MOLECULAR DYNAMICS SIMULATION

SIMULATION

Elementary Methods

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APPENDIX B

PRESSURE

To relate the pressure to molecular quantities, we usually rely on the virial theorem from classical dynamics [e.g., see 1], but the derivation of the virial theorem appears to fail for a system with periodic boundaries [2]. The difficulty can be summarized in the following way. For a system of N atoms, the derivation of the virial theorem starts with the quantity

$$I = \tfrac{1}{2} \sum_i^N m \mathbf{r}_i \cdot \mathbf{r}_i \qquad (B.1)$$

which is a measure of the shape of the object formed by the N atoms. Taking two time derivatives gives

$$\frac{d^2 I}{dt^2} = \sum_i^N m \dot{\mathbf{r}}_i^2 + \sum_i^N m \ddot{\mathbf{r}}_i \cdot \mathbf{r}_i \qquad (B.2)$$

Then using Newton's second law on the rhs and forming time averages give

$$\left\langle \frac{d^2 I}{dt^2} \right\rangle = m \left\langle \sum_i^N \dot{\mathbf{r}}_i^2 \right\rangle + \left\langle \sum_i^N \mathbf{F}_i \cdot \mathbf{r}_i \right\rangle \qquad (B.3)$$

Now in the usual development either external fields or container walls preserve the shape of the N-particle object (the shape measured by I), if not at each instant, then at least on a time average. Consequently, the lhs equals zero and the force F_i on the rhs divides into internal and external terms. But

in a system with periodic boundaries there are neither walls nor external forces to preserve I, and the usual derivation of the virial theorem appears problematic.

This appendix gives an alternative derivation in which the pressure is interpreted as a momentum flux. The derivation is given in some detail because the general strategy applies not only to the pressure but also to other macroscopic quantities [3].

B.1   GENERAL FORM

Consider N atoms that, at one instant, occupy a cubic region of space having volume V and side L (in molecular dynamics this is the usual shape of the primary cell). The collection of atoms is at equilibrium with zero total linear momentum. Imagine a planar surface of area $A = L^2$ inserted into the system and oriented perpendicular to the x-axis, as in Figure B.1. The pressure can be defined as the force per unit area acting normal to the surface,

$$P_x = \frac{F_x}{A} \qquad (B.4)$$

Using Newton's second law, this can be written as

$$P_x = \frac{1}{A} \frac{d(m v_x)}{dt} \qquad (B.5)$$

Thus, pressure is a momentum flux; it is the amount of momentum that crosses a unit area of the surface in unit time. In general, this flux is composed of two parts: (a) P_m, the momentum carried by the atoms themselves as they cross the area during dt, and (b) P_f, the momentum transferred as a result of forces acting between atoms that lie on different sides of the surface [4, 5],

$$P_x = P_{mx} + P_{fx} \qquad (B.6)$$

B.2   MOMENTUM FLUX CAUSED BY ATOMIC MOTION

The part of the pressure determined by atomic motion is the part usually derived in kinetic theory. We give an abbreviated derivation here; detailed derivations can be found in any good text on kinetic theory [e.g., 6]. On the

surface of area A = L^2

0   L

→ x

circular cross-
section of area
dS

← v_x dt →
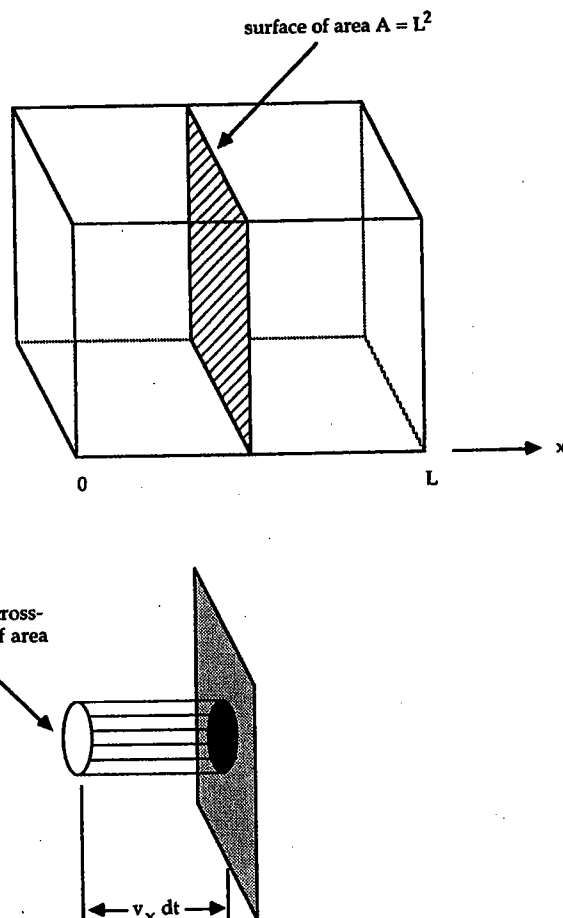
FIGURE B.1 *Top:* Imaginary plane inserted perpendicular to the x-axis across which the momentum flux will be evaluated. *Bottom:* Those atoms having velocities in dv_x about v_x and that cross an element dS on the plane A during interval dt must have been in the cylinder $\{v_x\, dt\, dS\}$ at some point during the time interval.

