Evaluation of Pressure Tensor in Constant-Volume Simulations of Hard and Soft Convex Bodies

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A method for calculating the pressure tensor in constant-volume Monte Carlo simulations of convex bodies is presented. In contrast to other approaches, the method requires only an isotropic scaling of the simulation box, and the counting of simple geometric quantities characterizing overlapping pairs. Non-sphericity presents no special difficulties. The result is expressed as a sum of pairwise contributions, and can therefore be used to compute pressure tensor profiles in a conventional way.

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I. INTRODUCTION

The purpose of this brief paper is to explain in detail a procedure to calculate the pressure tensor in constant-volume computer simulations of hard convex bodies. The term “hard” is used to denote particles whose interaction energy is infinite when they overlap, and zero when they do not; this paper will also consider “soft” convex bodies, meaning particles whose interaction energy takes a finite, positive, constant value $\epsilon$ when they overlap, and zero when they do not. The restriction to convex bodies is a simplification to ensure that an overlap between a pair of molecules may result when the distance between the molecular centres is reduced, but not when it is increased, while keeping all orientations fixed; extending the results to non-convex bodies is relatively straightforward but requires care. Calculation of the components of the pressure tensor, as opposed to the scalar pressure, is an important route to the surface tension of interfaces.

The motivation for this work is the recent paper by Gloor et al. which, as well as providing a near-comprehensive review of simulation techniques in this area, proposes a method for surface tension calculation based on perturbations in the cross-sectional area of a system containing the planar interface of interest. It is claimed that a key advantage of this “test-area” method for discontinuous potentials is the avoidance of the determination of delta-functions “which are impractical to evaluate, particularly in the case of non-spherical molecules”. The present paper demonstrates that this is not the case: that the pressure tensor components for such systems, and hence the surface tension, may be calculated by a simple extension of the standard approach of counting overlaps produced by an isotropic volume scaling. In fact, this method has already been used to determine the surface tension of the isotropic-nematic interface of hard ellipsoids, although the full details of the method were not explained in that paper.

Microscopic expressions for the pressure in a fluid are to be found in the standard references. Separate $P = P^{id} + P^{ex}$ where $P^{id} = \rho k_B T$ is the ideal gas contribution, and focus on the excess part, $P^{ex}$. The usual mechanical route to the pressure starts with the volume derivative of the excess Helmholtz free energy

$$\frac{P^{ex}}{k_B T} = -\frac{1}{k_B T} \frac{\partial F^{ex}}{\partial V} = \frac{1}{Q^{ex}} \frac{\partial Q^{ex}}{\partial V},$$

where $T$ is the temperature and $k_B$ Boltzmann’s constant. The excess partition function in the canonical ensemble, $Q^{ex}$, is written

$$Q^{ex} = V^{-N} \int \cdots \int e^{-U/k_B T} \; ds_1 \cdots ds_N,$$

where $U$ is the total potential energy. The $N$ particle centre-of-mass coordinates are denoted $r_j$, and scaled coordinates $s_j$ are defined by $r_j = L s_j$, assuming a cubic box of side $L$ and volume $V = L^3$. Particles may have orientational degrees of freedom; for example the orientation of a uniaxial molecule is specified by a unit vector $\hat{u}_j$ directed along the symmetry axis. However, for simplicity
here, and in most of what follows, the orientational dependence and the integrations over orientational degrees of freedom are not explicitly written. In the following, also for simplicity, pairwise-additive potentials \( U = \sum_{i<j} u_{ij} \) with \( u_{ij} = u(r_{ij}, \hat{u}_i, \hat{u}_j) \), where \( r_{ij} = r_i - r_j \), are assumed. For continuous potentials \( u_{ij} \), the volume differentiation within the integral of eqn (2) is readily carried out yielding the well-known expression

\[
\frac{P^{ex}}{k_B T} = -\frac{1}{3V k_B T} \left( \sum_{i<j} \left( \frac{\partial u_{ij}}{\partial r_{ij}} \right) \cdot r_{ij} \right) = -\frac{1}{3V k_B T} \left( \sum_{i<j} \left( \frac{\partial u_{ij}}{\partial r_{ij}} \right) r_{ij} \right). \tag{3}
\]

Any orientations (for example \( \hat{u}_i, \hat{u}_j \), and \( \hat{r}_{ij} = r_{ij}/r_{ij} \)) are held fixed in taking the derivative in the right-most expression in eqn (3).

