On the Equivalence of Atomic and Molecular Pressure[†]

Reinier L. C. Akkermans*

Unilever R&D Port Sunlight, Quarry Road East, Bebington, CH63 3JW United Kingdom

Giovanni Ciccotti

Department of Physics, University of Rome La Sapienza, Piazzale Aldo Moro 2, 1−00185 Roma, Italy

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We revisit the expressions for pressure in atomic and molecular coordinates. We elaborate on the proof of their equivalence, reported previously by one of us (*Comp. Phys. Rep.* **1986**, *4*, 345−392), by taking into account the boundary conditions appropriate to the system of interest. For systems subject to closed boundaries, we obtain the difference between atomic and molecular pressure, which is shown to vanish in the thermodynamic limit. For systems subject to periodic boundaries, we derive expressions for atomic and molecular pressure and proof their equivalence.

1. Introduction

The use of a barostat in the simulation of particle dynamics, as first put forward by H. C. Andersen[1] in 1980, has called for expressions for pressure in terms of the particle positions and momenta.[2−4] In case particles stand for molecules, composed of several atoms, there is ambiguity[5] on the pressure expression, as the pressure can be expressed in the positions and momenta of either the atoms or the molecular centers-of-mass. In turn, these two methods may be regarded as special cases of a generalized scheme in which the pressure is expressed in the positions and momenta of groups of atoms within a molecule.[6]

The equivalence of the various expressions for pressure was first reported by Ciccotti and Ryckaert[7] in 1984 and later by others.[8,9] In their derivation for the acceleration of an atom times its mass they substitute the total internal force due to interaction with all other particles, thereby neglecting potential external forces acting on the particles. Such is only justified in the thermodynamic limit. Yet the external forces are central to the definition of external pressure in finite systems subject to closed boundaries. It seems therefore more appropriate to first consider a finite system enclosed by boundaries and to subsequently take the thermodynamic limit. This will be the approach taken in section 2. In Appendix A, we derive the external pressure in a system with closed boundaries.

Simulations, on the other hand, are almost exclusively carried out for finite systems subject to periodic boundary conditions. As there are no external forces due to walls in such a system, pressure has to be obtained via the average momentum flux per volume.[10−15] In section 3, we therefore consider systems with periodic boundaries and derive equivalent expressions for pressure in terms of atomic and molecular coordinates. The momentum flux through a system with periodic boundaries is discussed in Appendix B.

Notation will be as follows: we consider N identical molecules consisting of n atoms with position $\mathbf{r}_{i\alpha}$ and mass m_i. Atomic and molecular properties will be denoted by lower and uppercase symbols, respectively. The force on atom i in mol-ecule α due to interaction with all other atoms is $\mathbf{f}_{i\alpha}$, whereas wall forces are denoted by $\mathbf{g}_{i\alpha}$. Mass, position, and forces of molecule α are respectively $M \equiv \sum_i m_i$, $\mathbf{R}_\alpha \equiv \sum_i m_i \mathbf{r}_{i\alpha}/M$, $\mathbf{F}_\alpha \equiv \sum_i \mathbf{f}_{i\alpha}$, and $\mathbf{G}_\alpha \equiv \sum_i \mathbf{g}_{i\alpha}$.

2. Closed Boundaries

If the system is enclosed by walls, each atom i in molecule α experiences a force $\mathbf{g}_{i\alpha} = \int\int_S d\mathbf{g}_{i\alpha}$ from the wall surface S, in addition to the interparticle forces $\mathbf{f}_{i\alpha}$. We define the instantaneous atomic pressure P_a as the normal force on the wall per unit area, due to the interaction of the wall with the atoms. As shown in Appendix A, we can approximate P_a by

$$P_a \approx -\frac{1}{3V}\sum_\alpha\sum_i \mathbf{g}_{i\alpha}\cdot\mathbf{r}_{i\alpha} \tag{1}$$

where V is the volume enclosed by S. In this equation, a surface term is neglected, which vanishes in the thermodynamic limit. Moreover, it is assumed that P_a is uniform over the surface.

