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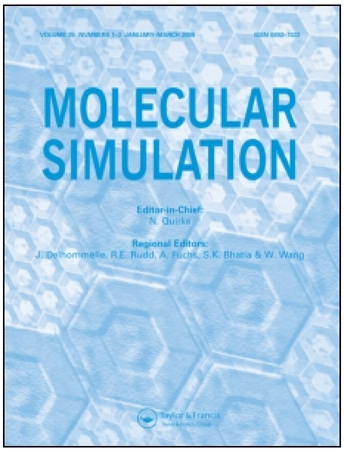

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Calculation of local and average pressure tensors in molecular simulations

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Calculation of local and average pressure tensors in molecular simulations

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A conceptually simple method to calculate local and average pressure tensors in simulations of molecular systems with discrete particles is presented. The pressure originates from the linear momentum of the particles as well as from n-body interactions between the particles, and consists of one additive contribution for every term in the expression of the total energy. The basis for the calculation is the analysis of the velocities of the particles and of the n-body interactions between the particles at the molecular scale to obtain local pressures, and averaging of the local pressure over areas and volumes to obtain average pressures (H. Heinz, W. Paul, K. Binder, *Phys. Rev. E.*, **72**, 066704 (2005)). The explicit consideration of many-body interactions (e.g. angles, torsions, cross-terms) provides simple derivations of existing methods (method of planes, virial expression) and a straightforward extension to periodic systems. In periodic systems original particles are translated into the box in the moment of pressure calculation and the pool of n-body interactions considered is the same as in the energy expression (particle–particle and particle–image interactions). Local and average pressure tensors are augmented by interactions including particles and images, and translational symmetry to judge dissection by specified areas A_α, compared to a non-periodic system. The method of planes and the virial expression, including the additional interactions in atom-based forces, are applicable without further changes in a periodic system.

Keywords: Pressure tensor; Nano-mechanics; Periodic boundary condition; Many-body interactions

1. Introduction

The calculation of pressure in molecular simulation serves to characterize the state of a system, as well as to analyze responses to strain, shear, heat or changes during phase transformations [1–8]. In particular, the calculation of elastic constants and interfacial tensions relies on the accurate computation of pressure tensors [2–8]. More recently, the three-dimensional analysis of pressure at the molecular level provides insight into nano-mechanical behavior, including fracture in composite materials and transport processes in biological systems [9–17].

The calculation of average pressures in an ensemble of particles with n-body interactions on the basis of the virial formula leads back to Rudolf Clausius and the origin of statistical mechanics [1–8,18]. The calculation of local pressure tensors was formulated in 1950 for systems with two-body interactions by Irving and Kirkwood [19] and recently extended to include n-body interactions ($n = 2, 3, 4, \ldots$) [20]. The explicit consideration of n-body interactions in the calculation of local pressures provides simple derivations for the method of planes [21] and for the virial formula to calculate average pressures over the entire system of particles, and allows the identification of additive contributions to the pressure (kinetic, bond stretching, angle bending, Coulomb, van-der-Waals, etc.) corresponding to the additive contributions to the total energy of the system. Our discussion will be focused on systems in mechanical equilibrium (no net force and no net velocity on its center of mass), however, local streaming velocities may be superimposed to simulate flow.

Less attention has been paid to the fact that pressure tensors are closely related to the free energy A according to $p = (\partial A/\partial V)_T$ [20] and to interfacial tensions according to $\gamma = (p_\perp - p_\parallel)\alpha_0$ [1] when two components form an interface of area A_α perpendicular to the α axis in a volume $V = A_\alpha \alpha_0$. These equivalences indicate the contribution of entropy terms S in addition to energy terms U to local and average pressures ($\Delta A = \Delta U - T\Delta S$). Therefore, averaging over a large number of degrees of freedom is part of the calculation of pressure tensors and a significant

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computational cost as well as large fluctuations can be involved [7]. The advantage is that changes in free energy and even in entropy (when the more easily accessible energy U is known) of a system or of a sub-system of particles can be obtained. The relations to thermodynamic state functions will not be pursued further, however, they are part of the motivation to describe a consistent method to calculate local and average pressure tensors.

The focus will be on the outline of a simple method and a solution for the treatment of periodic boundary conditions. Periodic systems are routinely in use [3–8,11,13,22–29], however, there are few discussions on the calculation of local and average pressure tensors under periodic boundary conditions [3,4,7,23] and they typically deal with modifications of the virial expression for the average pressure tensor over the entire, non-periodic box. This approach hinges on the original derivation of the virial expression, which involves the assumption of reflective box boundaries and disregards the influence of individual n-body interactions between the particles (a derivation in the presence of 2-body interactions was carried out by Haile [5]). Therefore, conclusions on local pressure tensors and periodic systems on that basis have been cumbersome. It will be shown that the formulation of the pressure tensor as a function of the n-body interactions between the particles eliminates these difficulties and allows a clear extension from non-periodic to periodic systems by adding particle–image interactions as in the energy expression and taking into account translational symmetry.

Short range contributions and long range (tail) contributions to interactions between particles will not be distinguished, since the underlying physics is the same and a separation can be performed anytime during the implementation of computational algorithms (e.g. Ewald summation). There are no restrictions on the range of interactions in the present treatment.

The structure of the paper is as follows. In Section 2, the calculation of local and average pressure tensors in systems of discrete particles in mechanical equilibrium in a non-periodic system is reviewed [20]. In Section 3, the partition of local and average pressure tensors into additive contributions is outlined. In Section 4, the calculation under periodic boundary conditions is examined . The applicability of various intermolecular potentials with the presented method is discussed in Section 5, followed by a summary in Section 6.

2. The calculation of local and average pressure tensors in systems bounded by walls

Perhaps the most widely used expression to calculate pressure tensors in computer simulations has been the virial formula for the average pressure over the entire box [1,3–8,18]:

$$\bar{p}_{\beta\alpha}(V) = \frac{1}{V}\left(\sum_{i=1}^{N} m_i v_{i\beta} v_{i\alpha} + \sum_{i=1}^{N} F_{i\beta}\alpha_i\right). \qquad (1)$$

Equation (1) signifies that the element $\bar{p}_{\beta\alpha}$ of the average pressure tensor over the entire volume V of a system bounded by walls with no force on its center of mass, $\sum_{i=1}^{N}\vec{F}_i = 0$, and no velocity on its center of mass, $\sum_{i=1}^{N} m_i\vec{v}_i = 0$, is given by the masses m_i and velocities $v_{i\alpha}$, $v_{i\beta}$ of the particles i, the total force $F_{i\beta}$ on each of the N particles due to the sum of interactions with all other particles, and the coordinate α_i of each of the N particles. Accordingly, the scalar pressure is

$$p(V) = \frac{1}{3} tr\{\overleftrightarrow{\bar{P}}(V)\} = \frac{1}{3V}\left(\sum_{i=1}^{N} m_i v_i^2 + \sum_{i=1}^{N} \vec{F}_i\cdot\vec{r}_i\right).$$

The original derivation equation (1) begins with Newton's equations of motion, leading to

$$0 = \left\langle \sum_{i=1}^{N} m_i v_{i\beta} v_{i\alpha} \right\rangle + \left\langle \sum_{i=1}^{N} F_{i\beta}\alpha_i \right\rangle$$

[1,6,18,24], and then reflective box boundaries are taken into account by adding the external virial

$$\left\langle \sum_{i=1}^{N} F_{i\beta}^{\text{ext}}\alpha_i \right\rangle = -\bar{p}_{\beta\alpha}(V)^* V$$

which introduces the pressure [6,18,24]. Equation (1) can also be derived from the definition of the pressure as a force across a unit area and taking into account all n-body interactions between the particles, followed by averaging over the box volume [5,20]. In the latter picture (outlined in Section 2.3), time averaging is not required and the influence of periodic boundary conditions can be analyzed because no reflective boundaries are involved in the derivation (outlined in Section 4).

