# Modified Virial Theorem for Total Momentum Fluctuations

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A modified form of the virial theorem, which relates the fluctuations in the total linear momentum to a "virial" of the external forces acting on a physical system, is proven both classically and quantum-mechanically.

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THE virial theorem of Clausius, which relates the mean kinetic energy of a system of particles to the pressure and a "virial" of the interparticle forces, has found many applications in physics. It is the purpose of this note to show that there exists also a relation between the fluctuations of the total momentum of a system and a "virial" involving only the external forces acting on the system. We assume for concreteness that the forces between the particles making up the system are two-body central forces. However, as is clear from the context, this restriction is not necessary.

Let $H$, the Hamiltonian of an $N$-particle system, be of the form

$$H=\sum_{i=1}^{N}(\mathbf{p}_i^2/2m)+\tfrac{1}{2}\sum_{i\neq j}V(r_{ij})+\sum_{i=1}^{N}U(\mathbf{r}_i), \tag{1}$$

$$\mathbf{r}_i=(x_i,y_i,z_i),\quad r_{ij}=|\mathbf{r}_i-\mathbf{r}_j|,$$

where $U(\mathbf{r})$ is the potential energy of a molecule at the point $\mathbf{r}$ due to external forces, such as gravity or boundary forces for instance. The classical equations of motion then have the form

$$(\dot{p}_x)_i=m\ddot{x}_i=-\sum_j\frac{\partial}{\partial x_i}V(r_{ij})-\frac{\partial}{\partial x_i}U(\mathbf{r}_i). \tag{2}$$

Summing these equations for all particles leads to an equation of motion for the center of mass from which the interparticle forces $V(r_{ij})$ have disappeared:

$$m\frac{d^2X}{dt^2}=-\sum_{i=1}^{N}\frac{\partial}{\partial x_i}U(\mathbf{r}_i);\quad X=\sum_{i=1}^{N}x_i. \tag{3}$$

If we now multiply this equation by $X$, we get

$$m\left(\frac{d^2X}{dt^2}\right)X=m\frac{d}{dt}(X\dot{X})-m(\dot{X})^2=-X\sum_{i=1}^{N}\frac{\partial}{\partial x_i}U(\mathbf{r}_i). \tag{4}$$

Hence, when $X$ and $\dot{X}$ are bounded,

$$\lim_{T\to\infty}\frac{1}{T}\int_0^T\frac{m}{2}(\dot{X})^2dt=\frac{1}{2m}\langle P_x^2\rangle_{\text{Av}}=\tfrac{1}{2}\sum_{i,j}\left\langle x_j\frac{\partial}{\partial x_i}U(\mathbf{r}_i)\right\rangle_{\text{Av}}, \tag{5}$$

where $P_x=\sum_{i=1}^{N}(p_x)_i$ is the $x$ component of the total momentum, and the $\langle\ \rangle_{\text{Av}}$ denotes the time average along a phase space trajectory. Similar theorems also hold for other elements of the tensor **PP**.

When our system is represented by a stationary Gibbs ensemble, we may replace this time average by an ensemble average denoted by $\langle\ \rangle$. Equation (5) now takes the form (see Appendix)

$$\frac{1}{2m}\langle P_x^2\rangle=\frac{1}{2}\int x_1\frac{\partial}{\partial x_1}U(\mathbf{r}_1)d\mathbf{r}_1+\frac{1}{2}\int\int x_1\frac{\partial}{\partial x_2}U(\mathbf{r}_2)\rho(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2, \tag{6}$$

where $\rho(\mathbf{r}_1)$ and $\rho(\mathbf{r}_1,\mathbf{r}_2)$ are the number density and the pair density, respectively. When the only external forces are those due to the walls, then

$$\int x_1\frac{\partial U(\mathbf{r}_1)}{\partial x_1}\rho(\mathbf{r}_1)d\mathbf{r}_1=p\Omega, \tag{7}$$

where $p$ is the pressure and $\Omega$ is the volume of the container.

The derivation of Eq. (5) holds also for a quantum mechanical system when $\mathbf{r}_i$, $\mathbf{p}_i$ are interpreted as Heisenberg operators. In a representation in which $H$ is diagonal the off-diagonal elements of $P_x^2$ oscillate in time and hence, their average vanishes. The diagonal elements are time independent and are just the expectation values of $P_x^2$ in an energy eigenstate. It is interesting though to derive Eq. (6) directly for a stationary state and show the modification required when $U(\mathbf{r})$ is infinite at the walls. Let $\psi$ be the wave function of such a state, satisfying

$$(H-E)\psi=0,\ H=\frac{-\hbar^2}{2m}\sum_{j=1}^{N}\nabla_j^2+\sum_{i\neq j}V(r_{ij})+\sum_{j=1}^{N}U(\mathbf{r}_j). \tag{8}$$

It follows from the definition of the operators $H$ and $P_x$ that

$$(H-E)X\psi=\frac{\hbar}{im}P_x\psi,\quad P_x=\frac{\hbar}{i}\sum_{j=1}^{N}\frac{\partial}{\partial x_j}. \tag{9}$$

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Hence

$$\left(X\psi, \frac{i}{2\hbar}[P_x, (H-E)]\psi\right)=\left(X\psi, \frac{-i}{2\hbar}(H-E)P_x\psi\right)$$

$$=\frac{1}{2m}\left(\frac{im}{\hbar}(H-E)X\psi, P_x\psi\right)=\left(\frac{1}{2m}\right)(P_x\psi,P_x\psi). \quad (10)$$

