Examples

The next case we shall consider here is that of a one-dimensional *simple harmonic oscillator*. The classical expression for the Hamiltonian of this system is

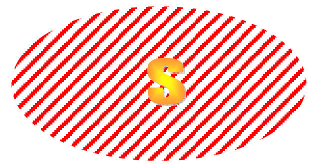
$$H(q,\,p) = \frac{1}{2}kq^2 + \frac{1}{2m}p^2$$

1-D Simple Harmonic Oscillator

$$H = cte. = E$$

$$H(q,\,p) = \frac{1}{2}kq^2 + \frac{1}{2m}p^2$$

$$\frac{q^2}{a^2} + \frac{q^2}{b^2} = 1$$



$$q = A\cos(\omega t + \phi)$$

$$p = m\dot{q} = -m\omega A \sin(\omega t + \phi)$$

$$\omega = \sqrt{(k/m)}$$

$$E = \frac{1}{2}kq^2 + \frac{1}{2m}p^2$$

$$E = \frac{1}{2}kA^2\cos^2(\omega t + \phi) + \frac{1}{2m}m^2\omega^2A^2\sin^2(\omega t + \phi)$$

$$E = \frac{1}{2}kA^2\cos^2(\omega t + \phi) + \frac{1}{2}m\omega^2A^2\sin^2(\omega t + \phi)$$

$$E = \frac{1}{2}kA^2\cos^2(\omega t + \phi) + \frac{1}{2}k^2A^2\sin^2(\omega t + \phi)$$

$$E = \frac{1}{2}kA^2\left(\cos^2(\omega t + \phi) + \sin^2(\omega t + \phi)\right) = \frac{1}{2}kA^2 = cte.$$

$$E = \frac{1}{2}kq^2 + \frac{p^2}{2m}$$

$$1 = \frac{1}{2E}kq^2 + \frac{p^2}{2mE}$$

$$1 = \frac{q^2}{2E/k} + \frac{p^2}{2mE}$$

$$1 = \frac{q^2}{\frac{2E}{m\omega^2}} + \frac{p^2}{2mE}$$

$$1 = \frac{q^2}{\left(\sqrt{\frac{2E}{m\omega^2}}\right)^2} + \frac{p^2}{\left(\sqrt{2mE}\right)^2} \qquad 1 = \frac{q^2}{a^2} + \frac{p^2}{b^2}$$

$$a = \sqrt{\frac{2E}{m\omega^2}}$$

$$b = \sqrt{2mE}$$

$$a \propto \sqrt{E}$$

$$b \propto \sqrt{E}$$

$$S \propto E$$

$$S = \pi ab = \pi\sqrt{\frac{2E}{m\omega^2}}\sqrt{2mE} = \pi\frac{2E}{\omega} \propto E$$

$$\omega = \int_{(E-1/2\Delta)\le H(q,p)\le(E+1/2\Delta)} \!\!\!\ldots\int dq\,dp = \left.\frac{2\pi E}{\omega}\right|_{E-1/2\Delta}^{E+1/2\Delta}$$

N.B. These two are different !

$$\omega = \left.\frac{2\pi E}{\omega}\right|_{E-1/2\Delta}^{E+1/2\Delta} = \frac{2\pi(E+1/2\Delta)}{\omega} - \frac{2\pi(E-1/2\Delta)}{\omega} = \frac{2\pi\Delta}{\omega}$$