The calculation of local pressures in simulations of particulate systems was introduced by Irving and Kirkwood [19] with the derivation of the equations of hydrodynamics and an expression for the stress tensor at a certain point in space (opposite equal to the pressure tensor) [11–13,20,21]. A limitation, however, is the assumption of pairwise interactions between the particles. The Irving–Kirkwood pressure tensor can be interpreted according to the mechanical definition of the pressure as a force across a unit area (figure 1):

$$p_{\beta\alpha}(x,y,z) = \frac{1}{2A_\alpha\Delta\alpha}\left\langle \sum_{i\in(\Delta V = 2A_\alpha\Delta\alpha)} m_i v_{i\beta} v_{i\alpha} \right\rangle + \frac{1}{A_\alpha}\left\langle \sum_{\vec{r}_{ij}\cap A_\alpha} F_{ij\beta} \right\rangle. \qquad (2)$$

Equation (2) signifies that the local pressure $p_{\beta\alpha}(x,y,z)$ at a certain coordinate (x,y,z) is given by the masses m_i and velocities v_i of the particles i in a small cube of volume $\Delta V = 2A_\alpha\Delta\alpha$ (figure 1) and by the two-body forces $\vec{F}_{ij}$

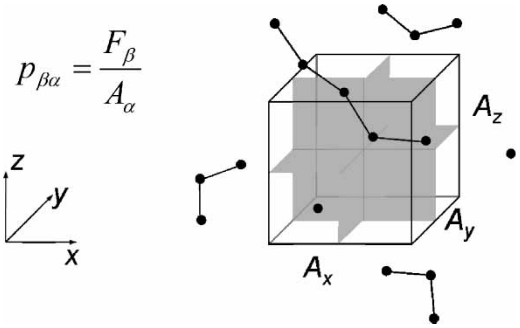

Figure 1. Model of a small cube $\Delta V = (2\Delta\alpha)^3$ to illustrate the definition of local pressure tensors. The three shaded faces $A_\alpha = (2\Delta\alpha)^2$ share a point of intersection in the geometric center of the cube. Some particles and molecules are also shown [20].

between particles whose connecting vector $\vec{r}_{ij}$ dissects the small area A_α (sign convention: $\vec{F}_{ij}$ is the force on the particle with higher α coordinate) in the limit $\Delta V \rightarrow 0$ as an average over time [30].

Considering different possibilities to define pressure [1,3,5–7,13,19,20,22], the mechanical definition of the local pressure tensor as a force across a unit area is preferred (figure 1). The elements of the pressure tensor are defined as $p_{\beta\alpha} = F_\beta/A_\alpha$ within a small volume element $\Delta V = (2\Delta\alpha)^3$ with three small areas $A_\alpha = (2\Delta\alpha)^2$ perpendicular to the coordinate axes, which possess a point of intersection (x, y, z) in the center of the cube (figure 1). This definition of a point pressure $p_{\beta\alpha}(x, y, z)$ is somewhat approximate in a computer simulation with discrete particles because averaging over a finite volume and a number of simulation steps is usually required. However, the definition is exact in the limit $\Delta V \rightarrow 0$ (Section 2.1) and extensible to calculate average pressure tensors over finite areas (Section 2.2) and finite volumes (Section 2.3). Equivalence with the thermodynamic definition of the pressure tensor has been shown [20].

2.1 The local pressure tensor

The force across the small area A_α, as illustrated in figure 1, consists of a contribution from the throughput of linear momentum, derived from the kinetic theory of gases, and an internal contribution due to dissected n-body interactions. The kinetic contribution has been derived elsewhere [5,22,24] and is the same as in equation (2). The force across A_α due to dissected n-body interactions can be obtained by splitting the energy E_n of an n-body interaction into atom-based forces $\vec{F}_i$:

$$\vec{F}_i = -\nabla_{\vec{r}_i} E_n. \qquad (3)$$

These forces, for example, on four atoms for an out-of-plane interaction, are internal so that the sum over the n atom-based forces is zero:

$$\vec{F}_1 + \vec{F}_2 + \cdots + \vec{F}_n = 0. \qquad (4)$$

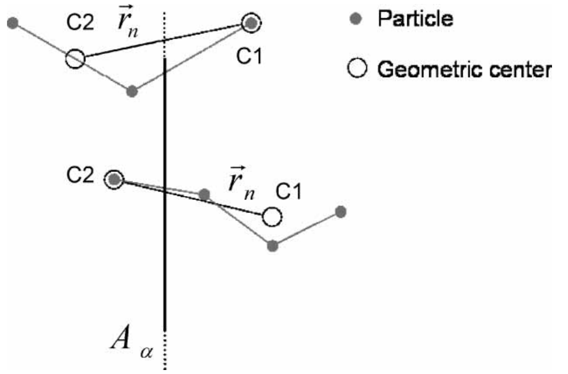

Figure 2. Example of a non-dissected 3-body interaction and a dissected 4-body interaction with respect to A_α. Note there are additional 3-body interactions and two-body interactions in this illustration that are not highlighted.

Accordingly, the forces due to an n-body interaction only make a contribution to the pressure if they are dissected by the area A_α (figure 2).

A criterion of dissection of n-body interactions with respect to the area A_α is vital to the uniqueness of the pressure tensor, and a decision on the basis of geometry appears to be appropriate [31]. The procedure consists of three steps:

1. If all particles pertaining to an n-body interaction are on either side of the plane defined by A_α, the n-body interaction is not dissected.
2. For an n-body interaction with k particles above the plane defined by A_α and $n - k$ particles below the plane defined by A_α, two centers of geometry (C1, C2) are defined for the particles on either side [31]:

$$\vec{c}_1 = \frac{1}{k}\sum_{i=1}^{k}\vec{x}_i, \quad \vec{c}_2 = \frac{1}{n-k}\sum_{i=k+1}^{n}\vec{x}_i. \qquad (5)$$

3. A connecting vector $\vec{r}_n = \vec{c}_1 - \vec{c}_2$ between the two centers is defined. If $\vec{r}_n$ passes through the area A_α, the n-body interaction is dissected and makes a contribution to the local pressure (figure 2). We designate this condition in the following by $\vec{r}_n \cap A_\alpha$.

Effectively, this scheme reduces n-body interactions to two-body interactions and is represented in the following notation:

$$p^{\text{int}}_{\beta\alpha}(x, y, z) = \frac{1}{2A_\alpha}\left\langle \sum_{\vec{r}_n \cap A_\alpha}\sum_{i=1}^{n} F_{i\beta}\,\text{sgn}(\alpha_i - \alpha)\right\rangle. \qquad (6)$$

Equation (6) states that the internal contribution to the local pressure across A_α is given by a summation over the n-body interactions that are dissected by A_α, and for each dissected interaction, the forces $F_{i\beta}$ on the n atoms due to the n-body potential are employed to calculate the

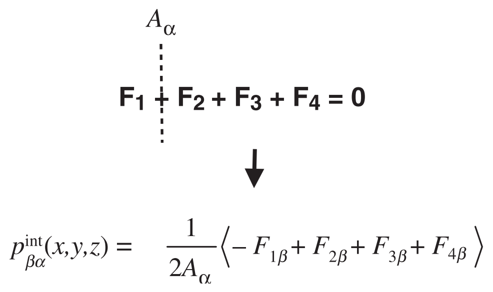

Figure 3. An example for the pressure contribution of a 4-body interaction, dissected between atom 1 and atom 2 (corresponds to the highlighted torsion in figure 2).

contribution to the pressure. The factor $\frac{1}{2}$ takes into account the effect of the sign function, which counts the forces on the area A_α twice (the forces above and below A_α are opposite equal as shown in figure 3).