II. PRESSURE FOR DISCONTINUOUS POTENTIALS

For discontinuous potentials, \( \partial Q^{ex}/\partial V \) may be estimated by finite differences. To highlight the connection with the method for determining the full pressure tensor, a derivation is presented here; this follows Eppenga and Frenkel, Perram et al., and the basic ideas go back to Vieillard-Baron, although the detailed approach and notation used here are different. Consider a volume change \( V \rightarrow V - \Delta V \).

\[
\frac{P^{ex}}{k_B T} = \frac{1}{Q^{ex}} \frac{\partial Q^{ex}}{\partial V} = \lim_{\Delta V \rightarrow 0} \frac{1}{\Delta V} \left( Q^{ex}(V) - Q^{ex}(V - \Delta V) \right) = \lim_{\Delta V \rightarrow 0} \frac{1}{\Delta V} \left[ 1 - \left( \frac{\epsilon}{k_B T} \right)^{\Delta u_{ij}} \right].
\]

The ensemble average is conducted in the unperturbed system and \( \Delta U = \sum_{i<j} \Delta u_{ij} \) is a sum of energy changes for each pair, arising from overlaps which are freshly generated by the volume change. Hence the Boltzmann factor is expressed as a product of terms. The expression is simplified by the assumption that the different pair overlaps are uncorrelated. This is reasonable at small \( \Delta V \), since the number of overlaps may be made vanishingly small.

\[
\frac{P^{ex}}{k_B T} = \lim_{\Delta V \rightarrow 0} \frac{1}{\Delta V} \left[ 1 - \exp\left( -\frac{\Delta u_{ij}}{k_B T} \right) \right] = \lim_{\Delta V \rightarrow 0} \frac{1}{\Delta V} \left[ 1 - \prod_{i<j} \exp\left( -\frac{\Delta u_{ij}}{k_B T} \right) \right].
\]

All pairs are now equivalent in this expression. For hard particles, each exponential is either 0 (signalling a newly-generated overlap) or 1 (when the volume scaling does not cause an overlap), and the average has the interpretation of a probability that any given pair will not overlap. For soft particles, every newly-generated overlap contributes \( \epsilon/k_B T \), while pairs whose overlap status remains unchanged contribute 1. In either case, it is convenient to define

\[
\phi_{ij} = \begin{cases} 1 - e^{-\Delta u_{ij}/k_B T} & \text{newly generated overlap} \\ 0 & \text{otherwise} \end{cases}
\]

\[
P_{ij}^{\text{overlap}} = \langle \phi_{ij} \rangle = 1 - \left\langle e^{-\Delta u_{ij}/k_B T} \right\rangle. \tag{5}
\]

\( P_{ij}^{\text{overlap}} \) will be loosely termed an “overlap probability”; for small \( \Delta V \), it is small compared with 1, simply because most pairs will have \( \Delta u_{ij} = 0 \). The indices \( i \) and \( j \) on \( P_{ij}^{\text{overlap}} \) are actually redundant. The product of terms is expanded to first order in the overlap probabilities:

\[
\frac{P^{ex}}{k_B T} = \lim_{\Delta V \rightarrow 0} \frac{1}{\Delta V} \left[ 1 - \frac{\prod_{i<j} \left( 1 - P_{ij}^{\text{overlap}} \right)}{\Delta V} \right] = \lim_{\Delta V \rightarrow 0} \frac{\sum_{i<j} P_{ij}^{\text{overlap}}}{\Delta V} = \lim_{\Delta V \rightarrow 0} \frac{\langle \phi_{ij}^{\text{overlap}} \rangle}{\Delta V}.
\]