Using $m_i\ddot{\mathbf{r}}_{i\alpha} = \mathbf{f}_{i\alpha} + \mathbf{g}_{i\alpha}$, and introducing brackets for time average, we find that

$$\langle m_i\dot{\mathbf{r}}_{i\alpha}{}^2 + \mathbf{r}_{i\alpha}\cdot(\mathbf{f}_{i\alpha} + \mathbf{g}_{i\alpha})\rangle$$

$$= m_i\left\langle\frac{d}{dt}(\dot{\mathbf{r}}_{i\alpha}\cdot\mathbf{r}_{i\alpha})\right\rangle$$

$$= m_i\lim_{t\to\infty}\frac{1}{t}[\dot{\mathbf{r}}_{i\alpha}(t)\cdot\mathbf{r}_{i\alpha}(t) - \dot{\mathbf{r}}_{i\alpha}(0)\cdot\mathbf{r}_{i\alpha}(0)] = 0$$

which vanishes as both $\dot{\mathbf{r}}_{i\alpha}$ and $\mathbf{r}_{i\alpha}$ are bounded (since the total energy is finite, and hence the velocity fluctuations). This is, of course, just Clausius' virial theorem, which combined with eq 1 results in

$$\langle P_a\rangle = \frac{1}{3V}\Big\langle\sum_\alpha\sum_i m_i\dot{\mathbf{r}}_{i\alpha}{}^2\Big\rangle + \frac{1}{3V}\Big\langle\sum_\alpha\sum_i \mathbf{r}_{i\alpha}\cdot\mathbf{f}_{i\alpha}\Big\rangle$$

Similarly, we define the instantaneous molecular pressure P_m as the normal force per unit area due to the interaction of the

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walls with the molecules, which can be approximated by

$$P_{\mathrm{m}} \approx -\frac{1}{3V}\sum_{\alpha}\mathbf{G}_{\alpha}\cdot\mathbf{R}_{\alpha} \tag{2}$$

which, since $\mathbf{R}_{\alpha}$ and $\dot{\mathbf{R}}_{\alpha}$ are bounded, gives

$$\langle P_{\mathrm{m}}\rangle = \frac{1}{3V}\langle\sum_{\alpha}M\dot{\mathbf{R}}_{\alpha}^2\rangle + \frac{1}{3V}\langle\sum_{\alpha}\mathbf{R}_{\alpha}\cdot\mathbf{F}_{\alpha}\rangle \tag{3}$$

Using eqs 1 and 2, the difference between the molecular and atomic pressure is

$$P_{\mathrm{m}} - P_{\mathrm{a}} = -\frac{1}{3V}\sum_{\alpha}\mathbf{G}_{\alpha}\cdot\mathbf{R}_{\alpha} + \frac{1}{3V}\sum_{\alpha}\sum_{i}\mathbf{g}_{i\alpha}\cdot\mathbf{r}_{i\alpha}$$

$$= \frac{1}{6V}\sum_{\alpha}\frac{1}{M}\sum_{i}\sum_{j}(\mathbf{r}_{i\alpha} - \mathbf{r}_{j\alpha})\cdot(m_j\mathbf{g}_{i\alpha} - m_i\mathbf{g}_{j\alpha}) \tag{4}$$

Interestingly, if $\mathbf{g}_{i\alpha} \propto m_i$ (such as gravitational forces), the difference does vanish. In general, however, there is no reason this should vanish on average. It should be noted, at the same time, that eqs 1 and 2 are only valid in the thermodynamic limit. In that limit eq 4 vanishes as S/V.