On addition of the kinetic contribution (equation (2)) to the internal contribution (equation (6)), we obtain the complete expression for the local pressure:

$$p_{\beta\alpha}(x,y,z) = \frac{1}{2A_\alpha\Delta\alpha}\left\langle \sum_{i\in(\Delta V = 2A_\alpha\Delta\alpha)} m_i v_{i\beta} v_{i\alpha}\right\rangle + \frac{1}{2A_\alpha}\left\langle \sum_{\vec{r}_n\cap A_\alpha}\sum_{i=1}^{n} F_{i\beta}\,\mathrm{sgn}(\alpha_i - \alpha)\right\rangle. \tag{7}$$

Equation (7) describes the local pressure $p_{\beta\alpha}(x,y,z)$ at a certain coordinate (x,y,z) by the masses m_i and velocities v_i of the particles i in a small cube of volume $\Delta V = 2A_\alpha\Delta\alpha$ and by the atom-centered forces $\vec{F}_i$ due to n-body interactions in the limit $\Delta V \rightarrow 0$. Only n-body interactions extending across A_α are counted, i.e. whose connecting vector $\vec{r}_n$ between the two geometric centers is dissected by A_α.

Equation (7) simplifies to equation (2) if exclusively two-body interactions between the particles are present. Effectively, the method reduces n-body interactions to two-body interactions represented by the geometric centers, and employs the concept of Irving and Kirkwood [19] to calculate local pressures.

2.2 The average pressure tensor over an area

The local pressure tensor in equation (7) can be averaged over an extended area perpendicular to the coordinate axis α. The infinitesimal area A_α in the volume element ΔV (figure 1) is expanded to the desired size A_α by integration along the other two coordinates, and $\Delta\alpha$ remains infinitely small to sample the velocities of particles in the interval $[\alpha - \Delta\alpha; \alpha + \Delta\alpha]$ for the kinetic contribution. The expression for the average pressure $\bar{p}_{\beta\alpha}(A_\alpha, \alpha)$ is otherwise the same as for the local pressure $p_{\beta\alpha}(x,y,z)$:

$$\bar{p}_{\beta\alpha}(A_\alpha, \alpha) = \frac{1}{2A_\alpha\Delta\alpha}\left\langle \sum_{i\in(\Delta V = 2A_\alpha\Delta\alpha)} m_i v_{i\beta} v_{i\alpha}\right\rangle + \frac{1}{2A_\alpha}\left\langle \sum_{\vec{r}_n\cap A_\alpha}\sum_{i=1}^{n} F_{i\beta}\,\mathrm{sgn}(\alpha_i - \alpha)\right\rangle. \tag{8}$$

Equation (8) represents the average pressure over an extended area A_α perpendicular to the coordinate axis α at a certain coordinate α (three tensor elements), given by the masses m_i and velocities $\vec{v}_i$ of the particles and the atom-centered forces $\vec{F}_i$ due to n-body interactions dissected by A_α in the limit $\Delta\alpha \rightarrow 0$.

When the area equals the cross-section of the box, A_α divides the box in two separate parts and the dissection of n-body interactions extending across the plane A_α automatically occurs at A_α (n-body interactions not extending across the plane A_α make zero contributions according to equation (4)). The analysis of dissection for individual n-body interactions is then not required, and the internal contribution to the average pressure simplifies to a summation over the net force $\vec{F}_i$ on every atom due to all n-body interactions with other particles [20]:

$$\bar{p}_{\beta\alpha}(\alpha) = \frac{1}{2A_\alpha\Delta\alpha}\left\langle \sum_{i\in(\Delta V = 2A_\alpha\Delta\alpha)} m_i v_{i\beta} v_{i\alpha}\right\rangle + \frac{1}{2A_\alpha}\left\langle \sum_{i=1}^{N} F_{i\beta}\,\mathrm{sgn}(\alpha_i - \alpha)\right\rangle. \tag{9}$$

Equation (9) represents the average pressure over the cross-sectional area A_α of the box perpendicular to the coordinate axis α at a certain coordinate α, given by the masses m_i and velocities $\vec{v}_i$ of the particles and their net forces $\vec{F}_i$ due to all n-body interactions with other particles in the limit $\Delta\alpha \rightarrow 0$. Equation (9) is identical with the method of planes result [21] derived on the basis of hydrodynamics.

2.3 The average pressure tensor over a volume

As a further step, pressure tensors can be averaged over a specified volume V. The volume is divided by cross-sectional areas A_α along the coordinate axes ($V = \int_{\alpha_1}^{\alpha_2} A_\alpha(\alpha)\,\mathrm{d}\alpha$) such that at least one cross-section is inserted between every particle along the respective axis α (figure 4). The average pressure tensor (nine elements) in the volume V is obtained as an integral over the average cross-sectional pressure along the three Cartesian axes:

$$\bar{p}_{\beta\alpha}(V) = \frac{1}{\alpha_2 - \alpha_1}\int_{\alpha_1}^{\alpha_2} \bar{p}_{\beta\alpha}(A_\alpha, \alpha)\,\mathrm{d}\alpha. \tag{10}$$

Insertion of equation (8) for the cross-sectional pressures $\bar{p}_{\beta\alpha}(A_\alpha, \alpha)$ yields:

$$\bar{p}_{\beta\alpha}(V) = \frac{1}{V}\left\langle \sum_{i\in V} m_i v_{i\beta} v_{i\alpha}\right\rangle + \frac{1}{\alpha_2 - \alpha_1}\int_{\alpha_1}^{\alpha_2} \frac{1}{2A_\alpha}\left\langle \sum_{\vec{r}_n\cap A_\alpha}\sum_{i=1}^{n} F_{i\beta}\,\mathrm{sgn}(\alpha_i - \alpha)\right\rangle \mathrm{d}\alpha. \tag{11}$$

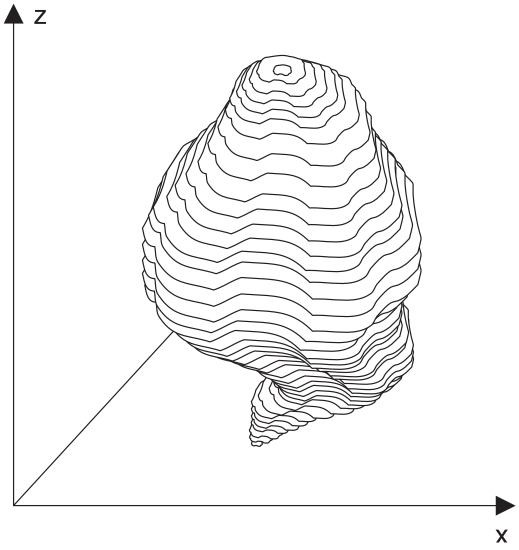

Figure 4. An arbitrary volume V inside a simulation box with schematic cross-sectional areas along the z direction to compute the elements $\bar{p}_{xz}(V)$, $\bar{p}_{yz}(V)$ and $\bar{p}_{zz}(V)$ of the average pressure tensor in this volume. The remaining 6 elements are obtained by insertion of cross-sections through the volume V along the x and y axes and following equation (11).