For hard particles, \( \phi_{ij}^{\text{overlap}} = N_{\text{overlap}} \), the number of overlaps in a configuration generated by the volume scaling, arising from summing the probabilities over all pairs. In the more general case of
soft particles

\[ \phi_{\text{overlap}} = \sum_{i<j} \phi_{ij} = \sum_{i<j} 1 - e^{-\Delta u_{ij}/k_B T} \]

\[ = N_{\text{overlap}} \left( 1 - e^{-\varepsilon/k_B T} \right), \]

re-emphasizing that \( N_{\text{overlap}} \) counts the number of new overlaps, since the original configuration may already contain overlaps if \( \varepsilon \) is finite, and these do not contribute.

Suppose now that the volume reduction comes from scaling the box lengths by a factor \((1 - \varepsilon)\), i.e. \( L \to L - \Delta L\) where \( \Delta L/L = \varepsilon \), then \( \Delta V/V \approx 3\varepsilon \) and

\[ \frac{P_{\text{ex}}}{k_B T} = \lim_{\Delta V \to 0^+} \frac{\left\langle \phi_{\text{overlap}} \right\rangle}{\Delta V} \]

\[ = \lim_{\varepsilon \to 0^+} \frac{\left\langle \phi_{\text{overlap}} \right\rangle}{3\varepsilon V} = \lim_{\varepsilon \to 0^+} \frac{\left\langle \sum_{i<j} \phi_{ij} \right\rangle}{3\varepsilon V}. \]  

(6)

Thus the pressure may be estimated by essentially counting the overlaps that result from a small isotropic volume scaling. The same expression (to leading order in \( \varepsilon \)) results if the overlaps result from scaling all linear particle dimensions by the factor \( 1 + \varepsilon \) instead of reducing the volume.

The expression of Perram et al.\(^6\) for convex spheroids is equivalent. It may be written

\[ \frac{P_{\text{ex}}}{k_B T} = \lim_{\varepsilon \to 0^+} \frac{\left\langle \sum_{i<j} F_{ij} \right\rangle}{3\varepsilon V}, \]  

(7)

with overlap function \( F_{ij} \) defined such that

- \( F_{ij} > 1 \), for non-overlapping \( i \& j \),
- \( F_{ij} = 1 \), for \( i \& j \) in contact,
- \( F_{ij} < 1 \), for overlapping \( i \& j \).

The sum in eqn (7) counts all distinct pairs for which \( 1 < F_{ij} < (1 + \varepsilon)^2 \approx 1 + 2\varepsilon \). The value \( F_{ij} \) within the sum can be replaced by 1. The overlap function defined by Perram et al.\(^6\) has the scaling behaviour \( F_{ij} = r^2 f_{ij}(\hat{r}_{ij}, \hat{u}_i, \hat{u}_j) \) so counting pairs for which \( 1 < F_{ij} \ll (1 + \varepsilon)^2 \) is equivalent to counting the overlaps generated by scaling all particle linear dimensions by \( 1 + \varepsilon \) as above.

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**FIG. 1:** Schematic geometry of two convex particles in contact (left) and near contact (right). The vectors \( \xi_i \) and \( \xi_j \), as well as the particle orientations, are kept fixed as the centre-centre vector \( r_{ij} \) is scaled uniformly.

I. PRESSURE TENSOR FOR DISCONTINUOUS POTENTIALS

Turning now to the pressure tensor, the ideal part is \( \frac{P_{\alpha\beta}}{k_B T} = \rho \delta_{\alpha\beta} \) and the excess part may be expressed\(^3\)

\[ \frac{P_{\text{ex}}}{k_B T} = -\frac{1}{V k_B T} \left\langle \sum_{i<j} \frac{\partial u(r_{ij})}{\partial r_{ij\alpha}} r_{ij\beta} \right\rangle, \alpha, \beta = x, y, z \]

