallel \mathrm{d}\boldsymbol{S}$ yields

$$Z_S = -2 \oint_S |\vec{\boldsymbol{p}}(\boldsymbol{r})| \boldsymbol{r} \cdot \mathrm{d}\boldsymbol{S}. \tag{21}$$

Because $|\vec{\boldsymbol{p}}|$ is a gas constant we have

$$Z_S = -2|\vec{\boldsymbol{p}}| \oint_S \boldsymbol{r} \cdot \mathrm{d}\boldsymbol{S}. \tag{22}$$

Gauss' theorem yields

$$Z_S = -2|\vec{\boldsymbol{p}}| \int_V \nabla \cdot \boldsymbol{r}\, \mathrm{d}V = -2|\vec{\boldsymbol{p}}| 3V. \tag{23}$$

The pressure is $P = 2|\vec{\boldsymbol{p}}|$, which yields

$$Z_S = -3PV. \tag{24}$$

This is the form of the surface flux virial Z_S for any gas of uniform and isotropic distribution of momentum. It is in fact valid for any volume of gas the momentum distribution of which is uniform and isotropic all over the surface, irrespective of the distribution in the rest of the volume.

In the special case of an ideal gas, the particles interact only via collision forces. Since these forces are equal and opposite for every collision, equation (19) assumes the form

$$2T = 3PV. \tag{25}$$

But the average kinetic energy per particle in an ideal gas is $\frac{3}{2}kT$, where k is Boltzmann's constant and T is temperature. If $\bar{N}$ is the average number of particles in V, we obtain

$$\bar{N}kT = PV \tag{26}$$

which is the ideal gas law. The present derivation is based on the exchange of momentum through imaginary walls. In the case of a petit ensemble, however, the corresponding derivation is based on the action of forces exerted on the particles by impenetrable walls.

Combining equations (24) and (25), we obtain

$$Z_S = -2T. \tag{27}$$

This result is of special interest for a Fermi gas such as electrons in a positive, neutralizing background. In a metal, for instance, Z_S can be approximately calculated from the total kinetic energy T of the conduction electrons in the observed volume.

4. Invariance criteria

The virial equation (1) for a petit ensemble is not unconditionally invariant under transformations. Let us study orthogonal transformations which always can be divided into one parallel translation and one pure rotation of the coordinate system.

Equation (1) is obviously invariant under pure rotation, since all T_i, $|\boldsymbol{r}_i|$, $|\boldsymbol{F}_i|$ and angles between vectors are unchanged. It is not necessarily invariant under translation, however. Let us go from the $\boldsymbol{r}$ system to an $\boldsymbol{r}'$ system through a parallel translation $\boldsymbol{x}$

$$\boldsymbol{r} = \boldsymbol{x} + \boldsymbol{r}'. \tag{28}$$

All T_i and $\boldsymbol{F}_i$ are invariant under this translation, but the petit virial is transformed according to

$$\sum \boldsymbol{r}_i \cdot \boldsymbol{F}_i = \boldsymbol{x} \cdot \sum \boldsymbol{F}_i + \sum \boldsymbol{r}'_i \cdot \boldsymbol{F}_i. \tag{29}$$

Thus, for an arbitrary translation $\boldsymbol{x}$ the petit virial (and equation (1)) is invariant if, and only if, the total force $\Sigma \boldsymbol{F}_i$ vanishes. Since Newton's third law demands that all interaction between particles in the system balances, the total force on the system amounts to the total *external* force.

Consequently we can state that the virial equation for a petit ensemble is invariant under orthogonal transformations *if, and only if, the long-time average of the external force resultant vanishes.*

This is easily understood, since the virial equation is a relation between mean values. If the time average of the external force were not equal to zero, no time average of the kinetic energy could exist.