Equation (11) is the average pressure $\bar{p}_{\beta\alpha}(V)$ over a specified volume V, given by the masses m_i and velocities v_i of the particles i in the volume V and the integral over the average internal pressure across the cross-sections A_α of the volume V along the coordinate axis α, defined by the atom-centered forces $\vec{F}_i$ of n-body interactions whose two geometric centers extend across the respective area A_α ($\vec{r}_n \cap A_\alpha$). At least one cross-section must be inserted between every particle along the axis α, and additional cross-sections are required as further interactions (e.g. between particles inside V and outside V) begin or end being dissected with respect to A_α during integration along the coordinate α.

When the volume corresponds to the entire rectangular box, the cross-sectional pressure can be expressed by equation (9), simplifying the integrand to

$$\frac{1}{2A_\alpha}\left\langle \sum_{i=1}^{N} F_{i\beta}\,\mathrm{sgn}(\alpha_i-\alpha)\right\rangle$$

and $\alpha_2-\alpha_1=\alpha_0$. The result according to equation (11) is:

$$\begin{aligned}\bar{p}_{\beta\alpha}(V) &= \frac{1}{V}\left\langle \sum_{i\in V} m_i v_{i\beta} v_{i\alpha}\right\rangle \\ &\quad + \frac{1}{\alpha_0}\int_0^{\alpha_0}\frac{1}{2A_\alpha}\left\langle \sum_{i=1}^{N} F_{i\beta}\,\mathrm{sgn}(\alpha_i-\alpha)\right\rangle \mathrm{d}\alpha.\end{aligned} \tag{12}$$

It is now imagined the N particles are numbered in the sequence of increasing α coordinate to perform a summation (integral) over N cross-sectional areas inserted between the particles just before every particle is reached. No planes in excess of N planes are needed because the cross-sections A_α act as infinite planes at the coordinate α and dissect the relevant interactions in the entire interval $\Delta\alpha$ between two particles. The duplicate summation associated with the sign function (figure 3) is rewritten as a single summation:

$$\bar{p}_{\beta\alpha}(V) = \frac{1}{V}\left\langle \sum_{i\in V} m_i v_{i\beta} v_{i\alpha}\right\rangle + \frac{1}{\alpha_0}\int_0^{\alpha_0}\frac{1}{A_\alpha}\left\langle \sum_{i=j}^{N} F_{i\beta}\right\rangle \mathrm{d}\alpha_j. \tag{13}$$

The integral now runs over N planes (j designates the number of the plane) and the summation of forces $\vec{F}_i$ runs over all particles above the plane j. The volume of the box $V=A_\alpha\alpha_0$ is introduced

$$\bar{p}_{\beta\alpha}(V) = \frac{1}{V}\left\langle \sum_{i\in V} m_i v_{i\beta} v_{i\alpha}\right\rangle + \frac{1}{V}\int_0^{\alpha_0}\left\langle \sum_{i=j}^{N} F_{i\beta}\right\rangle \mathrm{d}\alpha_j, \tag{14}$$

and the integral can be written out as single sum:

$$\left(\begin{array}{lllll} F_{1\beta}\Delta\alpha_1 & +F_{2\beta}\Delta\alpha_1 & +F_{3\beta}\Delta\alpha_1 & +\cdots & +F_{N\beta}\Delta\alpha_1 \\ & +F_{2\beta}\Delta\alpha_2 & +F_{3\beta}\Delta\alpha_2 & +\cdots & +F_{N\beta}\Delta\alpha_2 \\ & & +F_{3\beta}\Delta\alpha_3 & +\cdots & +F_{N\beta}\Delta\alpha_3 \\ & & & & \vdots \\ & & & & +F_{N\beta}\Delta\alpha_N \end{array}\right).$$

Note that this is not a matrix, instead every line contains the contribution from one plane j to the average pressure and the summation runs over all lines. The notation makes it easy to realize that the α coordinates of the particles can be extracted: $\alpha_1=\Delta\alpha_1$, $\alpha_2=\Delta\alpha_1+\Delta\alpha_2$, $\alpha_3=\Delta\alpha_1+\Delta\alpha_2+\Delta\alpha_3$, etc. Thus, the insertion of N planes between all N particles from $\alpha=0$ to $\alpha=\alpha_0$ just before every particle is reached allows rewriting the summation (integral) over N planes as a summation over N particles [20]:

$$\bar{p}_{\beta\alpha}(V) = \frac{1}{V}\left\langle \sum_{i\in V} m_i v_{i\beta} v_{i\alpha}\right\rangle + \frac{1}{V}\left\langle \sum_{i=1}^{N} F_{i\beta}\alpha_i\right\rangle. \tag{15}$$

Equation (15) is identical with the virial expression equation (1). Thus, the virial expression has been derived on the basis of the mechanical definition of the pressure tensor as a force across a unit area (figure 1), with no assumption of reflective box boundaries or time averaging (included here only for common simulation practice). This is an important result to determine the influence of periodic boundary conditions in Section 4. The identity of equation (15) with equation (11) for averaging over the total volume of the box is also supported by numerical examples [20].

3. Partition of the pressure tensor into additive contributions

According to the mechanical definition on the basis of momentum throughput and dissected n-body interactions, the pressure tensor consists of additive contributions due to every term in the expression of the total energy of the system [20]. In an atomistic simulation for example, these are the contributions due to the velocities of the particles, bond stretching, angle bending, torsions, out-of-plane interactions, cross terms/other contributions, Coulomb interactions and van-der-Waals interactions:

$$\begin{aligned} p_{\beta\alpha} = {} & p_{\beta\alpha}^{\text{kin}} + p_{\beta\alpha}^{2-\text{body bond}} + p_{\beta\alpha}^{3-\text{body angle}} + p_{\beta\alpha}^{4-\text{body torsion}} \\ & + p_{\beta\alpha}^{4-\text{body OOP}} + \cdots + p_{\beta\alpha}^{2-\text{body Coul}} + p_{\beta\alpha}^{2-\text{body vdW}} \end{aligned} \tag{16}$$

The sum of these contributions yields the total pressure $p_{\beta\alpha}$. In the following, equation (16) will be consistently applied to the cases in Section 2. Readers wishing to skip this discussion may proceed directly to Section 4.