For pairwise forces, we have $\mathbf{f}_{i\alpha} = \sum_{\beta}\sum_{j}\mathbf{f}_{i\alpha j\beta}$. Using Newton's third law $\mathbf{f}_{i\alpha j\beta} = -\mathbf{f}_{j\beta i\alpha}$, we can rewrite the virial part as a sum over pairs

$$\langle P_{\mathrm{a}}\rangle = \frac{1}{3V}\langle\sum_{\alpha}\sum_{i}m_i\dot{\mathbf{r}}_{i\alpha}^2\rangle + \frac{1}{6V}\langle\sum_{\alpha}\sum_{i}\sum_{\beta}\sum_{j}(\mathbf{r}_{i\alpha} - \mathbf{r}_{j\beta})\cdot\mathbf{f}_{i\alpha j\beta}\rangle \tag{5}$$

and, with $\mathbf{F}_{\alpha\beta} = \sum_i\sum_j\mathbf{f}_{i\alpha j\beta}$

$$\langle P_{\mathrm{m}}\rangle = \frac{1}{3V}\langle\sum_{\alpha}M\dot{\mathbf{R}}_{\alpha}^2\rangle + \frac{1}{6V}\langle\sum_{\alpha}\sum_{\beta}(\mathbf{R}_{\alpha} - \mathbf{R}_{\beta})\cdot\mathbf{F}_{\alpha\beta}\rangle \tag{6}$$

3. Periodic Boundaries

For simplicity, we consider a system of molecules in a cubic box with edge $L = (V)^{1/3}$ subject to periodic boundary conditions; that is, for every atom i in molecule α at position $\mathbf{r}_{i\alpha}$, there are images at positions $\mathbf{r}_{i\alpha} + \mathbf{n}L$ with the same velocity $\dot{\mathbf{r}}_{i\alpha}$, where $\mathbf{n}$ is a vector with three integer elements. In case of pairwise forces, the equation of motion for atom i in molecule α is

$$m_i\ddot{\mathbf{r}}_{i\alpha} = \mathbf{f}_{i\alpha} = \sum_{\beta}\sum_{j}\sum_{\mathbf{n}}\mathbf{f}_{i\alpha j\beta}^{\mathbf{n}}$$

where $\mathbf{f}_{i\alpha j\beta}^{\mathbf{n}}$ is the force exerted on atom i in molecule α by the image of atom j in molecule β at position $\mathbf{r}_{j\beta} + \mathbf{n}L$, with the condition $\mathbf{f}_{i\alpha i\alpha}^{\mathbf{0}} = \mathbf{0}$. Notice that for central forces, the force $\mathbf{f}_{i\alpha j\beta}^{\mathbf{n}}$ is a function of the distance $|\mathbf{r}_{i\alpha} - \mathbf{r}_{j\beta} - \mathbf{n}L|$ only. Using the equations of motion we again obtain the virial theorem

$$\langle\sum_{\alpha}\sum_{i}(m_i\dot{\mathbf{r}}_{i\alpha}^2 + \mathbf{r}_{i\alpha}\cdot\mathbf{f}_{i\alpha})\rangle = \langle\frac{\mathrm{d}}{\mathrm{d}t}\sum_{\alpha}\sum_{i}m_i\dot{\mathbf{r}}_{i\alpha}\cdot\mathbf{r}_{i\alpha}\rangle = 0 \tag{7}$$

which now vanishes since in the above equation the positions are unbounded, and hence increase as $\sqrt{t}$ in time, if governed by diffusion.

We rewrite the sum over individual particles in eq 7 as a double sum over pairs, using that (i) by symmetry $\sum_{\mathbf{n}}\mathbf{f}_{i\alpha j\beta}^{\mathbf{n}} = \sum_{\mathbf{n}}\mathbf{f}_{i\alpha j\beta}^{-\mathbf{n}}$ and (ii) by Newton's third law $\mathbf{f}_{i\alpha j\beta}^{\mathbf{n}} = -\mathbf{f}_{j\beta i\alpha}^{-\mathbf{n}}$

$$\sum_{\alpha}\sum_{i}\mathbf{r}_{i\alpha}\cdot\mathbf{f}_{i\alpha} = \frac{1}{2}\sum_{\alpha}\sum_{i}\sum_{\beta}\sum_{j}\sum_{\mathbf{n}}(\mathbf{r}_{i\alpha} - \mathbf{r}_{j\beta})\cdot\mathbf{f}_{i\alpha j\beta}^{\mathbf{n}}.$$