or

\[ \frac{P_{\text{ex}}}{k_B T} = -\frac{1}{V k_B T} \left\langle \sum_{i<j} \frac{\partial u(r_{ij})}{\partial r_{ij}} \otimes r_{ij} \right\rangle \]

where \( \otimes \) represents an outer product. To estimate this tensor in the case of discontinuous potentials, a more detailed consideration of pair geometry is required. When the particles are in contact, there is a common tangent plane at the point of contact; define a unit vector \( \hat{s}_{ij} \) normal to this plane, from \( j \) to \( i \), as shown in Fig. 1. For small displacements of the centre-centre vector \( r_{ij} \), keeping all angles, and the vectors \( \xi_i \) and \( \xi_j \) of the contact points relative to the molecular centres, fixed, the contact points and their associated tangent planes separate. Define the separation vector \( \xi_{ij} \), and the perpendicular separation between the tangent planes \( s_{ij} = \hat{s}_{ij} : \xi_{ij} \), as shown in the figure. Then \( s_{ij} \) takes positive values if the particles do not overlap, and negative values if they do overlap. Hence the step function \( \theta(s_{ij}) \) takes the value 0 (overlap) or 1 (no overlap), and a standard trick\(^3,10,11,12\) may be used to estimate the gradient of the potential.
Write
\[ e^{-u_{ij}/k_B T} = \theta(s_{ij}) + (1 - \theta(s_{ij})) e^{-\epsilon/k_B T}, \]
(the second term is zero for hard particles). Take the gradient of both sides and rearrange
\[ -\frac{1}{k_B T} \frac{\partial u(r_{ij})}{\partial r_{ij}} = \left( \frac{\partial s_{ij}}{\partial r_{ij}} \right) \delta(s_{ij} - 0_+) \times (1 - e^{-\epsilon/k_B T}) e^{+u_{ij}/k_B T}. \]

Note that the delta function may be taken to act at a separation infinitesimally outside contact, and so the exponential \( e^{-u_{ij}/k_B T} \) may be replaced by unity. Also, \( \left( \frac{\partial s_{ij}}{\partial r_{ij}} \right) = \hat{s}_{ij} \), so the expression simplifies:
\[ -\frac{1}{k_B T} \frac{\partial u(r_{ij})}{\partial r_{ij}} = \hat{s}_{ij} \delta(s_{ij} - 0_+) (1 - e^{-\epsilon/k_B T}). \]

This is a straightforward generalization of the expression of Boublik to include the case of soft particles. The connection to the pair distribution functions of hard convex body fluids at contact is set out elsewhere. For the present purposes, the delta function is approximated\(^{13}\) by the term in braces below:
\[ -\frac{1}{k_B T} \frac{\partial u(r_{ij})}{\partial r_{ij}} = \hat{s}_{ij} \times \left\{ \lim_{\Delta s \to 0_+} \frac{\theta(s_{ij}) - \theta(s_{ij} - \Delta s)}{\Delta s} \right\} (1 - e^{-\epsilon/k_B T}). \]

If the change results from a scaling \( r_{ij} \to r_{ij} - \Delta r_{ij} \) with \( \Delta r_{ij} = \epsilon r_{ij} \), then \( \Delta s = \hat{s}_{ij} \cdot \Delta s_{ij} = \hat{s}_{ij} \cdot \Delta r_{ij} = \epsilon \hat{s}_{ij} \cdot r_{ij} \). The remaining terms may be recognized as \( \phi_{ij} \), defined in eqn (4). The result becomes
\[ -\frac{1}{k_B T} \frac{\partial u(r_{ij})}{\partial r_{ij}} = \lim_{\epsilon \to 0_+} \frac{\phi_{ij} \hat{s}_{ij}}{\epsilon \hat{s}_{ij} \cdot r_{ij}}. \]

\[ \Rightarrow \frac{P_{\text{ex}}}{k_B T} = \lim_{\epsilon \to 0_+} \frac{1}{eV} \left\langle \sum_{i<j} \phi_{ij} \hat{s}_{ij} \otimes r_{ij} \right\rangle. \tag{8} \]