For the grand virial equation (14) the situation is different, however. By the same argument as earlier we realize that equation (14) is invariant under pure rotation. A translation $\boldsymbol{x}$ results in an extra term

$$(\boldsymbol{x} \cdot \sum \boldsymbol{F}_i)_{\text{av}} \tag{30}$$

in the petit virial, and an extra term

$$\boldsymbol{x} \cdot \oint_S (\tilde{\boldsymbol{p}}(\boldsymbol{r}) - \vec{\boldsymbol{p}}(\boldsymbol{r}))\, \mathrm{d}S \tag{31}$$

in the surface flux virial. Equation (14) therefore is invariant under an arbitrary translation $\boldsymbol{x}$ if, and only if, the condition

$$\left(\sum_{r_i \in V} \boldsymbol{F}_i\right)_{\mathrm{av}} + \oint_S (\tilde{\boldsymbol{p}}(\boldsymbol{r}) - \tilde{\boldsymbol{p}}(\boldsymbol{r}))\, \mathrm{d}S = 0 \tag{32}$$

is satisfied. It can be shown that this is always the case if a time average of the external force resultant exists. In exact analogy with the derivation of the surface flux virial in § 2 (replace M by $\Sigma \boldsymbol{p}_i$ and M by $\Sigma \boldsymbol{F}_i$) it is possible to show that equation (32) is then always satisfied.

Consequently we can state that *the mere existence of a finite long-time average value of external action is a necessary and sufficient condition for invariance* of the grand virial equation under orthogonal transformations.

This means that we can apply the grand virial equation to a system subjected to a non-vanishing external force resultant. In such a system some particles will suffer a net acceleration in their motion through the observed volume, and the total flux of momentum into the volume will not equal the total flux out of it.

5. Translations and subsystems

Assume that an assembly† of particles is divided into M subassemblies which may or may not overlap in space. Furthermore, assume that each subassembly has its own coordinate system (*subsystem*) which can be obtained from a *principal system* by a simple parallel translation $\boldsymbol{x}_m$

$$\boldsymbol{r}_i = \boldsymbol{x}_m + \boldsymbol{r}_{mk}; \qquad m = 1, 2, \ldots, M, \tag{33}$$

where i and k refer to the numbering of particles in the principal system and the mth subsystem, respectively. The total instantaneous number of particles in the principal assembly is L, and the number in a subassembly is l_m, i.e.

$$L = \sum_1^M l_m. \tag{34}$$

Let us adopt the notation Z_{P} for the petit virial of the principal assembly and $Z_{\mathrm{P}m}$ for the subassemblies

$$Z_{\mathrm{P}} = \sum_{i=1}^{L} \boldsymbol{r}_i \cdot \boldsymbol{F}_i \tag{35}$$

$$Z_{\mathrm{P}m} = \sum_{k=1}^{l_m} \boldsymbol{r}_{mk} \cdot \boldsymbol{F}_{mk}; \qquad m = 1, 2, \ldots, M. \tag{36}$$

The principal petit virial Z_{P} then can be expressed as

$$Z_{\mathrm{P}} = \sum_{i=1}^{L} \boldsymbol{r}_i \cdot \boldsymbol{F}_i = \sum_{m=1}^{M} \sum_{k=1}^{l_m} (\boldsymbol{x}_m + \boldsymbol{r}_{mk}) \cdot \boldsymbol{F}_{mk} = \sum_{m=1}^{M} \boldsymbol{x}_m \cdot \sum_{k=1}^{l_m} \boldsymbol{F}_{mk} + \sum_{m=1}^{M} \sum_{k=1}^{l_m} \boldsymbol{r}_{mk} \cdot \boldsymbol{F}_{mk}. \tag{37}$$

† Up to now we have used the word 'system' in two senses: systems of particles and coordinate systems. To avoid misunderstandings, in the following the word 'system' always refers to coordinate systems while the word 'assembly' is used for collections of particles.