Substituting this into eq 7 and adding a term $-\frac{1}{2}\langle\sum_{\alpha}\sum_{i}\sum_{\beta}\sum_{j}\sum_{\mathbf{n}}\mathbf{n}L\cdot\mathbf{f}_{i\alpha j\beta}^{\mathbf{n}}\rangle$ on both sides, we obtain

$$\langle\sum_{\alpha}\sum_{i}m_i\dot{\mathbf{r}}_{i\alpha}^2\rangle + \frac{1}{2}\langle\sum_{\alpha}\sum_{i}\sum_{\beta}\sum_{j}\sum_{\mathbf{n}}(\mathbf{r}_{i\alpha} - \mathbf{r}_{j\beta} - \mathbf{n}L)\cdot\mathbf{f}_{i\alpha j\beta}^{\mathbf{n}}\rangle =$$

$$-\frac{1}{2}\langle\sum_{\alpha}\sum_{i}\sum_{\beta}\sum_{j}\sum_{\mathbf{n}}\mathbf{n}L\cdot\mathbf{f}_{i\alpha j\beta}^{\mathbf{n}}\rangle \tag{8}$$

It is not difficult to show that the last term is the momentum flux through the periodic boundaries (see Appendix B). Hence, divided by $3V$, both expressions are suitable definitions for the atomic pressure in a system subject to periodic boundaries

$$\langle P_{\mathrm{a}}\rangle = \frac{1}{3V}\langle\sum_{\alpha}\sum_{i}m_i\dot{\mathbf{r}}_{i\alpha}^2\rangle +$$

$$\frac{1}{6V}\langle\sum_{\alpha}\sum_{i}\sum_{\beta}\sum_{j}\sum_{\mathbf{n}}(\mathbf{r}_{i\alpha} - \mathbf{r}_{j\beta} - \mathbf{n}L)\cdot\mathbf{f}_{i\alpha j\beta}^{\mathbf{n}}\rangle \tag{9}$$

$$= -\frac{1}{6V}\langle\sum_{\alpha}\sum_{i}\sum_{\beta}\sum_{j}\sum_{\mathbf{n}}\mathbf{n}L\cdot\mathbf{f}_{i\alpha j\beta}^{\mathbf{n}}\rangle \tag{10}$$

Notice that the expressions are different from eqs 1 and 5. We may call eqs 9 and 10 the internal and external atomic pressure, in analogy with eqs 5 and 1.

To arrive at an expression for pressure expressed in molecular coordinates, we consult once more the virial theorem

$$\langle\sum_{\alpha}(M\dot{\mathbf{R}}_{\alpha}^2 + \mathbf{R}_{\alpha}\cdot\mathbf{F}_{\alpha})\rangle = 0 \tag{11}$$

To obtain a working expression for the molecular pressure, we define $\mathbf{R}_{i\alpha}$ as the position of the center-of-mass of molecule α, to which atom i belongs. This allows to rewrite the molecular virial as a sum over pairs

$$\langle\sum_{\alpha}\mathbf{R}_{\alpha}\cdot\mathbf{F}_{\alpha}\rangle = \langle\sum_{\alpha}\sum_{i}\mathbf{R}_{i\alpha}\cdot\sum_{\beta}\sum_{j}\sum_{\mathbf{n}}\mathbf{f}_{i\alpha j\beta}^{\mathbf{n}}\rangle$$

$$= \frac{1}{2}\langle\sum_{\alpha}\sum_{i}\sum_{\beta}\sum_{j}(\mathbf{R}_{i\alpha} - \mathbf{R}_{j\beta})\cdot\sum_{\mathbf{n}}\mathbf{f}_{i\alpha j\beta}^{\mathbf{n}}\rangle$$

Substituting this expression into eq 11, dividing the result by $3V$, and subsequently adding eq 10, we find

$$\langle P_{\mathrm{a}}\rangle = \frac{1}{3V}\langle\sum_{\alpha}M\dot{\mathbf{R}}_{\alpha}^2\rangle +$$

$$\frac{1}{6V}\langle\sum_{\alpha}\sum_{\beta}[\sum_{\mathbf{n}}\sum_{i}\sum_{j}(\mathbf{R}_{i\alpha} - \mathbf{R}_{j\beta} - \mathbf{n}L)\cdot\mathbf{f}_{i\alpha j\beta}^{\mathbf{n}}]\rangle \tag{12}$$

We may call this expression the molecular pressure $\langle P_{\mathrm{m}}\rangle$, as only molecular velocities and separations occur in the last expression. The term in square brackets should be compared with $(\mathbf{R}_{\alpha} - \mathbf{R}_{\beta})\cdot\mathbf{F}_{\alpha\beta}$ in eq 6. The difference is that two molecules in a periodic system may interact through different images and that the respective center-of-mass separations have to be used in evaluating the virial.