$\Gamma(E;\,\Delta) = ?$

$$E_n = (n + 1/2)\hbar\omega;\quad n = 0, 1, 2, \ldots$$

$$n = \frac{E}{\hbar\omega} - 1/2$$

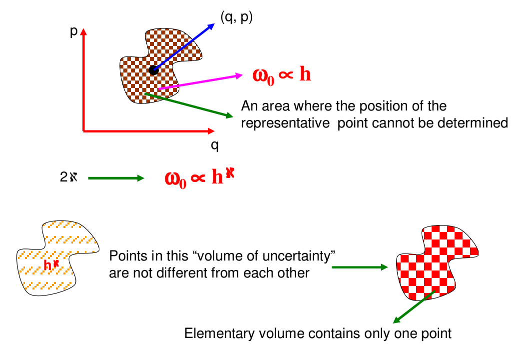
$$n = \Phi(E)$$

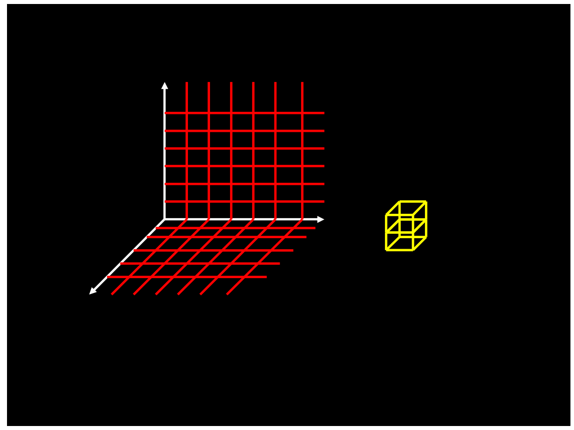
$$\Gamma(E;\Delta) = \frac{d\Phi}{dE}\delta E = \frac{1}{\hbar\omega}\Delta$$

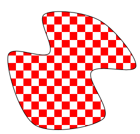
$$\omega_0 = \left.\frac{\omega}{\Gamma}\right)_{asymp.}$$

$$\omega_0 = \frac{\frac{2\pi\Delta}{\omega}}{\frac{\Delta}{\hbar\omega}} = 2\pi\hbar$$

$$\omega_0 = h$$ ☺







A photon gas

$$\int d^3q d^3 p = V\int d^3 p = V4/3\pi p^3 = \Sigma(p)$$

$$\omega = \delta p \frac{d\Sigma(p)}{dp} = V4\pi p^2 dp = V4\pi\left(\frac{h\nu}{c}\right)^2 \frac{h}{c} d\nu = V4\pi\frac{h^3\nu^2}{c^3} d\nu$$

Rayleigh relation in black body radiation yielding number of normal radiation modes:

$$V4\pi\frac{\nu^2}{c^3} d\nu \longrightarrow \Gamma(p;\Delta) \longrightarrow \omega_0 = \left.\frac{\omega}{\Gamma}\right)_{asymp.} = h^3$$

A two-fold multiplicity of these states (g=2) arises from the spin orientations of
The photon. This requires a multiplication of both expressions omega and gamma by
a factor of 2, leaving the omega_0 unchanged.

Two theorems :
The "equipartition" and the "virial"

The equipartition theorem

$$\left\langle x_i \frac{\partial H}{\partial x_j}\right\rangle = \delta_{ij} kT$$

$$\left\langle x_i \frac{\partial H}{\partial x_j}\right\rangle = \frac{\displaystyle\int\limits_{E-\Delta/2 \le H \le E+\Delta/2}\!\!\!\!\!\dots\int x_i \frac{\partial H}{\partial x_j} d\omega}{\displaystyle\int\limits_{E-\Delta/2 \le H \le E+\Delta/2}\!\!\!\!\!\dots\int d\omega}$$

$$= \frac{\Delta.\dfrac{\partial}{\partial E}\displaystyle\int\limits_{0\le H\le E}\!\!\dots\int x_i \frac{\partial H}{\partial x_j} d\omega}{\Delta.\dfrac{\partial}{\partial E}\displaystyle\int\limits_{0\le H\le E}\!\!\dots\int d\omega}$$

$$= \frac{\dfrac{\partial}{\partial E}\displaystyle\int\limits_{0\le H\le E}\!\!\dots\int x_i \frac{\partial H}{\partial x_j} d\omega}{\dfrac{\partial}{\partial E}\displaystyle\int\limits_{0\le H\le E}\!\!\dots\int d\omega}$$

$$\int\limits_{0\le H\le E}\!\!\dots\int x_i \frac{\partial H}{\partial x_j} d\omega = \int\limits_{0\le H\le E}\!\!\dots\int x_i \frac{\partial (H-E)}{\partial x_j} d\omega$$

$$\frac{\partial\big(x_i(H-E)\big)}{\partial x_j} = x_i \frac{\partial (H-E)}{\partial x_j} + (H-E)\frac{\partial x_i}{\partial x_j}$$

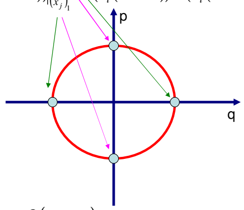
$$x_i \frac{\partial (H-E)}{\partial x_j} = \frac{\partial\big(x_i(H-E)\big)}{\partial x_j} - (H-E)\delta_{ij}$$

$$\int\limits_{0\le H\le E}\!\!\dots\int x_i \frac{\partial (H-E)}{\partial x_j} d\omega = \int\limits_{0\le H\le E}\!\!\dots\int \frac{\partial\big(x_i(H-E)\big)}{\partial x_j} d\omega - \int\limits_{0\le H\le E}\!\!\dots\int (H-E)\delta_{ij} d\omega$$

