LETTERS TO THE EDITOR

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NOTES

Virial pressure of periodic systems with long range forces

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The well known virial expression for the pressure valid for atomic or molecular systems confined in a container of impenetrable walls has to be modified to capture the particular geometry of a periodic system. We have derived pressure equations of state for two and three-dimensional periodic systems in Refs. 1, 2. In this note, the formulation for periodic systems with explicit long range Coulomb forces is presented, which demonstrates that the virial expression is identical to the thermodynamic definition of pressure.[3] Hence, the discrepancy between the virial and thermodynamic formulation of pressure observed in Ref. 3 is resolved.

The system of interest consists of N point particles with coordinates $\mathbf{r}_1,\ldots,\mathbf{r}_\mathbf{N}$, masses $m_1,\ldots,m_N$, and charges $q_1,\ldots,q_N$ in a box of volume V with periodic boundary conditions. (Please note, that particles are not reflected into a primary box when leaving that box on one side. The trajectories of the particles are rather followed through the infinite system.) The particles interact via pairwise (long and short range) potentials with each other and with periodic images at positions $\mathbf{r}_i+\mathbf{R}_\mathbf{n}$. For a cubic primary box the vector $\mathbf{R}_\mathbf{n}$ is given by

$$\mathbf{R}_\mathbf{n}=\mathbf{n}L, \tag{1}$$

where L is the length of the cube, $n_\alpha \in \mathbb{Z}$, and the index α denotes the Cartesian components. As shown in Ref. 1, the pressure (p) of a periodic system—corresponding to the mechanical definition p=*Force/Area* of a confining container—is given by

$$p=-\frac{1}{6V}\left\langle \sum_{i=1}^{N}\sum_{j=1}^{N}\sum_{\mathbf{n}}{}' \; \mathbf{F}_{ij}^{\mathbf{n}}\cdot \mathbf{R}_\mathbf{n}\right\rangle, \tag{2}$$

where $\langle\cdots\rangle=\int\cdots\exp(-\beta H)d\tau/Z$ denotes the thermal average, with H the Hamiltonian of the system and $\beta=1/k_BT$. (The prime indicates that $i\neq j$ for $\mathbf{n}=\mathbf{0}$.) The force $\mathbf{F}_{ij}^{\mathbf{n}}=\mathbf{F}_{ij}(\mathbf{r}_i-\mathbf{r}_j-\mathbf{R}_\mathbf{n})$ is the negative derivative of the (periodic) potential

$$U=\frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\sum_{\mathbf{n}}{}' \; U_{ij}(\mathbf{r}_i-\mathbf{r}_j-\mathbf{R}_\mathbf{n}). \tag{3}$$

The virial pressure is then given by

$$pV=Nk_BT+\frac{1}{6}\sum_{i=1}^{N}\sum_{j=1}^{N}\sum_{\mathbf{n}}{}' \; \langle \mathbf{F}_{ij}^{\mathbf{n}}\cdot[\mathbf{r}_i-\mathbf{r}_j-\mathbf{R}_\mathbf{n}]\rangle. \tag{4}$$

In brief, this equation is obtained starting from Newton's equations of motion,[1]

$$m_i\ddot{x}_{i\alpha}=F_{i\alpha}=\sum_{j=1}^{N}\sum_{\mathbf{n}}{}' \; F_{ij\alpha}^{\mathbf{n}}. \tag{5}$$

Multiplication of the equation by $x_{i\beta}$ and summation over all particles yields

$$\frac{d}{dt}\sum_{i=1}^{N} m_i\dot{x}_{i\alpha}x_{i\beta}=\sum_{i=1}^{N} m_i\dot{x}_{i\alpha}\dot{x}_{i\beta} +\frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\sum_{\mathbf{n}}{}' \; F_{ij\alpha}^{\mathbf{n}}(x_{i\beta}-x_{j\beta}). \tag{6}$$

As can easily be shown, the average of the left-hand side of this equation is zero for any standard statistical ensemble. Similar the time average is zero for a system of particles with a mean square displacement increasing with time by a power smaller than two. As a consequence, we find the relation

$$\left\langle \sum_{i=1}^{N} m_i\dot{x}_{i\alpha}\dot{x}_{i\beta}\right\rangle+\left\langle \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\sum_{\mathbf{n}}{}' \; F_{ij\alpha}^{\mathbf{n}}(x_{i\beta}-x_{j\beta})\right\rangle=0, \tag{7}$$