3.1 Contributions to the local pressure tensor

Let us first consider the contributions to the local pressure tensor given by equation (7). The first term is due to the kinetic energy, i.e. momentum transfer through the respective infinitesimal area A_α:

$$p_{\beta\alpha}^{\text{kinetic}}(x,y,z) = \frac{1}{2A_\alpha \Delta\alpha} \left\langle \sum_{i \in (\Delta V = 2A_\alpha \Delta\alpha)} m_i v_{i\beta} v_{i\alpha} \right\rangle \tag{17}$$

The second term in equation (7) is due to the potential energy (force field), i.e. n-body interactions between the particles. Separation of the various n-body interactions across the area A_α yields the individual contributions, e.g. 2-body bond stretch, 2-body Coulomb, 2-body van-der-Waals, 3-body angle, 4-body torsion, 4-body out-of-plane, etc.:

$$\begin{aligned} & p_{\beta\alpha}^{2-\text{body bond}}(x,y,z) \\ & \qquad = \frac{1}{2A_\alpha} \left\langle \sum_{\substack{\text{dissected bonds} \\ \vec{r}_n \cap A_\alpha}} \sum_{i=1}^{2} F_{i\beta} \operatorname{sgn}(\alpha_i - \alpha) \right\rangle \\ & p_{\beta\alpha}^{3-\text{body angle}}(x,y,z) \\ & \qquad = \frac{1}{2A_\alpha} \left\langle \sum_{\substack{\text{dissected angles} \\ \vec{r}_n \cap A_\alpha}} \sum_{i=1}^{3} F_{i\beta} \operatorname{sgn}(\alpha_i - \alpha) \right\rangle \\ & p_{\beta\alpha}^{4-\text{body torsion}}(x,y,z) \\ & \qquad = \frac{1}{2A_\alpha} \left\langle \sum_{\substack{\text{dissected torsions} \\ \vec{r}_n \cap A_\alpha}} \sum_{i=1}^{4} F_{i\beta} \operatorname{sgn}(\alpha_i - \alpha) \right\rangle \\ & \qquad \cdots \end{aligned} \tag{18}$$

For example, $p_{\beta\alpha}^{2-\text{body bond}}(x,y,z)$ is the contribution to the local pressure $p_{\beta\alpha}(x,y,z)$ caused only by bond stretching interactions across A_α, $p_{\beta\alpha}^{2-\text{body angle}}(x,y,z)$ is the contribution to the local pressure $p_{\beta\alpha}(x,y,z)$ caused only by angle bending interactions across A_α, etc. The partition continues for every type of n-body potential between the particles and facilitates the analysis of the relative weight in relation to the total local pressure $p_{\beta\alpha}(x,y,z)$ described by equation (7).

3.2 Contributions to the average pressure tensor over an area

The average pressure over an area of finite size is obtained by expansion of the infinitesimal area A_α and equation (8). Only 3 elements of the pressure tensor are relevant, and the contributions $\bar{p}_{\beta\alpha}^{\text{kinetic}}(A_\alpha, \alpha)$, $\bar{p}_{\beta\alpha}^{2-\text{body bond}}(A_\alpha, \alpha)$, etc. read the same as in equations (17) and (18).

In the simplifying case that the area A_α equals the cross-section of the box, equation (9) can be employed for the average pressure tensor over the area. The kinetic contribution $\bar{p}_{\beta\alpha}^{\text{kinetic}}(\alpha)$ equals equation (17) and the internal contributions to the pressure are contained in net forces $F_{i\beta}$ on every atom i:

$$\begin{aligned} \vec{F}_i = {} & \vec{F}_i^{\text{bond}} + \vec{F}_i^{\text{angle}} + \vec{F}_i^{\text{torsion}} + \vec{F}_i^{\text{out-of-plane}} + \cdots \\ & + \vec{F}_i^{\text{Coulomb}} + \vec{F}_i^{\text{van-der-Waals}}. \end{aligned} \tag{19}$$

Therefore, the atom-based force $\vec{F}_i$ is composed of contributions due to the 2-body bond stretching potential $\vec{F}^{\text{bond}}$, 3-body angle bending potential $\vec{F}^{\text{angle}}$, and so forth, of atom i with other atoms. The corresponding contributions to the average cross-sectional pressure tensor are:

$$\begin{aligned} \bar{p}_{\beta\alpha}^{2-\text{body bond}}(\alpha) &= \frac{1}{2A_\alpha} \left\langle \sum_{i=1}^{N} F_{i\beta}^{\text{bond}} \operatorname{sgn}(\alpha_i - \alpha) \right\rangle \\ \bar{p}_{\beta\alpha}^{3-\text{body angle}}(\alpha) &= \frac{1}{2A_\alpha} \left\langle \sum_{i=1}^{N} F_{i\beta}^{\text{angle}} \operatorname{sgn}(\alpha_i - \alpha) \right\rangle \\ \bar{p}_{\beta\alpha}^{4-\text{body torsion}}(\alpha) &= \frac{1}{2A_\alpha} \left\langle \sum_{i=1}^{N} F_{i\beta}^{\text{torsion}} \operatorname{sgn}(\alpha_i - \alpha) \right\rangle \\ & \cdots \end{aligned} \tag{20}$$

3.3 Contributions to the average pressure tensor over a volume

The average pressure over a volume is given by equation (11). The first term corresponds to the kinetic contribution:

$$\bar{p}_{\beta\alpha}^{\text{kinetic}}(V) = \frac{1}{V} \left\langle \sum_{i \in V} m_i v_{i\beta} v_{i\alpha} \right\rangle. \tag{21}$$

The second term in equation (11) contains the internal contributions, and the partition is obtained by separation of the different types of n-body interactions in the integrand:

$$
\begin{aligned}
\bar{p}^{\,2-\text{body bond}}_{\beta\alpha}(V) &= \frac{1}{\alpha_2-\alpha_1}\int_{\alpha_1}^{\alpha_2}\frac{1}{2A_\alpha}\left\langle \sum_{\substack{\text{dissected bonds}\\ \vec{r}_n\cap A_\alpha}}\sum_{i=1}^{2}F_{i\beta}\,\mathrm{sgn}(\alpha_i-\alpha)\right\rangle \mathrm{d}\alpha\\
\bar{p}^{\,3-\text{body angle}}_{\beta\alpha}(V) &= \frac{1}{\alpha_2-\alpha_1}\int_{\alpha_1}^{\alpha_2}\frac{1}{2A_\alpha}\left\langle \sum_{\substack{\text{dissected angles}\\ \vec{r}_n\cap A_\alpha}}\sum_{i=1}^{3}F_{i\beta}\,\mathrm{sgn}(\alpha_i-\alpha)\right\rangle \mathrm{d}\alpha\\
\bar{p}^{\,4-\text{body torsion}}_{\beta\alpha}(V) &= \frac{1}{\alpha_2-\alpha_1}\int_{\alpha_1}^{\alpha_2}\frac{1}{2A_\alpha}\left\langle \sum_{\substack{\text{dissected torsions}\\ \vec{r}_n\cap A_\alpha}}\sum_{i=1}^{4}F_{i\beta}\,\mathrm{sgn}(\alpha_i-\alpha)\right\rangle \mathrm{d}\alpha\\
&\dots
\end{aligned}
\tag{22}
$$

For example, $\bar{p}^{\,2-\text{body bond}}_{\beta\alpha}(V)$ contains only contributions from bond stretching interactions across A_α, $\bar{p}^{\,3-\text{body angle}}_{\beta\alpha}(V)$ contains only contributions from angle bending interactions across A_α, and so forth. The sum of all contributions yields $\bar{p}_{\beta\alpha}(V)$ in equation (11). For the numerical evaluation of the integrals, cross-sections of the volume must be inserted along the axis α at least between every particle involved in the respective type of interaction, and additional cross-sections are required as further interactions (e.g. between particles inside V and outside V) begin or end being dissected with respect to A_α during integration along the coordinate α.