Introduce $\boldsymbol{F}_m = \sum_{k=1}^{l_m} \boldsymbol{F}_{mk}$, which is the total force acting on the mth subassembly and amounts to the total *external* force (exerted by other subassemblies, for instance). Thus we obtain

$$Z_P = \sum_{m=1}^{M} \boldsymbol{x}_m \cdot \boldsymbol{F}_m + \sum_{m=1}^{M} Z_{Pm}. \tag{38}$$

It is now possible to divide an assembly with complicated symmetry properties into subassemblies, convenient for calculating the principal petit virial Z_P from the subvirials Z_{Pm} and the total external forces $\boldsymbol{F}_m$ acting on each subassembly.

Similarly, the calculation of the surface flux virial Z_S (equation (16)) may be simplified by a division into subassemblies. In this case, however, the subassemblies should not overlap in space, but rather constitute a non-overlapping partition of the entire volume of the principal assembly.

If Z_S denotes the surface flux virial of the the entire assembly of the principal system, and Z_{Sm} is the notation for subassembly m in the subsystem, we have:

$$Z_S = \oint_S \boldsymbol{r} \cdot (\tilde{\boldsymbol{p}}(\boldsymbol{r}) - \vec{\boldsymbol{p}}(\boldsymbol{r}))\, \mathrm{d}\boldsymbol{S}, \tag{39}$$

$$Z_{Sm} = \oint_{S_m} \boldsymbol{r}_m \cdot (\tilde{\boldsymbol{p}}(\boldsymbol{r}_m) - \vec{\boldsymbol{p}}(\boldsymbol{r}_m))\, \mathrm{d}\boldsymbol{S}; \qquad m = 1, 2, \ldots, M. \tag{40}$$

The translation $\boldsymbol{r} = \boldsymbol{x}_m + \boldsymbol{r}_m$ substituted into (39) yields

$$\begin{aligned} Z_S &= \sum_{m=1}^{M} \oint_{S_m} (\boldsymbol{x}_m + \boldsymbol{r}_m) \cdot (\tilde{\boldsymbol{p}}(\boldsymbol{r}) - \vec{\boldsymbol{p}}(\boldsymbol{r}))\, \mathrm{d}\boldsymbol{S} \\ &= \sum_{m=1}^{M} \boldsymbol{x}_m \cdot \oint_{S_m} (\tilde{\boldsymbol{p}}(\boldsymbol{r}) - \vec{\boldsymbol{p}}(\boldsymbol{r}))\, \mathrm{d}\boldsymbol{S} + \sum_{m=1}^{M} \oint_{S_m} \boldsymbol{r}_m \cdot (\tilde{\boldsymbol{p}}(\boldsymbol{r}_m) - \vec{\boldsymbol{p}}(\boldsymbol{r}_m))\, \mathrm{d}\boldsymbol{S}. \end{aligned} \tag{41}$$

To obtain the first equality we have utilized the fact that all contributions to Z_S from interfaces between neighbouring subassemblies cancel (since $\tilde{\boldsymbol{p}}(\boldsymbol{r})$ in one subassembly must equal $\vec{\boldsymbol{p}}(\boldsymbol{r})$ in the neighbouring one)†. In the last term of the last equality we have utilized the fact that $\vec{\boldsymbol{p}}$ and $\tilde{\boldsymbol{p}}$ are invariants under translations. From equation (32) it is seen that the integral in the first part of the last term equals $-(\boldsymbol{F}_m)_{av} = -(\sum_{k=1}^{l_m} \boldsymbol{F}_{mk})_{av}$, i.e. the negative of the total external force on subassembly m. Thus we obtain (cf equation (38))

$$Z_S = -\sum_{m=1}^{M} \boldsymbol{x}_m \cdot (\boldsymbol{F}_m)_{av} + \sum_{m=1}^{M} Z_{Sm}. \tag{42}$$

For a non-overlapping partition of the entire volume of the principal assembly, neither the principal petit virial Z_P nor the principal surface flux virial Z_S can be divided into simple sums of subvirials (cf equations (38) and (42)). This, however, is possible for the grand virial

$$Z = Z_P + Z_S = \sum_{m=1}^{M} (Z_{Pm} + Z_{Sm}) \qquad \text{(time averages tacitly implied).} \tag{43}$$