This is the main result: pressure tensor components in constant-volume Monte Carlo simulations of general convex bodies can be calculated almost as simply as the scalar pressure, by summing over pairs which would overlap as a result of an isotropic scaling of coordinates. The term \( \phi_{ij} \) acts to select such pairs (and for soft particles, it also incorporates the appropriate energy-dependent scale factor): the only additional requirement is to compute the surface normal for the near-contact pairs, which is almost always straightforwardly done. The above derivation follows closely that of Trokhymchuk and Alejandro\(^{13}\), although that paper explicitly considered only the spherically symmetric case. Taking one third of the trace of eqn \( 5 \) regenerates eqn \( 6 \).

This expression is consistent with the form of pressure tensor calculated in collisional molecular dynamics simulations
\[ P_{\text{ex}} = \frac{1}{Vt} \sum_{\text{colls}} \Delta p_{ij} \hat{s}_{ij} \otimes r_{ij} \]

which is a sum over collisions occurring in time \( t \), where the colliding particles are labelled \( i \) and \( j \), and the impulsive momentum transfer of magnitude \( \Delta p_{ij} \) is directed along the common surface normal \( \hat{s}_{ij} \). For continuous potentials, the analogous formula is proportional to \( f_{ij} \otimes r_{ij} \) where \( f_{ij} \) is the pair force. Indeed, eqn \( 5 \) may be written down almost immediately, knowing that pair contributions must be proportional to \( \hat{s}_{ij} \otimes r_{ij} \), and that the isotropic pressure is given by eqn \( 6 \).

To evaluate the surface tension \( \gamma \) of a planar interface normal to the \( z \) direction, the difference in components \( \Delta P(z) \equiv P_{zz} - \frac{1}{2}(P_{xx}(z) + P_{yy}(z)) \) is calculated as a function of \( z \) and integrated across the interface. The integrals may be computed implicitly, yielding \( \gamma \) as a single number, but the above formalism makes explicit the contributions of each pair to the total for each component of \( P \), and therefore the definition of a local pressure tensor \( P(z) \) via the Irving-Kirkwood or Harasima convention\(^{14,15,16}\) is handled in exactly the same way as for continuous potentials. The integration of \( \Delta P(z) \) is then performed numerically. As emphasized by Holcomb et al.\(^{17}\) and Trokhymchuk and Alejandro\(^{13}\), monitoring pressure tensor profiles in inhomogeneous systems is an important test of equilibrium, as well as providing useful information about interface structure. This aspect is missing from the test-area method as described in Ref.\(^{18}\), although it could probably be incorporated.
IV. CONCLUSIONS

This paper has demonstrated that all components of the pressure tensor may be straightforwardly computed in constant-volume simulations by counting the pair overlaps resulting from isotropic scaling of the simulation box, and including a simple geometrical tensor formed from the surface normal at contact and the centre-centre vector. Non-spherical particles with discontinuous interaction potentials present no great difficulties and special anisotropic scaling moves are not required. The method makes it easy to resolve the pressure tensor profile, for use in surface tension calculations.

No explicit comparisons of techniques are performed here, but it should be noted that equation (8) has been used to calculate pressure tensor profiles, and the surface tension, of the equilibrium isotropic-nematic interface in the hard ellipsoid fluid and comparisons made there with results for a closely-related continuous potential model. There is a trade-off between minimizing statistical errors (favoured by large numbers of overlaps) and systematic errors (favoured by small volume changes), in the choice of the scaling parameter $\epsilon$, so usually it will be necessary to examine several values. As has been emphasized, the method is essentially equivalent to a numerical estimate of the (orientationally-averaged) pair distribution function at contact, and so the same caveats apply as to the calculation of that quantity near contact, the function may vary quite sharply, so the extrapolation to small $\epsilon$ may require care. These observations apply equally to the test-area method, and all other finite perturbation methods of this kind.

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