When the volume equals the entire volume of the box, the virial formula equation (1) can be applied. The first term is the kinetic contribution:

$$\bar{p}^{\,\text{kinetic}}_{\beta\alpha}(V) = \frac{1}{V}\sum_{i=1}^{N} m_i v_{i\beta} v_{i\alpha}, \tag{23}$$

and the second term the internal contribution

$$\bar{p}^{\,\text{int}}_{\beta\alpha}(V) = \frac{1}{V}\sum_{i=1}^{N} F_{i\beta}\alpha_i$$

As stated in equation (19), the net atom-based forces $\vec{F}_i$ are the sum of the individual contributions. Therefore, the partition continues as follows:

$$
\begin{aligned}
\bar{p}^{\,2-\text{body bond}}_{\beta\alpha}(V) &= \frac{1}{V}\sum_{i=1}^{N} F^{\text{bond}}_{i\beta}\alpha_i\\
\bar{p}^{\,3-\text{body angle}}_{\beta\alpha}(V) &= \frac{1}{V}\sum_{i=1}^{N} F^{\text{angle}}_{i\beta}\alpha_i\\
\bar{p}^{\,4-\text{body torsion}}_{\beta\alpha}(V) &= \frac{1}{V}\sum_{i=1}^{N} F^{\text{torsion}}_{i\beta}\alpha_i\\
&\dots
\end{aligned}
\tag{24}
$$

The equivalence of equation (24) with equation (22) for averaging over the total volume of the box has been shown in Section 2.3 and numerical examples have been given [20]. The partition of the pressure tensor in additive contributions demonstrates the relation to the inner energy.

4. The calculation of local and average pressure tensors in periodic systems

The discussion so far has been limited to systems bounded by walls whereas simulations are most often carried out in periodic systems [3–8,11,13,22–29]. As mentioned in the introduction, the influence of periodic boundary conditions on the calculation of pressure tensors has been an ongoing discussion [3,4,7,23] and the results in Sections 2 and 3 facilitate a consistent treatment of periodic boundary conditions.

The introduction of periodic boundaries results in three significant changes: interactions between the particles are altered by adding particle–image interactions, particles

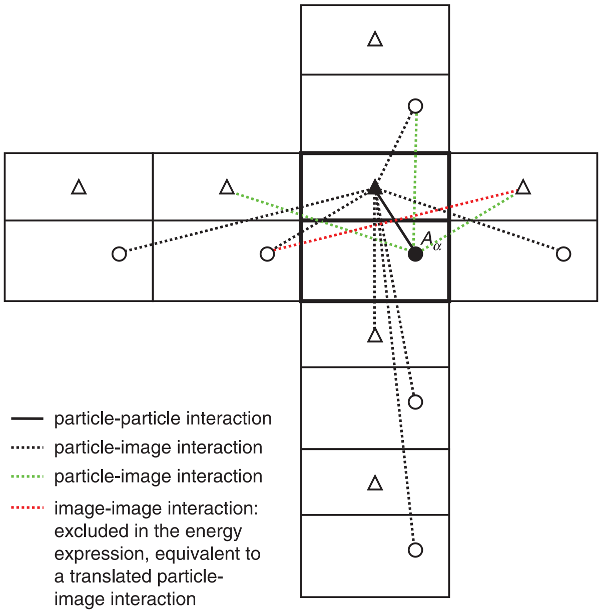

Figure 5. Scheme of a box (thick boundary) with two particles, a cross-section A_α, and periodic images. Possible interactions are illustrated. For simplicity, the box is two-dimensional and only two-body interactions are shown.

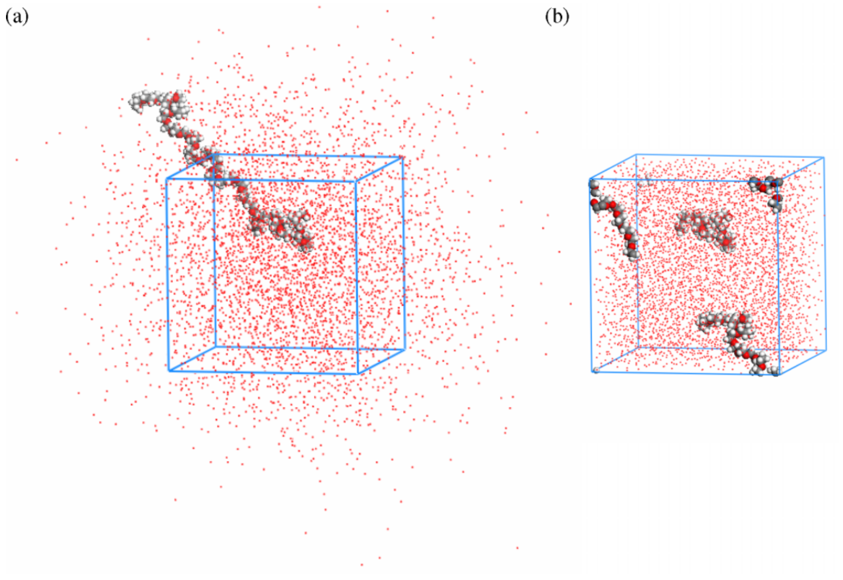

Figure 6. Snapshot of a chain molecule (PEO) in a solvent (water) (a) with original positions of the particles and (b) after translation of the particles into the box using combinations of box vectors. Energy and pressure are identical in (a) and (b).

are allowed to diffuse out of the box, and both particles and interactions can be translated by any combination of box vectors without changing the energy or the pressure. These relations are illustrated in figures 5 and 6. Given no further principal differences between periodic and non-periodic systems, the following criteria are sufficient to calculate pressure tensors in periodic systems:

(1) in the moment of pressure calculation, all particles must be placed back into the box (the location of which can be freely chosen),
(2) the pool of evaluated interactions must be the same as in the energy expression (particle–particle and particle–image interactions), and
(3) the dissection of n-body interactions is equally possible by the original area A_α or images of the area A_α in image boxes, and every n-body interaction contributes no more than once if dissected multiple times.

The first criterion serves mainly to collect the original particles and is not strictly required for the method of planes (average pressure over a cross-section of the box). The second criterion includes that the same cutoffs should be used in the energy calculation and in the pressure calculation, e.g. to avoid errors in computed surface tensions or free energies. In the following sections, local and average pressure tensors are discussed again to exemplify the above criteria.

4.1 Local pressure tensors

The calculation of the local pressure tensor is based on a small volume element $\Delta V = 2A_\alpha \Delta\alpha$ inside the box (figure 1 and equation (7)) in the limit $\Delta V \to 0$. When particles move out of the box in a periodic system, some of them may belong to ΔV after translation (figure 6) and it is essential to translate all particles back into the box. Subsequently, the kinetic contribution to the pressure tensor can be calculated (first term in equation (7)). The calculation of the internal contributions to the pressure tensor must include all particle–particle and particle–image interactions dissected by the area A_α in ΔV. In addition to interactions dissected by the original area A_α (figure 5), some long-range particle–image interactions across several boxes may be dissected by images of A_α in image boxes (some of the dotted black lines in figure 5). These interactions contribute equally to the internal pressure due to the translation symmetry of particles and interactions by any combination of box vectors. If an interaction is dissected multiple times by A_α, one, or more images of A_α (some black dotted lines in figure 5), it contributes only once to the pressure tensor, as it does to the energy. The result is represented as follows:

$$p_{\beta\alpha}(x,y,z) = \frac{1}{2A_\alpha \Delta\alpha}\left\langle \sum_{i\in(\Delta V = 2A_\alpha\Delta\alpha)} m_i v_{i\beta} v_{i\alpha} \right\rangle + \frac{1}{2A_\alpha}\left\langle \sum_{\substack{\vec{r}_n \cap A_\alpha \\ \bullet\ \text{include all } n-\text{body interactions} \\ \text{involving particles and images once} \\ \bullet\ \vec{r}_n \text{ must be dissected by } A_\alpha \\ \text{or an image of } A_\alpha}} \sum_{i=1}^{n} F_{i\beta}\, \mathrm{sgn}(\alpha_i - \alpha) \right\rangle \quad (25)$$

In summary, all particles are translated into the box and all n-body interactions comprised by particles or by particles and images are analyzed as described in Section 2.1. An n-body interaction makes exactly one contribution to the local pressure $p_{\beta\alpha}(x, y, z)$ if the connecting vector $\vec{r}_n$ between the two geometric centers is dissected by the original area A_α or by an image of A_α in any of the image boxes, or several times. Equation (25) assumes $\Delta V \to 0$.