0

$$= \int \big(x_i(H-E)\big)\Big|_{(x_j)_1}^{(x_j)_2} dx_i - \delta_{ij}\int\limits_{0\le H\le E}\!\!\dots\int (H-E)d\omega$$

$$(x_i(H-E))\Big|_{(x_j)_1}^{(x_j)_2} = (x_i(E-E)) - (x_i(E-E)) = 0$$



$$\int_{0\le H\le E}\!\!\ldots\!\int x_i \frac{\partial(H-E)}{\partial x_j}\, d\omega = -\delta_{ij}\int_{0\le H\le E}\!\!\ldots\!\int (H-E)\,d\omega$$

$$\int_{0\le H\le E}\!\!\ldots\!\int x_i \frac{\partial(H-E)}{\partial x_j}\, d\omega = \delta_{ij}\int_{0\le H\le E}\!\!\ldots\!\int (E-H)\,d\omega$$

$$\left\langle x_i \frac{\partial H}{\partial x_j}\right\rangle = \frac{\dfrac{\partial}{\partial E}\displaystyle\int_{0\le H\le E}\!\!\ldots\!\int x_i \frac{\partial H}{\partial x_j}\, d\omega}{\dfrac{\partial}{\partial E}\displaystyle\int_{0\le H\le E}\!\!\ldots\!\int d\omega}$$

$$= \delta_{ij}\frac{\dfrac{\partial}{\partial E}\displaystyle\int_{0\le H\le E}\!\!\ldots\!\int (E-H)\,d\omega}{\dfrac{\partial}{\partial E}\displaystyle\int_{0\le H\le E}\!\!\ldots\!\int d\omega}$$

$$\frac{\partial}{\partial\alpha}\int_{x=f(\alpha)}^{x=g(\alpha)} F(\alpha,x) = \int_{x=f(\alpha)}^{x=g(\alpha)}\left(\frac{\partial F(\alpha,x)}{\partial\alpha}\right)_{x=cte.} dx + \left\{\frac{\partial g(\alpha)}{\partial\alpha}F[\alpha,g(\alpha)] - \frac{\partial f(\alpha)}{\partial\alpha}F(\alpha,f(\alpha))\right\}$$

$$\frac{\partial}{\partial E}\int_{0\le H\le E}\!\!\ldots\!\int (E-H)\,d\omega = \int_{0\le H\le E}\!\!\ldots\!\int \cancelto{1}{\left(\frac{\partial(E-H)}{\partial E}\right)_{H=cte.}} d\omega + \cancelto{0}{\{\ldots\}} = \int_{0\le H\le E}\!\!\ldots\!\int d\omega$$

$$\{\ldots\} = \left\{\frac{\partial E}{\partial E}\cancelto{0}{[E-E]} - \cancelto{0}{\frac{\partial 0}{\partial E}}[E-0]\right\}$$

$$\frac{\partial}{\partial E}\int_{0\le H\le E}\!\!\ldots\!\int (E-H)\,d\omega = \int_{0\le H\le E}\!\!\ldots\!\int d\omega$$

$$\left\langle x_i \frac{\partial H}{\partial x_j}\right\rangle = \delta_{ij}\frac{\displaystyle\int_{0\le H\le E}\!\!\ldots\!\int d\omega}{\dfrac{\partial}{\partial E}\displaystyle\int_{0\le H\le E}\!\!\ldots\!\int d\omega} = \delta_{ij}\frac{1}{\dfrac{\partial}{\partial E}\ln\left\{\displaystyle\int_{0\le H\le E}\!\!\ldots\!\int d\omega\right\}} = \delta_{ij}\frac{k}{\left(\dfrac{\partial S}{\partial E}\right)_{N,V}} = \delta_{ij}kT$$

$$\left\langle x_i \frac{\partial H}{\partial x_j}\right\rangle = \delta_{ij}kT \quad ☺$$

$$\left\langle \sum_i p_i \frac{\partial H}{\partial p_i}\right\rangle = \left\langle \sum_i p_i \dot{q}_i\right\rangle = 3NkT$$

