# Pressure in the Average-Atom Model

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**Abstract**

The (well-known) quantum mechanical expression for the stress tensor is derived and applied to obtain a formula for the pressure in the average-atom model. This average-atom pressure formula reduces to the (well-known) expression for the pressure in a classical free-electron gas when the average-atom continuum wave functions are replaced by free-electron wave functions.

## 1 Derivation

We start with the time-dependent Schrödinger equation for an electron in a potential $V(r)$,

$$-\frac{\hbar}{i}\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\nabla^2\psi + V\psi \tag{1}$$

The expectation value of $i$-th component of the electron's momentum inside a region $R$ is

$$\langle p_i\rangle = \int_R d\tau\, \psi^\dagger p_i \psi. \tag{2}$$

The rate of increase of momentum in $R$ is

$$\begin{aligned}\frac{d}{dt}\langle p_i\rangle &= \int_R d\tau \left[\frac{\partial\psi^\dagger}{\partial t} p_i\psi + \psi^\dagger p_i \frac{\partial\psi}{\partial t}\right] \\ &= -\frac{i\hbar}{2m}\int_R d\tau \left[\nabla^2\psi^\dagger p_i\psi - \psi^\dagger p_i \nabla^2\psi\right] \\ &\quad -\frac{i}{\hbar}\int_R d\tau\, \psi^\dagger \left[p_i V - V p_i\right]\psi. \end{aligned}\tag{3}$$

This expression can be rewritten as

$$\frac{d}{dt}\langle p_i\rangle = -\frac{i\hbar}{2m}\int_R d\tau\, \nabla\cdot\left[\nabla\psi^\dagger p_i\psi - \psi^\dagger p_i\nabla\psi\right]$$
$$-\frac{i}{\hbar}\int_R d\tau\, \psi^\dagger\left[p_i, V\right]\psi. \tag{4}$$

With the aid of Gauss' theorem, Eq. (4) reduces to:

$$\begin{aligned}\frac{d}{dt}\langle p_i\rangle &= -\frac{i\hbar}{2m}\int_R dS\,\sum_j n_j\left[\frac{\partial\psi^\dagger}{\partial x_j}p_i\psi - \psi^\dagger p_i\frac{\partial\psi}{\partial x_j}\right] - \frac{i}{\hbar}\int_R d\tau\,\psi^\dagger\left[p_i, V\right]\psi \\ &= -\frac{\hbar^2}{2m}\int_R dS\,\sum_j n_j\left[\frac{\partial\psi^\dagger}{\partial x_j}\frac{\partial\psi}{\partial x_i} - \psi^\dagger\frac{\partial^2\psi}{\partial x_i\partial x_j}\right] - \int_R d\tau\,\psi^\dagger\frac{\partial V}{\partial x_i}\psi \end{aligned} \tag{5}$$

The first integral is the $i$-th component of the surface force on the region and the second gives the $i$-th component of the volume force. We introduce the stress-tensor

$$T_{ji} = \frac{\hbar^2}{2m}\left[\frac{\partial\psi^\dagger}{\partial x_j}\frac{\partial\psi}{\partial x_i} - \psi^\dagger\frac{\partial^2\psi}{\partial x_i\partial x_j}\right] \tag{6}$$

and the volume force

$$F_i = -\left\langle\frac{\partial V}{\partial x_i}\right\rangle.$$

We find that the time rare of change of momentum is

$$\frac{d}{dt}\langle p_i\rangle = -\int_R dS\,\sum_j T_{ij}\,n_j + F_i. \tag{7}$$

From this expression it follows that $-\sum_j T_{ij}n_j$ is the $i$-th component of the force per unit area exerted by the surroundings on the region $R$ through the surface. Therefore $T_{ij}$ is the $i$-th component of the force/area, on a surface with normal in direction $n_j$ exerted by the electrons in the region $R$ on the surroundings. The pressure is related to the trace of the stress tensor by

$$P = \frac{1}{3}\sum_i T_{ii}. \tag{8}$$

In the stationary state, we must have

$$\int_R dS\,\sum_j T_{ij}\,n_j = F_i, \tag{9}$$

which reduces to

$$\sum_j \frac{\partial T_{ij}}{\partial x_j} = -\psi^\dagger \psi \, \frac{\partial V}{\partial x_i} \tag{10}$$

in differential form.