Therefore, the calculation is very similar to a non-periodic system. The partition of the pressure tensor into individual contributions (kinetic, 2-body bond stretch, 2-body van-der-Waals, etc.) follows as in Section 3.1:

$$
\begin{aligned}
p_{\beta\alpha}^{\text{kinetic}}(x, y, z) &= \frac{1}{2A_\alpha \Delta\alpha} \left\langle \sum_{i \in (\Delta V = 2A_\alpha \Delta\alpha)} m_i v_{i\beta} v_{i\alpha} \right\rangle \\
p_{\beta\alpha}^{2-\text{body bond}}(x, y, z) &= \frac{1}{2A_\alpha} \left\langle \sum_{\substack{\text{dissected bonds} \\ \vec{r}_n \cap A_\alpha \\ \bullet\ \text{include all bonds between} \\ \text{particles and images once} \\ \bullet\ \vec{r}_n \text{ must be dissected by } A_\alpha \\ \text{or an image of } A_\alpha}} \sum_{i=1}^{2} F_{i\beta} \operatorname{sgn}(\alpha_i - \alpha) \right\rangle \\
p_{\beta\alpha}^{3-\text{body angle}}(x, y, z) &= \frac{1}{2A_\alpha} \left\langle \sum_{\substack{\text{dissected angles} \\ \vec{r}_n \cap A_\alpha \\ \bullet\ \text{include all angles involving} \\ \text{particles and images once} \\ \bullet\ \vec{r}_n \text{ must be dissected by } A_\alpha \\ \text{or an image of } A_\alpha}} \sum_{i=1}^{3} F_{i\beta} \operatorname{sgn}(\alpha_i - \alpha) \right\rangle \\
p_{\beta\alpha}^{4-\text{body torsion}}(x, y, z) &= \frac{1}{2A_\alpha} \left\langle \sum_{\substack{\text{dissected torsions} \\ \vec{r}_n \cap A_\alpha \\ \bullet\ \text{include all torsions involving} \\ \text{particles and images once} \\ \bullet\ \vec{r}_n \text{ must be dissected by } A_\alpha \\ \text{or an image of } A_\alpha}} \sum_{i=1}^{4} F_{i\beta} \operatorname{sgn}(\alpha_i - \alpha) \right\rangle \\
p_{\beta\alpha}^{2-\text{body Coulomb}}(x, y, z) &= \frac{1}{2A_\alpha} \left\langle \sum_{\substack{\text{dissected Coulomb interactions} \\ \vec{r}_n \cap A_\alpha \\ \bullet\ \text{include all Coulomb interactions} \\ \text{involving particles and images once} \\ \bullet\ \vec{r}_n \text{ must be dissected by } A_\alpha \text{ or} \\ \text{an image of } A_\alpha}} \sum_{i=1}^{2} F_{i\beta} \operatorname{sgn}(\alpha_i - \alpha) \right\rangle \\
&\dots
\end{aligned}
\tag{26}
$$

Equation (26) include the so-called minimum image convention. For example, if a bond extends across the box boundary, the nearest image is considered and the corresponding original atom on the opposite side of the box is disregarded to avoid double counting of the same interaction. The cutoff of n-body interactions (if any) determines the number of neighbor boxes with images of particles and images of the area A_α to be included and should be the same as in the energy expression.

4.2 Average pressure tensor over an area

The average pressure tensor over an extended area $\bar{p}_{\beta\alpha}(A_\alpha, \alpha)$ is obtained from the local pressure tensor by extension over a larger area A_α and comprises only three elements. The calculation consists of the translation of all particles into the box, and the analysis of the pool of n-body interactions involving particles and combinations of particles and images with respect to the original area A_α and with respect to image areas A_α in adjacent boxes. The result for $\bar{p}_{\beta\alpha}(A_\alpha, \alpha)$ in a periodic system equals equation (25) in the limit $\Delta\alpha \to 0$, and the partition in $\bar{p}_{\beta\alpha}^{\text{kinetic}}(A_\alpha, \alpha)$, $\bar{p}_{\beta\alpha}^{2-\text{body bond}}(A_\alpha, \alpha)$, etc. is obtained as in equation (26) in the limit $\Delta\alpha \to 0$.

When the area A_α equals a cross section of the box, equation (9) can be applied in non-periodic systems. In a periodic system, the atom-based forces $\vec{F}_i$ contain all interactions between particles as well as between particles and images. n-body interactions involving only particles and extending across the plane A_α are then automatically dissected by the cross-section A_α. Figure 5 illustrates that the interactions between particles and images extending across the plane A_α are also dissected by A_α or adjacent images of A_α since the cross-section A_α

acts as an infinite plane in periodic systems as well. Interactions involving particles and images may also experience multiple dissections when extended over several box lengths (some black dotted lines in figure 5). However, these interactions count only once as a contribution to the energy and subsequently to the pressure across A_α. Therefore, the method of planes equation (9) yields $\bar{p}_{\beta\alpha}(\alpha)$ in periodic systems as well (translation of the particles into the box is not strictly required but recommended for further analysis). The partition into additive contributions $\bar{p}_{\beta\alpha}^{\text{2−body bond}}(\alpha)$, $\bar{p}_{\beta\alpha}^{\text{3−body angle}}(\alpha)$, etc. follows equation (20).

4.3 Average pressure tensor over a volume

The calculation of average pressure tensors over a volume $\bar{p}_{\beta\alpha}(V)$ relies on inserting cross-sectional areas A_α between the particles in the volume V along the three coordinate axes (equation (11)). The extension to periodic systems requires the translation of all particles into the box, the analysis of n-body interactions between the particles as well as between particles and images, and translational symmetry to determine dissection by A_α:

$$\bar{p}_{\beta\alpha}(V) = \frac{1}{V}\left\langle \sum_{i\in V} m_i v_{i\beta} v_{i\alpha}\right\rangle + \frac{1}{\alpha_2-\alpha_1}\int_{\alpha_1}^{\alpha_2} \frac{1}{2A_\alpha}\left\langle \sum_{\substack{\vec{r}_n \cap A_\alpha \\ \bullet\ \text{include all } n\text{−body interactions} \\ \text{involving particles and images once} \\ \bullet\ \vec{r}_n \text{ must be dissected by } A_\alpha \\ \text{or an image of } A_\alpha}} \sum_{i=1}^{n} F_{i\beta}\,\mathrm{sgn}(\alpha_i-\alpha)\right\rangle \mathrm{d}\alpha \tag{27}$$