Notice that eq 12 can also be obtained from eq 9 by combining the virial theorems eqs 7 and 11, from which

$$\left\langle \sum_\alpha \sum_i m_i \dot{\mathbf{r}}_{i\alpha}^2 \right\rangle = \left\langle \sum_\alpha (M\dot{\mathbf{R}}_\alpha^2 + \mathbf{R}_\alpha \cdot \mathbf{F}_\alpha - \sum_i \mathbf{r}_{i\alpha} \cdot \mathbf{f}_{i\alpha}) \right\rangle$$

which, when substituted in eq 9 leads to eq 12.

We end with some remarks on eq 12: (i) For "molecules" consisting of a single atom eq 12 reduces to eq 9 for the internal atomic pressure. (ii) Even if there is just one molecule in the periodic system (i.e., $N = 1$), eq 12 still gives a finite pressure, as a molecule will interact with its own images. (iii) If atoms i and j belong to the same image of molecule α, then $\mathbf{R}_{i\alpha} - \mathbf{R}_{j\beta} - \mathbf{n}L = \mathbf{0}$. Consequently all bonded interactions, as well as nonbonded interactions within the same molecular image, do not contribute to the molecular pressure.

4. Conclusion

We conclude that to obtain expressions for the pressure, the boundary conditions appropriate to the system of interest have to be taken into account. For systems subject to closed boundaries we obtained eqs 1 and 5 for the external and internal pressure, which are well defined in the thermodynamic limit. This can be done using both atomic and molecular coordinates. In the thermodynamic limit, we have shown that the difference between the atomic and molecular variant vanishes. For a system enclosed by periodic boundaries, we can define pressure via the momentum flux through the periodic boundaries. This leads to eqs 9 and 10 for the internal and external pressure expressed in atomic positions and velocities. By straightforward manipulation, we derived an equivalent expression eq 12 in terms of molecular velocities and positions.

The only ingredients to derive the pressure expressions are the virial theorems in atomic and molecular coordinates. These theorems, of course, do not refer to the time scale on which the properties vanish. These time scales may be different in the atomic and molecular case. Also, it does not tell anything about the fluctuations in the quantity. It is possible, for example, that the external atomic pressure is subject to much larger fluctuations than the internal expression.

Appendix A. External Pressure in a System with Closed Boundaries

In this appendix, we shall derive eqs 1 and 2 for the atomic and molecular pressure in systems subject to closed boundaries.[16] We introduce the atomic pressure tensor $\mathbf{P}_a(\mathbf{r}, t)$ such that $\mathbf{P}_a(\mathbf{r}, t) \cdot \mathbf{e}(\mathbf{r})$ is the force per unit area exerted by the atoms at time t on a surface element located at $\mathbf{r}$, where $\mathbf{e}$ is the unit vector normal to, and outward to, the surface at $\mathbf{r}$. The force on an infinitesimal area dS around $\mathbf{r}$ is thus $dS\mathbf{P}_a \cdot \mathbf{e}$. Let $d\mathbf{g}_{i\alpha}(\mathbf{r}, t)$ be the force on atom i in molecule α at time t due to the surface element dS at $\mathbf{r}$. One has

$$dS\mathbf{P}_a \cdot \mathbf{e} = -\sum_i \sum_\alpha d\mathbf{g}_{i\alpha}$$

and

$$\mathbf{g}_{i\alpha} = \int\int_S d\mathbf{g}_{i\alpha}$$

where the integral runs over the surface S. Hence

$$\sum_i \sum_\alpha \mathbf{r}_{i\alpha} \cdot \mathbf{g}_{i\alpha} = \int\int_S \sum_i \sum_\alpha \mathbf{r}_{i\alpha} \cdot d\mathbf{g}_{i\alpha}$$