It is not difficult to verify the differential form of the momentum conservation law above directly from the single-particle Schrödinger equation. We start with the equation for $\partial\psi/\partial x_i$

$$-\frac{\hbar^2}{2m}\nabla^2 \frac{\partial \psi}{\partial x_i} = (E - V)\, \frac{\partial \psi}{\partial x_i} - \frac{\partial V}{\partial x_i}\, \psi. \tag{11}$$

We left multiply this by $\psi^\dagger$ to obtain

$$-\frac{\hbar^2}{2m}\psi^\dagger\, \nabla^2 \frac{\partial \psi}{\partial x_i} = (E - V)\, \psi^\dagger \frac{\partial \psi}{\partial x_i} - \psi^\dagger \frac{\partial V}{\partial x_i}\, \psi. \tag{12}$$

We next consider the equation for $\psi^\dagger$ right multiplied by $\partial\psi/\partial x_i$.

$$-\frac{\hbar^2}{2m}\nabla^2\, \psi^\dagger \frac{\partial \psi}{\partial x_i} = (E - V)\, \psi^\dagger \frac{\partial \psi}{\partial x_i}. \tag{13}$$

Subtracting (13) from (12), one obtains

$$\frac{\hbar^2}{2m}\left[\nabla^2\, \psi^\dagger \frac{\partial \psi}{\partial x_i} - \psi^\dagger\, \nabla^2 \frac{\partial \psi}{\partial x_i}\right] = -\psi^\dagger \frac{\partial V}{\partial x_i}\, \psi. \tag{14}$$

This equatiom may be simplifed to

$$\frac{\hbar^2}{2m}\boldsymbol{\nabla}\cdot\left[\boldsymbol{\nabla}\, \psi^\dagger \frac{\partial \psi}{\partial x_i} - \psi^\dagger\, \boldsymbol{\nabla} \frac{\partial \psi}{\partial x_i}\right] = -\psi^\dagger \frac{\partial V}{\partial x_i}\, \psi. \tag{15}$$

Setting

$$T_{ij} = \frac{\hbar^2}{2m}\left[\frac{\partial \psi^\dagger}{\partial x_j}\, \frac{\partial \psi}{\partial x_i} - \psi^\dagger\, \frac{\partial^2 \psi}{\partial x_i \partial x_j}\right],$$

we see that Eq. (15) becomes

$$\sum_j \frac{\partial T_{ij}}{\partial x_j} = -\psi^\dagger \psi \frac{\partial V}{\partial x_i},$$

which is precisely the differential form of the momentum conservation law given earlier in Eq. (10).

## 2 Evaluation of Pressure

We first evaluate the formula for pressure given in Eq. (8) for an electron in state $(nlm)$ with wave function

$$\psi_{nlm}(\boldsymbol{r}) = \frac{1}{r} P_{nl}(r)\, Y_{lm}(\hat{r}) \ .$$

Ultimately, we sum the electron partial pressures over closed subshells. For one electron, we have

$$P = \frac{\hbar^2}{6m} \left[ \boldsymbol{\nabla}\psi^\dagger \ \cdot \boldsymbol{\nabla}\psi - \psi^\dagger \boldsymbol{\nabla}^2 \psi \right] \tag{16}$$

We note that

$$\boldsymbol{\nabla}\psi_{nlm}(\boldsymbol{r}) = \frac{d}{dr}\left(\frac{P_{nl}(r)}{r}\right) \boldsymbol{Y}^{(-1)}_{lm}(\hat{r}) + \frac{P_{nl}(r)}{r} \frac{\sqrt{l(l+1)}}{r} \boldsymbol{Y}^{(1)}_{lm}(\hat{r}). \tag{17}$$

Thus

$$\begin{aligned} \boldsymbol{\nabla}\psi^\dagger_{nlm} \ \cdot \boldsymbol{\nabla}\psi_{nlm} = & \\ & \left[\frac{d}{dr}\left(\frac{P_{nl}(r)}{r}\right)\right]^2 (-1)^m \ \boldsymbol{Y}^{(-1)}_{l-m}(\hat{r}) \cdot \boldsymbol{Y}^{(-1)}_{lm}(\hat{r}) \\ + \frac{\sqrt{l(l+1)}}{r} \ \frac{P_{nl}(r)}{r} \ \frac{d}{dr}\left(\frac{P_{nl}(r)}{r}\right) & (-1)^m \left[ \boldsymbol{Y}^{(-1)}_{l-m}(\hat{r}) \cdot \boldsymbol{Y}^{(1)}_{lm}(\hat{r}) + \boldsymbol{Y}^{(1)}_{l-m}(\hat{r}) \cdot \boldsymbol{Y}^{(-1)}_{lm}(\hat{r}) \right] \\ & + \frac{l(l+1)}{r^2} \ \left(\frac{P_{nl}(r)}{r}\right)^2 \ (-1)^m \ \boldsymbol{Y}^{(1)}_{l-m}(\hat{r}) \cdot \boldsymbol{Y}^{(1)}_{lm}(\hat{r}) \ . \end{aligned} \tag{18}$$