planar surface of area A, construct a circular element of area dS. Let

$$N(v_x)\, dv_x = \begin{array}{l}\text{number of atoms having velocities} \\ \text{within } dv_x \text{ of } v_x \text{ and that cross} \\ \text{element } dS \text{ in } +x \text{ direction during } dt\end{array} \qquad (B.7)$$

$$= \begin{array}{l}\text{volume of cylinder containing} \\ \text{those atoms that have the} \\ \text{specified velocities and that} \\ \text{approach } dS \text{ during } dt\end{array} \times \begin{array}{l}\text{density of} \\ \text{atoms having} \\ \text{the specified} \\ \text{velocities}\end{array} \qquad (B.8)$$

The volume of the cylinder is $\{v_x\, dt\, dS\}$ (see Figure B.1), while the density of atoms having the specified velocities is proportional to the velocity distribution $f(v_x, t)$. Recall from Section 2.7.1 that the velocity distribution is

$$f(v_x, t)\, dv_x = \begin{array}{l}\text{fraction of } N \text{ atoms that have, at} \\ \text{time } t, \text{ velocities within } dv_x \text{ of } v_x\end{array} \qquad (2.54)$$

So (B.8) becomes

$$N(v_x)\, dv_x = [v_x\, dt\, dS] \times \left[\frac{N}{V} f(v_x, t)\, dv_x\right] \qquad (B.9)$$

Then the total component of momentum normal to dS carried by the atoms that cross dS (in both directions) per unit area in unit time is

$$P_{mx} = \int m v_x v_x \frac{N}{V} f(v_x, t)\, dv_x \qquad (B.10)$$

This integral is, according to (2.56), proportional to the average of v_x^2,

$$P_{mx} = \frac{Nm}{V} \overline{v_x^2} \qquad (B.11)$$

Averaging over time produces

$$\langle P_{mx}\rangle = \frac{Nm}{V} \langle \overline{v_x^2}\rangle = \frac{2N}{V} \langle E_{kx}\rangle \qquad (B.12)$$

where E_k is the kinetic energy per atom. After repeating this procedure in the y- and z-directions, we can form the total convective contribution to the pressure and thereby obtain the ideal-gas law,

$$\langle P_m\rangle = \frac{2N}{3V}\left[\langle E_{kx}\rangle + \langle E_{ky}\rangle + \langle E_{kz}\rangle\right] = \frac{2N}{3V}\langle E_k\rangle \qquad (B.13)$$

B.3 MOMENTUM FLUX CAUSED BY INTERMOLECULAR FORCES

While kinetic theory gives (B.13) as a standard result, kinetic theory is rarely used to obtain an expression for P_f, the contribution resulting from inter-molecular forces. We therefore give the following derivation in some detail. An analogous derivation is given by Hill [7], except that he immediately obtains the virial in terms of the radial distribution function.

At any instant, the second term in (B.7), P_{fx}, is the total force (per unit area) acting normal to the surface A, where the forces are caused by atoms
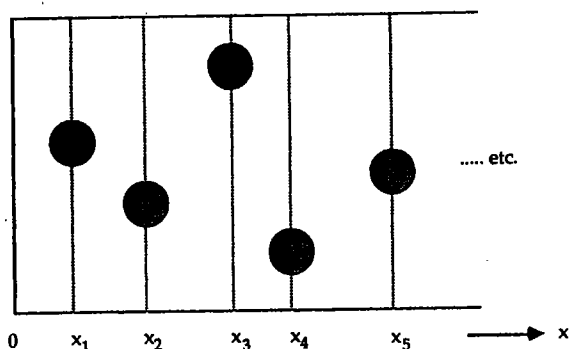
..... etc.

0   x_1 x_2 x_3 x_4 x_5 $\longrightarrow$ x

FIGURE B.2 Labeling of atoms to help evaluation of (B.15), which involves the average over all positions of the imagined surface (dotted lines) inserted perpendicular to the x-axis.

on one side of the surface interacting with atoms on the other side. Assuming the intermolecular forces are pairwise additive, P_{fx} can be written as

$$P_{fx} = \frac{1}{A} \sum_i' \sum_j'' \mathbf{F}_{ij} \cdot \hat{\mathbf{x}} \qquad (B.14)$$

where $\hat{\mathbf{x}}$ is the unit vector in the $+ x$-direction. The primes on the summation signs are to remind us that neither sum is over all N atoms; specifically, index i runs over all atoms on one side of the surface, while index j runs over all atoms on the other side. Averaging over all possible locations of the imaginary surface that is positioned along the x-axis, we obtain

$$\bar{P}_{fx} = \frac{1}{AL} \int_0^L \sum_i' \sum_j'' F_{xij} \, dx \qquad (B.15)$$