Considering that $\mathbf{r}_{i\alpha} \cdot d\mathbf{g}_{i\alpha}$ is only nonzero if $\mathbf{r}_{i\alpha} \approx \mathbf{r}$, i.e., for atoms close to the boundary, the above integral can be approximated by

$$\int\int_S \mathbf{r} \cdot \sum_i \sum_\alpha d\mathbf{g}_{i\alpha} = -\int\int_S dS\, \mathbf{r} \cdot \mathbf{P}_a \cdot \mathbf{e}$$

which by the divergence theorem leads to

$$-\int\int\int_V dV\, \nabla \cdot (\mathbf{r} \cdot \mathbf{P}_a) = -\int\int\int_V dV\, Tr(\mathbf{P}_a) -$$
$$\int\int\int_V dV\, \mathbf{r} \cdot \nabla \cdot \mathbf{P}_a^T$$

where the integral runs over the volume V. Finally, if $\mathbf{P}_a$ is independent of $\mathbf{r}$, we obtain eq 1, after identifying P_a with $\frac{1}{3}Tr(\mathbf{P}_a)$. An entirely similar reasoning leads to eq 2 for the molecular pressure P_m.

As shown above, the approximation eq 1 is valid if

$$\int\int_S \sum_i \sum_\alpha (\mathbf{r}_{i\alpha} - \mathbf{r}) \cdot d\mathbf{g}_{i\alpha}$$

can be neglected with respect to $\sum_i \sum_\alpha \mathbf{r}_{i\alpha} \cdot \mathbf{g}_{i\alpha}$. To estimate this contribution, we assume that for each surface element, dS, only the particles in a volume element dSl directly adjacent to it will experience a force, where l is the typical range of the wall potential. The position of those particles is such that $\mathbf{r}_{i\alpha} - \mathbf{r} \approx -\frac{1}{2}l\mathbf{e}$, whereas the force will be $d\mathbf{g}_{i\alpha} \approx -f(l/2)\mathbf{e}$, with $f(z)$ the force at a distance z from the surface. Hence we find

$$\int\int_S \sum_i \sum_\alpha (\mathbf{r}_{i\alpha} - \mathbf{r}) \cdot d\mathbf{g}_{i\alpha} \approx \int\int_S dS\, l\rho \frac{1}{2}lf(l/2) =$$
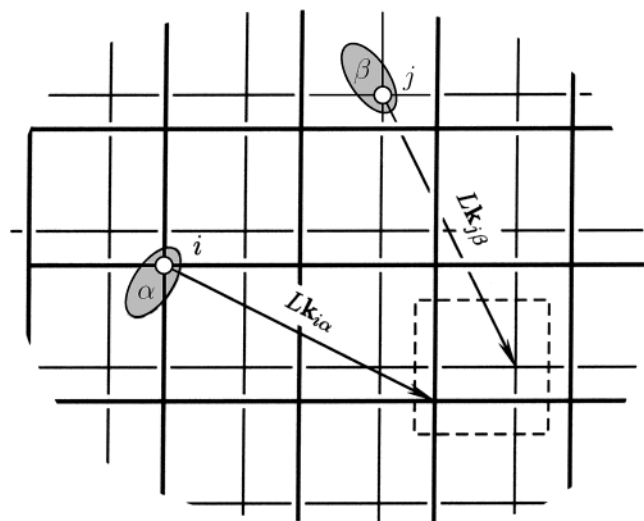$$\frac{1}{2}\rho l^2 f(l/2)S$$

where ρ is the density, so that $dSl\rho$ is the number of terms that contribute to $\sum_i \sum_\alpha (\mathbf{r}_{i\alpha} - \mathbf{r}) \cdot d\mathbf{g}_{i\alpha}$. Potential correlations have been neglected. Since the term $\sum_i \sum_\alpha \mathbf{r}_{i\alpha} \cdot \mathbf{g}_{i\alpha}$ is proportional to the volume V, the approximation is valid in the thermodynamic limit, for which $S/V \to 0$.