Consequently, for a volume partitioned in the above manner, it is possible to find the

† Note that the directions of $\mathrm{d}\boldsymbol{S}$ (positive or negative) must be the same in all subsystems as in the principal system. Thus, for an interface, $\mathrm{d}\boldsymbol{S}$ is directed inwards for one subassembly if it is directed outwards for the neighbouring subassembly.

grand virial of the principal assembly simply by the summation of the grand virials of the subassemblies; irrespective of the choice of subsystems and of the external forces on the subassemblies.

6. Internal and external virials

In order to clarify the cause and origin of the different parts of the grand virial, it is useful to divide it into different parts: $Z = Z_I + Z_X$, where Z_I is the 'internal virial' due to internal interactions and Z_X is the 'external virial' caused by external influences. Z_X can be further divided into the 'constraint virial' Z_C due to external forces of constraint, and the surface flux virial Z_S caused by the exchange of momentum through the limiting surfaces. The relation between the different Z is given by

$$Z = \underbrace{Z_I + \overbrace{Z_C + Z_S}^{Z_X}}_{Z_P}. \tag{44}$$

For electrostatic type of interaction we have $Z_I = U$ (internal potential energy).

In the literature (Slater 1933, March 1958, Löwdin 1959, Ross 1969) virial relationships of the type

$$2T + U = -3V\frac{\partial E}{\partial V}\left(= -r\frac{\partial E}{\partial r}\right) \tag{45}$$

are currently encountered for electrostic interaction. E is the total energy $T + U$ (time averages are tacitly implied). These expressions, however, are derived for *petit* ensembles. Only in the special case of a gas of homogeneous and isotropic distribution (in space) of momentum are they applicable to grand ensembles. A non-vanishing space derivative of E in the right-hand side of equation (45) implies that the assembly is subjected to external constraint, the energy of which is not included in $E = T + U$. In a homogeneous gas, for instance, $-\partial E/\partial V$ is the wall pressure P. Thus, the petit virial of equation (45) is

$$Z_P = U + 3V\frac{\partial E}{\partial V} \tag{46}$$

where the first term is Z_I and the second term is Z_C.

Imagine a homogeneous gas of limited volume V. For a *petit* ensemble (i.e. V is enclosed by walls) $Z_C \neq 0$ and $Z_S = 0$, but for a *grand* ensemble (no walls) $Z_C = 0$ and $Z_S \neq 0$. As discussed above, $Z_{C(\text{petit})} = -3PV$, which, according to equation (24), equals $Z_{S(\text{grand})}$. This is the reason why equation (45) can be applied directly to a grand ensemble in a homogeneous gas. In the general case, however, both Z_C and Z_S are non-vanishing, and a grand virial equation which includes both types of virials must be used.

7. Summary

The petit virial equation suffers from the restrictions that it can only be applied to an assembly of a fixed number of particles and subjected to no external net action. By

introduction of a surface flux virial these restrictions are removed in the grand virial equation. Furthermore, the grand virial equation is, contrary to the petit equation, applicable to any arbitrary chosen part of a larger assembly.

As pointed out in § 6, petit virial relationships are sometimes applied to *grand* ensembles. This is possible only in cases where the surface flux virial equals the constraint virial of the corresponding *petit* ensemble, as for instance in a gas of isotropic and homogeneous distribution of momentum. This fact, however, is rarely pointed out in the literature.

Some quantum mechanical virial equations, resembling the classical grand virial equation derived in the present work, are found in the literature. These equations are either derived from the Schrödinger equation by means of Slater's (1933) original method (Weislinger and Olivier 1974, Srebrenik and Bader 1974), or from the Heisenberg equation (McLellan 1974). In a subsequent publication, the present author derives a quantum grand virial equation by a similar method to that used in the present work. It is thereby possible to express the quantum surface flux virial in the same easily interpreted manner as the classical Z_S.

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