Now label the atoms sequentially from 1 to N as their x-position increases from zero to L; that is, as in Figure B.2, label the atoms so that

$$x_1 \leq x_2 \leq x_3 \leq \cdots \leq x_N$$

and divide the edge of length L along the x-axis into $N+1$ intervals of unequal widths Δx_k, where

$$\Delta x_k = x_{k+1} - x_k \equiv x_{k,k+1} \qquad (B.16)$$

We use a sum over these intervals Δx_k to approximate the integral in (B.15),

$$\bar{P}_{fx} = \frac{1}{V} \sum_{k=0}^{N} \sum_i' \sum_j'' F_{xij} \Delta x_k \qquad (B.17)$$

Thus, the distances between adjacent atoms serve as the integration intervals Δx (recall the analysis so far is all at one instant). Note that the first and last intervals Δx_0 and Δx_N do not contribute to the momentum flux because, in both cases, all N atoms lie on one side of the surface A; so

$$\bar{P}_{fx} = \frac{1}{V} \sum_{k=1}^{N-1} \sum_i' \sum_j'' F_{xij} x_{k,k+1} \qquad (B.18)$$

Further, when the surface lies between atoms k and $k+1$, index i runs from 1 to k, while index j runs from $k+1$ to N; thus

$$\bar{P}_{fx} = \frac{1}{V} \sum_{k=1}^{N-1} \sum_{i=1}^{k} \sum_{j=k+1}^{N} F_{xij} x_{k,k+1} \qquad (B.19)$$

Note also that if two atoms happen to have the same x-position, then that interval $\Delta x = 0$; that is, those two atoms cannot fall on different sides of the surface A, and so their interaction does not contribute to a force in the $\pm x$-direction.

Let us examine the first few terms in (B.19):

$$\bar{P}_{fx} = \frac{1}{V} [x_{12}(F_{x12} + F_{x13} + F_{x14} + \cdots)$$

$$+ x_{23}(F_{x13} + F_{x14} + \cdots + F_{x23} + F_{x24} + \cdots)$$

$$+ x_{34}(F_{x14} + \cdots + F_{x24} + \cdots + F_{x34} + \cdots) + \cdots] \qquad (B.20)$$

These can be rearranged to give

$$\bar{P}_{fx} = \frac{1}{V} [F_{x12} x_{12} + F_{x13}(x_{12} + x_{23}) + F_{x14}(x_{12} + x_{23} + x_{34})$$

$$+ \cdots + F_{x23} x_{23} + F_{x24}(x_{23} + x_{34}) + \cdots + F_{x34} x_{34} + \cdots] \qquad (B.21)$$

Or in general,

$$\bar{P}_{fx} = \frac{1}{V} \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} F_{xij} \sum_{k=i}^{j} x_{k,k+1} \qquad (B.22)$$

But

$$\sum_{k=i}^{j} x_{k,k+1} = x_{ij} \qquad (B.23)$$

For example, $x_{12} + x_{23} + x_{34} = x_{14}$. Thus,

$$\bar{P}_{fx} = \frac{1}{V} \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} F_{xij} x_{ij} \qquad (B.24)$$

This is still at one instant; now average over time,

$$\langle P_{fx} \rangle = \frac{1}{V} \left\langle \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} F_{xij} x_{ij} \right\rangle \qquad (B.25)$$

Repeating this procedure for surfaces oriented perpendicular to the y- and z-axes produces analogous expressions for P_{fy} and P_{fz}. Then

$$\langle P_f \rangle = \frac{1}{3V} \left[\left\langle \sum_{i<j} \sum F_{xij} x_{ij} \right\rangle + \left\langle \sum_{i<j} \sum F_{yij} y_{ij} \right\rangle + \left\langle \sum_{i<j} \sum F_{zij} z_{ij} \right\rangle \right] \qquad (B.26)$$

or

$$\langle P_f \rangle = \frac{1}{3V} \left\langle \sum_{i<j} \sum \mathbf{F}_{ij} \cdot \mathbf{r}_{ij} \right\rangle \qquad (B.27)$$

which is the virial. Combining (B.13) and (B.27) gives the complete expression for the pressure,

$$P = \frac{2N}{3V} \langle E_k \rangle + \frac{1}{3V} \left\langle \sum_{i<j} \sum \mathbf{F}_{ij} \cdot \mathbf{r}_{ij} \right\rangle \qquad (B.28)$$

where E_k is the kinetic energy per atom. For systems with periodic boundaries this becomes

$$P = \frac{2N}{3V} \langle E_k \rangle + \frac{1}{3V} \left\langle \sum_{\alpha} \sum_{i<j} \sum (\mathbf{r}_{ij} - \alpha L) \cdot \mathbf{F}_{ij} (\mathbf{r}_{ij} - \alpha L) \right\rangle \qquad (B.29)$$

where α is the cell translation vector defined in Section 2.9.

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