Appendix B. Momentum Flux through a Periodic System

In this appendix, we will show that eq 8 represents the momentum flux through a periodic system. To this end, let us define for each atom i of molecule α a vector $L\mathbf{k}_{i\alpha}(t)$ that translates the position $\mathbf{r}_{i\alpha}(t)$ of the atom at time t to a fixed reference box. This is illustrated in Figure 1. We introduce a vector $\mathbf{m}(\mathbf{r}_{i\alpha}, \mathbf{r}_{j\beta}, \mathbf{n})$ such that

$$\mathbf{m} = \mathbf{k}_{i\alpha} - \mathbf{k}_{j\beta} - \mathbf{n}$$

The force $\mathbf{f}_{i\alpha j\beta}^n$ is evaluated at the distance $|(\mathbf{r}_{i\alpha} - L\mathbf{k}_{i\alpha}) - (\mathbf{r}_{j\beta} - L\mathbf{k}_{j\beta}) + L\mathbf{m}|$. Clearly, the entries of $\mathbf{m}$ represent the

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Figure 1. Illustration of the notation used in Appendix B, showing two molecules α and β, with atoms i and j respectively, at time t. The vectors $Lk_{i\alpha}$ and $Lk_{j\beta}$ translate the position of the atoms to a fixed volume enclosed by the dashed line.

number of times that this particular interaction crosses the respective boundaries, where opposite boundaries carry a different sign. Substituting the above into eq 8

$$-\Big\langle \frac{1}{2}\sum_{\alpha}\sum_{i}\sum_{\beta}\sum_{j}\sum_{\mathbf{n}}\mathbf{n}L\cdot\mathbf{f}^{\mathbf{n}}_{i\alpha j\beta} \Big\rangle =$$
$$-\frac{L}{2}\Big\langle \sum_{\alpha}\sum_{i}\sum_{\beta}\sum_{j}(\mathbf{k}_{i\alpha}-\mathbf{k}_{j\beta})\cdot\sum_{\mathbf{n}}\mathbf{f}^{\mathbf{n}}_{i\alpha j\beta} \Big\rangle +$$
$$\frac{L}{2}\Big\langle \sum_{\alpha}\sum_{i}\sum_{\beta}\sum_{j}\sum_{\mathbf{n}}\mathbf{m}\cdot\mathbf{f}^{\mathbf{n}}_{i\alpha j\beta} \Big\rangle \quad (13)$$

Since $\mathbf{m}$ stands for the number of boundary crossings of the

interaction $\mathbf{f}^{\mathbf{n}}_{i\alpha j\beta}$, we can immediately identify the last term with the momentum flux through the boundaries due to interactions intercepted by those boundaries.

The first term in eq 13 can be written as a single sum

$$-\frac{L}{2}\Big\langle \sum_{\alpha}\sum_{i}\sum_{\beta}\sum_{j}(\mathbf{k}_{i\alpha}-\mathbf{k}_{j\beta})\cdot\sum_{\mathbf{n}}\mathbf{f}^{\mathbf{n}}_{i\alpha j\beta} \Big\rangle = -L\Big\langle \sum_{\alpha}\sum_{i}\mathbf{k}_{i\alpha}\cdot\mathbf{f}_{i\alpha} \Big\rangle$$
$$= L\Big\langle \sum_{\alpha}\sum_{i}\dot{\mathbf{k}}_{i\alpha}\cdot m_i\dot{\mathbf{r}}_{i\alpha} \Big\rangle$$

where we have used $\mathbf{f}_{i\alpha}=m_i\ddot{\mathbf{r}}_{i\alpha}$ and the time symmetry property of the correlation function. Since $\dot{\mathbf{k}}_{i\alpha}$ is a delta-function counting the passes of atom i in molecule α through the boundaries, this is the kinetic contribution to the momentum flux.

Hence, we conclude that eq 8 is the total momentum flux through the boundaries due to both the motion of particles and the interactions. The pressure is finally obtained as the momentum flux per unit volume.

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