$$\left\langle \sum_i q_i \frac{\partial H}{\partial q_i}\right\rangle = -\left\langle \sum_i q_i \dot{p}_i\right\rangle = 3NkT$$

$$H = \sum_j A_j P_j^2 + \sum_j B_j Q_j^2$$

$$\sum_j\left(P_j\frac{\partial H}{\partial P_j} + Q_j\frac{\partial H}{\partial Q_j}\right) = \sum_j\left(P_j(2A_jP_j) + Q_j(2B_jQ_j)\right) =$$

$$= 2\sum_j\left(A_jP_j^2 + B_jQ_j^2\right) = 2H$$

$$\langle 2H\rangle = \left\langle \sum_j\left(P_j\frac{\partial H}{\partial P_j} + Q_j\frac{\partial H}{\partial Q_j}\right)\right\rangle$$

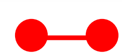
$$\left\langle x_i \frac{\partial H}{\partial x_j}\right\rangle = \delta_{ij}kT$$

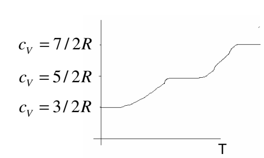
$$\langle 2H\rangle = \left\langle \sum_j\left(P_j\frac{\partial H}{\partial P_j} + Q_j\frac{\partial H}{\partial Q_j}\right)\right\rangle$$

$$\langle 2H\rangle = 3NkT + 3NkT = 6NkT = fkT$$

$$\langle H\rangle = 3NkT = \frac{1}{2}fkT$$

In our subsequent study we shall find that the equipartition theorem as stated here is not always valid; it applies only when the relevant degrees of freedom can be *freely* excited. At a given temperature T, there may be certain degrees of freedom which, due to the insufficiency of the energy available, are more or less "frozen". Such degrees of freedom do not make a significant contribution towards the internal energy of the system or towards its specific heat; see, for example, Secs 6.5, 7.3 and 8.3. Of course, the higher the temperature of the system the better the validity of this theorem.





The virial theorem

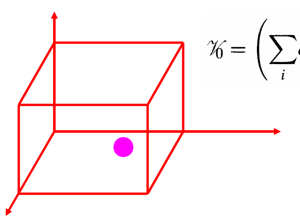
$$\sum_i q_i \dot{p}_i = \mathscr{V} = -3NkT$$

$$\left\langle \sum_i q_i \frac{\partial H}{\partial q_i} \right\rangle \equiv -\left\langle \sum_i q_i \dot{p}_i \right\rangle = 3NkT$$

We now consider the implications of formula (6). First of all, we note that this formula embodies the so-called *virial theorem* of Clausius (1870) for the quantity $\langle \sum_i q_i \dot{p}_i \rangle$, which is the expectation value of the sum of the products of the coordinates of the various particles in the system and the respective forces acting on them; this quantity is referred to as the *virial* of the system and is generally denoted by the symbol $\mathscr{V}$. The virial theorem then states that

$$\mathscr{V} = -3NkT$$

The relationship between the virial and other physical quantities of the system is best understood by first looking at a classical gas of non-interacting particles. In this case, the only forces that come into play are the ones arising from the walls of the container; these forces can be designated by an external pressure P that acts upon the system by virtue of the fact that it is bounded by the walls of the container. Consequently, we have here a force $-P\,d\boldsymbol{S}$ associated with an element of area $d\boldsymbol{S}$ of the walls; the negative sign appears because the force is directed *inward* while the vector $d\boldsymbol{S}$ is directed outward. The virial of the gas is then given by



$$\mathscr{V}_0 = \left(\sum_i q_i F_i \right)_0 = -P \oint_S \boldsymbol{r} \cdot d\boldsymbol{S}$$

$$\mathscr{V}_0 = -P \oint_S \boldsymbol{r} \cdot d\boldsymbol{S}$$

$$\mathscr{V}_0 = -P \int_V (\operatorname{div} \boldsymbol{r})\, dV = -P \int_V 3dV = -3P \int_V dV = -3PV$$

$$\mathscr{V}_0 = -3PV$$

$$\mathscr{V} = -3NkT$$

$$PV = NkT$$

The internal energy of the gas, which in this case is wholly kinetic, follows from the equipartition theorem (9) and is equal to $\frac{3}{2}NkT$, $3N$ being the number of degrees of freedom. Comparing this result with (10), we obtain the classical relationship