On the other hand, by directly evaluating the commutator of $P_x$ and $(H-E)$, we obtain

$$\left(\frac{i}{\hbar}\right)[P_x, (H-E)]=\sum_{j=1}^{N}\frac{\partial}{\partial x_j}. \quad (11)$$

We are thus again led to Eq. (6) except that now the one and two particle distribution functions are computed from the wave function. In Eq. (10) we have used our assumption that $U(\mathbf{r})$ is sufficiently well behaved so that no boundary terms appear when $(H-E)$ is replaced by its conjugate. When the walls are treated as rigid, the potential $U(\mathbf{r})$ is replaced by the requirement that $\psi$ vanish at the boundaries. Then, by arguments similar to those by Fierz,[1] we get for a quantum-mechanical system confined to a cube with sides $L$

$$\frac{1}{2m}\langle P_x^2\rangle=\tfrac{1}{2}p\Omega+\left(\frac{\hbar^2}{8m}\right)\times\int x_1\left\{\frac{\partial^2}{\partial x_2^2}\rho(\mathbf{r}_1,\mathbf{r}_2)\right\}\Bigg|_{x_2=0}^{x_2=L}d\mathbf{r}_1dy_2dz_2. \quad (12)$$

When a classical system is confined to a box with rigid walls, Eq. (6) assumes the form

$$\frac{1}{2m}\langle P_x^2\rangle=\tfrac{1}{2}p\Omega+kT\int x_1\{\rho(\mathbf{r}_1,\mathbf{r}_2)\}\Bigg|_{x_2=0}^{x_2=L}d\mathbf{r}_1dy_2dz_2. \quad (13)$$

We thus have the same correspondence between the classical and quantum expression for the virial of the external forces when the walls are rigid that exists for the virial of the internal forces when the particles are rigid spheres.[1]

It is interesting to compare Eq. (6) with the virial theorem of Clausius

$$\frac{N}{2m}\langle p_x^2\rangle=\tfrac{1}{3}\langle\text{K.E.}\rangle=\frac{1}{2}\int x_1\frac{\partial}{\partial x_2}V(r_{12})\rho(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2+\frac{1}{2}\int x_1\frac{\partial}{\partial x_1}U(\mathbf{r}_1)d\mathbf{r}_1. \quad (14)$$

In a classical system (represented by a canonical ensemble) there is no correlation between the momentum of different particles; hence

$$\langle P_x^2\rangle=N\langle p_x^2\rangle=NmkT. \quad (15)$$

[1] M. Fierz, Phys. Rev. **106**, 412 (1957); **107**, 1736 (1957).

This implies, by combining Eqs. (6) and (14), that

$$\int x_1\frac{\partial U(\mathbf{r}_2)}{\partial x_2}\rho(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2=\int x_1\frac{\partial}{\partial x_2}V(r_{12})\rho(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2 \quad (16)$$

for a *classical* system. We have here a relation between a quantity, the right side, which depends on the bulk properties, and another quantity, the left side, which depends on the surface properties of our system.

In general, subtracting Eq. (6) from Eq. (14) yields the following:

$$\left(\frac{1}{2m}\right)[N\langle p_x^2\rangle-\langle P_x^2\rangle]=\frac{1}{2}\int x_1\frac{\partial}{\partial x_2}[V(r_{12})-U(\mathbf{r}_2)]\rho(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_1d\mathbf{r}_2. \quad (17)$$

It is shown elsewhere[2] that for liquid helium II, at very low temperatures, an extreme quantum liquid, $\langle P_x^2\rangle=NmkT$, its classical value. This result probably holds quite generally. Hence, the right side of Eq. (17) represents the deviation of the kinetic energy of a quantum system from its classical value.

## APPENDIX

For a classical system represented by a canonical ensemble, Eq. (6) or (13), can be derived directly from the $N$-particle distribution in $\Gamma$ space $\mu_N(\mathbf{r}^N,\mathbf{p}^N)=(1/Z)e^{-[\beta H]}$. When $U(\mathbf{r})$ is continuous, we have

$$\frac{1}{Z}\sum_{i=1}^{N}\int\frac{\partial}{\partial x_i}(Xe^{-\beta H})d\mathbf{r}^Nd\mathbf{p}^N=0=N-\beta\sum\left\langle x_j\frac{\partial}{\partial x_i}U(\mathbf{r}_i)\right\rangle, \quad (\text{A1})$$

while for rigid boundaries

$$\frac{1}{Z}\sum_{i=1}^{N}\int\frac{\partial}{\partial x_i}(Xe^{-\beta H})d\mathbf{r}^Nd\mathbf{p}^N\times\frac{1}{Z}\sum_{i=1}^{N}\int[Xe^{-\beta H}]dS_{x_i}=N, \quad (\text{A2})$$

where $S_{x_i}$ is a surface in $\Gamma$ space on which $x_i$ is constant. These equations are the same as (6) and (13), respectively. Since the virial theorem is also derivable from the canonical distribution, Eq. (16) also follows from that distribution.

[2] J. L. Lebowitz and L. Onsager, Program of the Fifth International Conference on Low-Temperature Physics and Chemistry, The University of Wisconsin, Madison, Wisconsin, 1957 (to be published), p. 50.