Furthermore, we have

$$\begin{aligned} & \psi^\dagger_{nlm} \boldsymbol{\nabla}^2 \psi_{nlm} = \\ & \frac{P_{nl}(r)}{r} \ \left[ \frac{1}{r^2} \frac{d}{dr} r^2 \frac{d}{dr}\left(\frac{P_{nl}(r)}{r}\right) - \frac{l(l+1)}{r^2} \frac{P_{nl}(r)}{r} \right] (-1)^m \ Y_{l-m}(\hat{r}) Y_{lm}(\hat{r}) \end{aligned} \tag{19}$$

### 2.1 Useful Identities

One may easily establish the following theorem:

$$\sum_m (-1)^m Y_{l-m}(\hat{r}) Y_{lm}(\hat{r}) = \frac{[l]}{4\pi}. \tag{20}$$

We expand the vector harmonics as

$$\boldsymbol{Y}^{(1)}_{JM}(\hat{r}) =\sqrt{\frac{J+1}{[J]}}\ \boldsymbol{Y}_{JJ-1M}(\hat{r}) + \sqrt{\frac{J}{[J]}}\ \boldsymbol{Y}_{JJ+1M}(\hat{r}) \tag{21}$$

$$\boldsymbol{Y}^{(0)}_{JM}(\hat{r}) =\sqrt{\frac{J+1}{[J]}}\ \boldsymbol{Y}_{JJM}(\hat{r}) \tag{22}$$

$$\boldsymbol{Y}^{(-1)}_{JM}(\hat{r}) =\sqrt{\frac{J}{[J]}}\ \boldsymbol{Y}_{JJ-1M}(\hat{r}) - \sqrt{\frac{J+1}{[J]}}\ \boldsymbol{Y}_{JJ+1M}(\hat{r}). \tag{23}$$

We can prove by diagrammatic methods that

$$\sum_M (-1)^M \boldsymbol{Y}_{JK-M}(\hat{r}) \cdot \boldsymbol{Y}_{JLM}(\hat{r}) = (1)^{J+L+1}\frac{[J]}{4\pi}\ \delta_{KL}. \tag{24}$$

With the aid of this result, it follows that

$$\sum_M (-1)^M \boldsymbol{Y}^{(\lambda)}_{J-M}(\hat{r}) \cdot \boldsymbol{Y}^{(\mu)}_{JM}(\hat{r}) = (-1)^{\lambda+1}\ \frac{[J]}{4\pi}\ \delta_{\lambda\mu}. \tag{25}$$

### 2.2 Summary

Combining Eqs. (18) and (19), we find

$$\sum_m \left[\boldsymbol{\nabla}\psi^\dagger_{nlm} \cdot \boldsymbol{\nabla}\psi_{nlm} - \psi^\dagger_{nlm}\boldsymbol{\nabla}^2\psi_{nlm}\right] = \frac{[l]}{4\pi}\left\{\left[\frac{d}{dr}\left(\frac{P_{nl}(r)}{r}\right)\right]^2 - \frac{P_{nl}(r)}{r^2}\ \frac{d^2P_{nl}(r)}{dr^2} + \frac{2l(l+1)}{r^2}\left(\frac{P_{nl}(r)}{r}\right)^2\right\}. \tag{26}$$

The partial pressure from a closed subshell $nl$ point $r$ may, therefore, be written

$$P = \frac{\hbar^2}{6m}\ \frac{2[l]}{4\pi r^2}\ \left\{r^2\ \left[\frac{d}{dr}\left(\frac{P_{nl}(r)}{r}\right)\right]^2 + \frac{l(l+1)}{r^2}P^2_{nl}(r) + \frac{2m}{\hbar^2}\left(E_{nl} - V(r)\right)P^2_{nl}(r)\right\}. \tag{27}$$

If we choose $r$ to be the radius of the average atom $V(R) = 0$ then

$$P = \frac{\hbar^2}{6m}\ \frac{2[l]}{4\pi}\ \left\{\left[\frac{d}{dr}\left(\frac{P_{nl}(r)}{r}\right)\right]^2 + \frac{l(l+1)}{r^2}\left(\frac{P_{nl}(r)}{r}\right)^2 + \frac{2m}{\hbar^2}E_{nl}\left(\frac{P_{nl}(r)}{r}\right)^2\right\}_R. \tag{28}$$