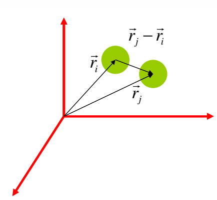
$$\langle H \rangle = \langle K \rangle = K = \frac{1}{2} fkT = \frac{1}{2} 3NkT = \frac{3}{2} NkT$$

$$\mathscr{V}_0 = -3PV = -3NkT$$

$$K = \frac{3}{2} NkT = \frac{3}{2}\left(-\frac{1}{3}\right)\mathscr{V}_0$$

$$\mathscr{V}_0 = -2K$$

It is straightforward to carry out an extension of this study to a system of particles interacting through a two-body potential $u(\boldsymbol{r}_j - \boldsymbol{r}_i)$. The virial $\mathscr{V}$ then draws a contribution from the interior as well. Assuming the interparticle potential to be central and denoting it by the symbol $u(r)$, where $r = |\boldsymbol{r}_j - \boldsymbol{r}_i|$, the contribution arising from the pair of particles i and j, with position vectors $\boldsymbol{r}_i$ and $\mathbf{r}_j$, is given by



$$\mathcal{V}_p = \left\langle \vec{r}_i \cdot \left(-\frac{\partial u(r)}{\partial r_i} \right) + \vec{r}_j \cdot \left(-\frac{\partial u(r)}{\partial r_j} \right) \right\rangle =$$

$$\vec{F}_i = -\vec{\nabla}_{\vec{r}_i} u(r) \qquad \vec{F}_j = -\vec{\nabla}_{\vec{r}_j} u(r)$$

$$= \left\langle \vec{r}_i \cdot \left(-\frac{\partial u(r)}{\partial r^2} \frac{\partial r^2}{\partial r_i} \right) + \vec{r}_j \cdot \left(-\frac{\partial u(r)}{\partial r^2} \frac{\partial r^2}{\partial r_j} \right) \right\rangle =$$

$$= \left\langle \vec{r}_i \cdot \left(-\frac{\partial u(r)}{\partial r^2} \frac{\partial |\vec{r}_j - \vec{r}_i|^2}{\partial r_i} \right) + \vec{r}_j \cdot \left(-\frac{\partial u(r)}{\partial r^2} \frac{\partial |\vec{r}_j - \vec{r}_i|^2}{\partial r_j} \right) \right\rangle =$$

$$= -\left\langle \frac{\partial u(r)}{\partial r^2} \left(\vec{r}_i \cdot \frac{\partial |\vec{r}_j - \vec{r}_i|^2}{\partial r_i} + \vec{r}_j \cdot \frac{\partial |\vec{r}_j - \vec{r}_i|^2}{\partial r_j} \right) \right\rangle$$

$$= \left\langle -\frac{\partial u(r)}{\partial r^2} \left(\vec{r}_i \cdot \vec{\nabla}_{\vec{r}_i} |\vec{r}_j - \vec{r}_i|^2 + \vec{r}_j \cdot \vec{\nabla}_{\vec{r}_j} |\vec{r}_j - \vec{r}_i|^2 \right) \right\rangle$$

$$= \left\langle -\frac{\partial u(r)}{\partial r^2} \left(\vec{r}_i \cdot \vec{\nabla}_{\vec{r}_i} \left((x_j - x_i)^2 + (y_j - y_i)^2 + (z_j - z_i)^2 \right) + \vec{r}_j \cdot \vec{\nabla}_{\vec{r}_j} \left((x_j - x_i)^2 + (y_j - y_i)^2 + (z_j - z_i)^2 \right) \right) \right\rangle$$

$$= \left\langle -\frac{\partial u(r)}{\partial r^2} \left(\vec{r}_i \cdot \left(-2\left[(x_j - x_i)\hat{i} + (y_j - y_i)\hat{j} + (z_j - z_i)\hat{k} \right] \right) + \vec{r}_j \cdot \left(2\left[(x_j - x_i)\hat{i} + (y_j - y_i)\hat{j} + (z_j - z_i)\hat{k} \right] \right) \right) \right\rangle$$

$$= \left\langle -\frac{\partial u(r)}{\partial r^2} \left(\vec{r}_i \cdot \left(-2[\vec{r}_j - \vec{r}_i] \right) + \vec{r}_j \cdot \left(2[\vec{r}_j - \vec{r}_i] \right) \right) \right\rangle =$$