For the numerical evaluation, it is important to insert cross-sections of the volume V at every coordinate α when n-body interactions begin or end being dissected by A_α. The partition into additive contributions is analogous to equations (21) and (22) for non-periodic systems:

$$\bar{p}_{\beta\alpha}^{\text{kinetic}}(V) = \frac{1}{V}\left\langle \sum_{i\in V} m_i v_{i\beta} v_{i\alpha}\right\rangle$$

$$\bar{p}_{\beta\alpha}^{\text{2−body bond}}(V) = \frac{1}{\alpha_2-\alpha_1}\int_{\alpha_1}^{\alpha_2} \frac{1}{2A_\alpha}\left\langle \sum_{\substack{\text{dissected bonds} \\ \vec{r}_n \cap A_\alpha \\ \bullet\ \text{include all bonds involving} \\ \text{particles and images once} \\ \bullet\ \vec{r}_n \text{ must be dissected by } A_\alpha \\ \text{or an image of } A_\alpha}} \sum_{i=1}^{2} F_{i\beta}\,\mathrm{sgn}(\alpha_i-\alpha)\right\rangle \mathrm{d}\alpha$$

$$\bar{p}_{\beta\alpha}^{\text{3−body angle}}(V) = \frac{1}{\alpha_2-\alpha_1}\int_{\alpha_1}^{\alpha_2} \frac{1}{2A_\alpha}\left\langle \sum_{\substack{\text{dissected angles} \\ \vec{r}_n \cap A_\alpha \\ \bullet\ \text{include all angles involving} \\ \text{particles and images once} \\ \bullet\ \vec{r}_n \text{ must be dissected by } A_\alpha \\ \text{or an image of } A_\alpha}} \sum_{i=1}^{3} F_{i\beta}\,\mathrm{sgn}(\alpha_i-\alpha)\right\rangle \mathrm{d}\alpha$$

When averaging is performed over the volume of the entire box, it is sufficient to insert N cross-sectional areas A_α between the N particles along the three coordinate axes to evaluate the integral in equation (27) (Section 2.3) since A_α acts as an infinite plane in periodic systems (Section 4.2). Under the condition that all particles are translated into the box and the atom-based forces $\vec{F}_i$ take all interactions between particles as well as between particles and images into account, equation (9) describes the average pressure over cross-sections of the box in a periodic system (Section 4.2) and the derivation of the virial expression in a periodic system is the same as in a non-periodic system (Section 2.3). Therefore, equation (15) describes the average pressure over the entire box under periodic boundary conditions. This is in agreement with earlier findings [3,23] and the partition into contributions follows equations (23) and (24).

In summary, the calculation of pressure tensors in periodic systems is a straightforward extension from non-periodic systems. Particles must be translated into the box, and interactions between particles as well as between particles and images must be taken into account as in the energy expression. The dissection of individual interactions may occur at the considered area A_α or at any of the images of A_α in image boxes. The method of planes equation (9) and the virial expression equation (15), which relate to cross-sectional areas of the box, fulfill the dissection criteria inherently and can be applied directly to periodic systems (after translation and inclusion of

$$\bar{p}^{4-\text{body torsion}}_{\beta\alpha}(V) = \frac{1}{\alpha_2-\alpha_1}\int_{\alpha_1}^{\alpha_2}\frac{1}{2A_\alpha}\left\langle \sum_{\substack{\text{dissected torsions}\\ \vec{r}_n\cap A_\alpha \\ \bullet\ \text{include all torsions involving}\\ \text{particles and images once}\\ \bullet\ \vec{r}_n\ \text{must be dissected by}\ A_\alpha\\ \text{or an image of}\ A_\alpha}} \sum_{i=1}^{4} F_{i\beta}\,\mathrm{sgn}(\alpha_i-\alpha)\right\rangle \mathrm{d}\alpha \tag{28}$$

$$\ldots$$

particle–particle and particle–image interactions in the atom-based forces $\vec{F}_i$).

5. Applicability to various potentials

It has been shown in the previous sections that the pressure tensor is closely related to the energy expression (Hamiltonian). The approach is general for systems of discrete particles with a total energy determined by additive *n*-body interactions. The energy contributions should be differentiable with respect to the particle coordinates to obtain the forces and there are no restrictions on the functional form of the potentials. For example, harmonic, Morse, Lennard–Jones, Buckingham, Rydberg, Gaussian, Stillinger–Weber, Coulomb, Urey–Bradley, Murrell–Mottram, torsion, out-of-plane, cross-term or custom-made *n*-body potentials may be included.

The method can also be used with embedded atom [32] and bond-order potentials [33,34], however, pressure tensors are computationally more expensive with increasing complexity of the energy expression. A simple way to apply the methods for the calculation of local and average pressure tensors discussed in the previous sections is an explicit write out of the total energy as a function of the coordinates of the particles. This permits the computation of the forces for all two-body interactions (which are the majority), and then the analysis of the total number of interactions to determine forces across specified areas A_α. Alternatively, the atom-based forces $\vec{F}_i = -\nabla_{\vec{r}_i}E_{\text{pot}}$ due to all interactions of atom i with other atoms can be computed for use in the method of planes equation (9) or in the virial expression equation (15).

6. Summary

A method to calculate local and average pressure tensors in computer simulations of discrete particles in non-periodic and in periodic systems has been outlined on the basis of the mechanical definition of the pressure as a force acting across an area. The systematic analysis of *n*-body interactions between the particles yields a consistent overview of existing methods for pressure calculations as well as the partition of pressure tensors into additive contributions corresponding to the additive contributions in the total energy expression.

In a non-periodic system, the point function pressure tensor is given by equation (7), the average pressure tensor over an area by equation (8) (for cross-sections of the entire box also equation (9)), and the average pressure tensor over a volume by equation (11) (for the volume of the entire box also equation (15)). The partition into additive contributions is detailed in Section 3.

The calculation of pressure tensors under periodic boundary conditions is a straightforward extension from non-periodic systems. All particles must be translated into the box in the moment of pressure calculation. Then, the evaluation of all *n*-body interactions contributing to the total energy of the system is carried out, i.e. interactions between particles as well as between particles and images. *n*-body interactions dissected by the respective area A_α or by one of the images of A_α in other boxes (or multiply dissected interactions) make exactly one contribution to the pressure tensor.

In a periodic system, the point function pressure tensor is given by equation (25), the average pressure tensor over an area also by equation (25) assuming an area of finite-size (for cross-sections of the entire box also equation (9)), and the average pressure tensor over a volume by equation (27) (for the volume of the entire box also equation (15)). The method of planes and the virial formula fulfill the dissection criteria inherently and remain the same in periodic systems, provided the atom-based net forces $\vec{F}_i$ include *n*-body interactions with other particles and with images. The partition into additive contributions is detailed in Section 4.

Moreover, there are no restrictions on energy models and on the range of interactions between the particles. Pressure tensors are closely related to the free energy so that insight into local free energy changes can be obtained. As a consequence, the large number of degrees of freedom involved may render the calculation of pressure tensors computationally expensive, particularly in arbitrarily shaped volumes and when complex energy models are employed. However, it is hoped the three-dimensional analysis of pressure tensors with respect to freely chosen areas and volumes will help solve current challenges in understanding mechanics and thermodynamics at the nanoscale.

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[30] For conceptual clarity, the symbol A_α in this paper is employed to represent infinitesimal areas ΔA_α, finite-size areas A_α, and cross-sections A_α of the box. The meaning is identified in the context.

[31] Arguably, centers of mass could be employed instead of centers of geometry, however, the problem appears to be rather geometric in nature.

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