There are two contributions to the pressure at the surface of the average atom sphere:

$$P_{\text{bound}} = \frac{1}{24\pi m} \sum_{nl} \frac{2(2l+1)}{1+e^{(\epsilon_{nl}-\mu)/kT}}$$
$$\left\{ \left[ \frac{d}{dr}\left(\frac{P_{nl}(r)}{r}\right)\right]^2 + \frac{l(l+1)}{r^2}\left(\frac{P_{nl}(r)}{r}\right)^2 + \frac{2m}{\hbar^2}E_{nl}\left(\frac{P_{nl}(r)}{r}\right)^2 \right\}_R \quad (29)$$
$$P_{\text{contin}} = \frac{1}{24\pi m} \int_0^\infty \frac{d\epsilon}{1+e^{(\epsilon-\mu)/kT}} \sum_l 2(2l+1)$$
$$\left\{ \left[ \frac{d}{dr}\left(\frac{P_{nl}(r)}{r}\right)\right]^2 + \frac{l(l+1)}{r^2}\left(\frac{P_{nl}(r)}{r}\right)^2 + p^2\left(\frac{P_{nl}(r)}{r}\right)^2 \right\}_R \quad (30)$$

## 2.3 Free Electron Gas

For a free electron gas,

$$P_{\epsilon l}(r) = \sqrt{\frac{2m}{\pi p}}\, pr\, j_l(pr).$$

The corresponding pressure at the surface of the average atom sphere $R$ is

$$P_{\text{free}} = \frac{\hbar^2}{24\pi m} \int_0^\infty \frac{d\epsilon}{1+e^{(\epsilon-\mu)/kT}} \frac{2m}{\pi p} p^4$$
$$\sum_l 2(2l+1) \left\{ \left(\frac{dj_l(z)}{dz}\right)^2 + \frac{l(l+1)}{z^2} j_l^2(z) + j_l^2(z) \right\}_{z=pR} \quad (31)$$

Now, we state a few useful theorems:

1. First we use Eq. (10.1.50) in [1]

$$\sum_l (2l+1) j_l^2(z) = 1.$$

2. Differentiating with respect to $z$ gives

$$\sum_l (2l+1) j_l(z) \frac{dj_l(z)}{dz} = 0.$$

3. Differentiating once again, one finds

$$\sum_l (2l+1)\left(\frac{dj_l(z)}{dz}\right)^2 = -\sum_l (2l+1) j_l(z) \frac{d^2 j_l(z)}{dz^2}.$$

4. Substituting from the differential equation for spherical Bessel functions,

$$\begin{aligned}
&\sum_l (2l+1)\left(\frac{dj_l(z)}{dz}\right)^2 \\
&\qquad = \sum_l (2l+1)\left[\frac{2}{z} j_l(z)\frac{dj_l(z)}{dz} + \left(1 - \frac{l(l+1)}{z^2}\right) j_l^2(z)\right] \\
&\qquad = \sum_l (2l+1)\left(1 - \frac{l(l+1)}{z^2}\right) j_l^2(z)
\end{aligned}$$

5. From this, it follows that

$$\begin{aligned}
&\sum_l 2(2l+1)\left\{\left(\frac{dj_l(z)}{dz}\right)^2 + \frac{l(l+1)}{z^2} j_l^2(z) + j_l^2(z)\right\} \\
&\qquad\qquad = 4\sum_l (2l+1) j_l^2(z) = 4. \qquad (32)
\end{aligned}$$

With the aid of Eq. (32), we we may rewrite the expression for the pressure as

$$\begin{aligned}
P_{\mathrm{free}} =& \frac{(2m)^{3/2}}{3\pi^2}\int_0^\infty \frac{\epsilon^{3/2} d\epsilon}{1 + e^{(\epsilon-\mu)/kT}} \\
=& \frac{(2mkT)^{5/2}}{6m\pi^2}\int_0^\infty \frac{y^{3/2} dy}{1 + e^{(y-x)}} \\
=& \frac{(2mkT)^{5/2}}{6m\pi^2} I_{3/2}(x) \qquad (33)
\end{aligned}$$

where $x = kT$. This expression agrees with the classical expression for the pressure of a free electron gas given, for example, in Feynman et al. [2]

## References


[1] M. Abramowitz and I. A. Stegun, eds., *Handbook of Mathematical Functions*, Applied Mathematics Series 55 (U. S. Government Printing Office, Washington D. C., 1964).

[2] R. P. Feynman, N. Metropolis, and E. Teller, Phys. Rev. **75**, 1561 (1949).