$$= \left\langle -\frac{\partial u(r)}{\partial r^2} \left(2[\vec{r}_j - \vec{r}_i](\vec{r}_j - \vec{r}_i) \right) \right\rangle = \left\langle -\frac{\partial u(r)}{\partial r^2} (2r^2) \right\rangle$$

$$\mathcal{V}_p = \left\langle -\frac{\partial u(r)}{\partial r^2} (2r^2) \right\rangle = \left\langle -\frac{\partial u(r)}{\partial r} \frac{\partial r}{\partial r^2} (2r^2) \right\rangle =$$

$$= \left\langle -\frac{\partial u(r)}{\partial r} \frac{1}{\frac{\partial r^2}{\partial r}} (2r^2) \right\rangle =$$

$$= \left\langle -\frac{\partial u(r)}{\partial r} \frac{1}{2r} (2r^2) \right\rangle =$$

$$= \left\langle -r \frac{\partial u(r)}{\partial r} \right\rangle$$

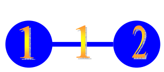
$$\mathcal{V}_p = \left\langle -r \frac{\partial u(r)}{\partial r} \right\rangle$$

$$\mathcal{V} = -3NkT$$

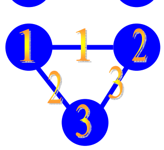
$$\mathcal{V}_0 = -3PV$$

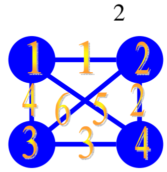
$$\mathcal{V}_p = \left\langle -r \frac{\partial u(r)}{\partial r} \right\rangle$$

$$\mathcal{V}_p = \frac{1}{2} N^2 \left\langle -r \frac{\partial u(r)}{\partial r} \right\rangle$$



Number of pair particles $= \frac{2 \times (2-1)}{2} = 1$





Number of pair particles $= \frac{3 \times (3-1)}{2} = 3$

Number of pair particles $= \frac{4 \times (4-1)}{2} = 6$

Number of pair particles $= \frac{N \times (N-1)}{2} \approx \frac{1}{2} N^2$

$N >> 1$

$$\mathcal{V}_p = \frac{1}{2} N^2 \left\langle -r \frac{\partial u(r)}{\partial r} \right\rangle$$

$$= -\frac{1}{2} N^2 \int_0^\infty r \frac{\partial u(r)}{\partial r} g(r) \frac{4\pi r^2 dr}{V}$$

$$\mathcal{V} = \mathcal{V}_0 + \mathcal{V}_p$$

$$= -3PV - \frac{1}{2} \frac{N}{V} N \int_0^\infty r \frac{\partial u(r)}{\partial r} g(r) 4\pi r^2 dr$$

$$= -3PV - \frac{2\pi n}{1} N \int_0^\infty \frac{\partial u(r)}{\partial r} g(r) r^3 dr$$

$$= -3NkT$$

$$-3NkT = -3PV - \frac{2\pi n}{1} N \int_0^\infty \frac{\partial u(r)}{\partial r} g(r) r^3 dr$$

$$3PV = 3NkT - 2\pi n N \int_0^\infty \frac{\partial u(r)}{\partial r} g(r) r^3 dr$$

$$PV = NkT - \frac{2\pi n N}{3} \int_0^\infty \frac{\partial u(r)}{\partial r} g(r) r^3 dr$$

$$PV = NkT \left\{ 1 - \frac{2\pi n}{3kT} \int_0^\infty \frac{\partial u(r)}{\partial r} g(r) r^3 dr \right\}$$

$$E = \frac{3}{2} NkT + \frac{N^2}{2} \int_0^\infty u(r) g(r) \frac{4\pi r^2 dr}{V}$$

$$= \frac{3}{2} NkT + \frac{4\pi N}{2V} N \int_0^\infty u(r) g(r) r^2 dr$$

$$= \frac{3}{2} NkT + 2\pi n N \int_0^\infty u(r) g(r) r^2 dr$$

$$= \frac{3}{2} NkT \left\{ 1 + \frac{2\pi n N}{\frac{3}{2} NkT} \int_0^\infty u(r) g(r) r^2 dr \right\}$$

$$E = \frac{3}{2} NkT \left\{ 1 + \frac{4\pi n N}{3kT} \int_0^\infty u(r) g(r) r^2 dr \right\}$$