which is valid for any standard ensemble. Equation (7) has been confirmed in Ref. 1 for a system with short range interactions. Using $\alpha=\beta$, summing over the various space directions, and adding Eq. (2) on both sides of Eq. (7) we find the pressure of Eq. (4). This demonstrates the identity between Eqs. (2) and (4). Alternatively, Eq. (4) is obtained by Green's method based on the partition function. A detailed derivation along this line is presented in Refs. 2, 4. It is important to realize that in addition to the double sum over i and j, which is already present in the virial of a confined system, a sum over all periodic images appears. (Naturally, the double sum can be reduced to a single sum by using Newton's third law: $\frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\sum_{\mathbf{n}}'\mathbf{F}_{ij}^{\mathbf{n}}\cdot[\mathbf{r}_i-\mathbf{r}_j-\mathbf{R}_\mathbf{n}]=\sum_{i=1}^{N}\sum_{\mathbf{n}}\mathbf{F}_{i}^{\mathbf{n}}\cdot[\mathbf{r}_i-\mathbf{R}_\mathbf{n}/2]$, with $\mathbf{F}_i^{\mathbf{n}}=\sum_{j=1}^{N}\mathbf{F}_{ij}^{\mathbf{n}}$.) If only short range interactions are present, the minimum image convention can be applied, which reduces the sum over **n** to $n_\alpha = 0, \pm 1$, if attention is paid to the N particles of the primary box only.[7] In case of long range forces, all the different images given by the various **n** values have to be taken into account.

For the considered cubic primary box, the instantaneous pressure of Eq. (2) can be written as

$$p = -\frac{\partial U}{\partial V} = -\frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\sum_{\mathbf{n}}{}' \frac{\partial U_{ij}(\mathbf{r}_i - \mathbf{r}_j - \mathbf{R}_\mathbf{n})}{\partial V}. \tag{8}$$

A similar representation of pressure is provided in Refs. 5, 6. In these references the pressure is split into a contribution by short range interactions using minimum image distances only and a contribution (denoted by W_e) which includes terms with explicit volume dependence. The same separation of Eq. (8) into short range terms plus other volume dependent terms yields an expression similar to W_e.

For the Coulomb interaction, the potential U_{ij}^C is given by $U_{ij}^C = q_i q_j / [\epsilon |\mathbf{r}_i - \mathbf{r}_j - \mathbf{R}_\mathbf{n}|]$. Hence the force is

$$\mathbf{F}_{ij}^{\mathbf{n}C} = \frac{q_i q_j}{\epsilon} \frac{\mathbf{r}_i - \mathbf{r}_j - \mathbf{R}_\mathbf{n}}{|\mathbf{r}_i - \mathbf{r}_j - \mathbf{R}_\mathbf{n}|^3}. \tag{9}$$

Inserting Eq. (9) into Eq. (4) leads to the well-known expression (see Ref. 3, and references therein)

$$pV = Nk_BT + \frac{1}{6}\sum_{i=1}^{N}\sum_{j=1}^{N}\sum_{\mathbf{n}}{}' \langle \mathbf{F}_{ij}^{\mathbf{n},sr} \cdot [\mathbf{r}_i - \mathbf{r}_j - \mathbf{R}_\mathbf{n}]\rangle + \frac{\langle U^C\rangle}{3V}, \tag{10}$$

when we assume only Coulomb long range forces and otherwise short range forces ($\mathbf{F}_{ij}^{\mathbf{n},sr}$). This expression is identical to the pressure derived by Green's method and is denoted thermodynamic pressure in Ref. 3. This demonstrates that the appropriate formulation of the virial of a periodic system yields an expression for the pressure which is unique and independent from the way it is derived.

Equation (4) is easily extended to obtain a stress (pressure) tensor of an anisotropic system (cf. Ref. 1),

$$\sigma_{\alpha\beta} V = -\sum_{i=1}^{N} \langle m_i \dot{x}_{i\alpha} \dot{x}_{i\beta}\rangle - \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N}\sum_{\mathbf{n}}{}' \langle F_{ij\alpha}^{\mathbf{n}}[x_{i\beta} - x_{j\beta} - R_{\mathbf{n}\beta}]\rangle. \tag{11}$$

To evaluate the virial term with long range forces sufficiently fast, e.g., in a computer simulation, the splitting in a real space part and a Fourier space part may be useful.[7] However, since the sum over the lattice vectors **n** appears in the virial term, it is not possible to first transform the forces and then multiply them by the position or distances $[x_{i\beta} - x_{j\beta} - R_{\mathbf{n}\beta}]$ of the particles.[3] Instead, the term in angular brackets has to be transformed as a whole otherwise some contributions to the pressure or stress tensor would be missing. There are various ways to obtain the appropriate stress tensor representation. Expressions for the stress tensor (11) have been derived in Refs. 8, 9 using Ewald sums. A detailed discussion of the evaluation of the thermal average is presented in Ref. 10.

In summary, a virial expression for the pressure of periodic systems with long range Coulomb forces has been presented. For a system confined in a container with impenetrable walls and surface interactions of negligible range (for details cf. Ref. 2) the virial contains the sum over all the confined particles ($\Sigma_i \langle \mathbf{F}_i \cdot \mathbf{r}_i\rangle$). In a periodic system the summation over all the periodic images is additionally required [see Eq. (4)]. As shown here, the adequate treatment of the lattice sum leads to a virial expression of the pressure identical to the thermodynamic definition.

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