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Subtleties in the calculation of the pressure and pressure tensor of anisotropic particles from volume-perturbation methods and the apparent asymmetry of the compressive and expansive contributions

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12 **RESEARCH ARTICLE**
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15 **Subtleties in the calculation of the pressure and pressure tensor of**
16 **anisotropic particles from volume-perturbation methods and the**
17 **apparent asymmetry of the compressive and expansive**
18 **contributions.**
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21 Paul E. Brumby[†], Andrew J. Haslam[†], Enrique de Miguel[‡] and George Jackson^{†*}

22 [†]*Department of Chemical Engineering, Imperial College London, South Kensington*
23 *Campus, London SW7 2AZ, UK;* [‡]*Facultad de Ciencias Experimentales, Departamento*
24 *de Física Aplicada, Universidad de Huelva, 21071 Huelva, Spain*
25

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29 An efficient and versatile method to calculate the components of the pressure tensor for hard-
30 body fluids of generic shape from the perspective of molecular simulation is presented. After
31 due consideration of all the possible repulsive contributions exerted by molecules upon their
32 surroundings during an anisotropic system expansion, it is observed that such a volume change
33 can, for non-spherical molecules, give rise to configurations where overlaps occur. This feature
34 of anisotropic molecules has to be taken into account rigorously as it can lead to discrepancies
35 in the calculation of tensorial contributions to the pressure. Using the condition of detailed
36 balance as a basis, a perturbation method developed for spherical molecules has been extended
37 so that it is applicable to non-spherical and non-convex molecules. From a series of ‘ghost’
38 anisotropic volume perturbations the residual contribution to the components of the pressure
39 tensor may be accurately calculated. Comparisons are made with prior methods, and where
40 relevant results are evaluated against existing data. For inhomogeneous systems this method
41 provides a particularly convenient route to the calculation of the interfacial tension (surface
42 free energy) from molecular simulations.

43 **Keywords:** Monte Carlo; Pressure tensor; Perturbation, Surface tension; Hard-core
44 particles; Non-convex particles; Detailed balance
45

46 **1. Introduction**
47

48 A knowledge of a system’s pressure is a vital component in our understanding
49 of phase behaviour and phase transitions. In molecular simulation studies using
50 constant-volume ensembles an independent methodology is required to evaluate
51 the pressure [1, 2]. When a constant-pressure ensemble [3] is used, it is fundamen-
52 tal that the correct value of pressure is maintained; while this is straightforward in
53 simulations of simple systems, as we shall show for inhomogeneous systems involv-
54 ing molecules of complex shape, unexpected (and non-intuitive) contributions to
55 the pressure may be present; any such contributions must therefore be taken into
56 account. The first task in any molecular-simulation study is the choice of ensem-
57 ble in which the simulation is to be performed, and the microcanonical (constant
58 number of particles N , volume V , and energy E) or canonical (constant N , V , and
59 temperature T) ensembles are often a convenient choice. A disadvantage of the use
60

*Corresponding author. Email: g.jackson@imperial.ac.uk

of these ensembles is that the pressure is not specified *a priori*. Consequently, a method for the calculation of the pressure is required.

The approaches most commonly encountered fall into two broad classes that may be described as the mechanical and the thermodynamic routes: the first is based on the use of the pressure virial of Clausius [4, 5], while the second is developed from the thermodynamic definition of the pressure as the derivative of the Helmholtz free energy with respect to the change in volume (at constant T and N) [5]. Since the early days of molecular simulation the mechanical (virial) route has been used in a routine manner to compute the pressure of systems of molecules interacting through continuous potentials [1, 2]. In molecular dynamics this is the technique of choice as the forces acting on the particles have to be evaluated to solve the equations of motion, so that the virials are directly accessible. It is relatively straightforward, even for large molecules represented with models at the atomistic level of detail, to determine the pressure by considering all of the appropriate site-site contributions to the virial. Care has to be taken in the case of discontinuous potentials; here the forces are impulsive and the corresponding virials are delta functions which must be evaluated accurately. This is important also in the case of otherwise-continuous potentials that are truncated at a finite distance; the contribution at the discontinuity is often not negligible [1]. The thermodynamic route, which involves a computation of the change in free energy accompanying test (virtual) infinitesimal perturbations in the volume with an appropriate scaling of the particle positions, is less prevalent. We note, however, that this type of thermodynamic perturbation approach is used frequently to determine the chemical potential with the so-called test-particle method of Widom [6], and a similar test-area method is now commonly employed to determine the surface tension [7]. Eppenga and Frenkel [8] were the first to adopt this type of procedure for the pressure in studies of the isotropic and nematic phases of systems of hard discs; as the simulations involved particles with discontinuous repulsive potentials, in this case the pressure was obtained by examining the probability of obtaining configurations with overlapping particles after vanishingly small isotropic volume perturbations (compressions). This methodology has now been extended to provide a route for the computation of the bulk pressure of systems with attractive interactions such as Lennard-Jones [9], square-well [10] or Gay-Berne [11] fluids. Related approaches based on the virial expression for the pressure together with a direct enumeration of the number of overlaps from a test volume contraction (to give the contact value of the pair distribution function) have also been used for systems with discontinuous potentials [12–22]. Though the formal equivalence of the virial (mechanical) and thermodynamic (volume derivative of the free energy) routes to the pressure has been known for some time [23, 24], there are important differences in the practical implementation of the two approaches, which lead to numerical differences in the value of the pressure that is computed: one method involves the explicit estimate of the averages of the virial for each molecule, while the other involves the evaluation of the average Boltzmann factor of the energy associated with infinitesimal volume deformations.

The virial and thermodynamic approaches also provide a means of determining the tensorial components of the pressure during a molecular simulation (see, for example, references [10, 11, 19, 21, 22]). Such an approach is relatively straightforward for systems of spherical particles, but there can be complications in the case of volume deformations involving hard-core particles of general non-spherical shape, as we show in this paper. Allen [21] has shown that for systems comprising hard-body molecules, one can determine the components of the pressure tensor from isotropic volume perturbations using an overlap algorithm, provided that one can find a

mutual plane at the point of contact between the two overlapping molecules. This method is, however, applicable only to convex shaped molecules, as only compressive perturbations are made; for more geometrically complex hard-body molecules another method is required.

Our principal aim in this paper is to provide a versatile method for calculating the pressure and components of the pressure tensor of systems of convex and non-convex hard-body molecules. Our method is straightforward to implement and is general for hard-body molecules of generic shape. By making a series of ‘ghost’ perturbations to the system it is possible to evaluate the configurational component of the pressure to a high level of accuracy [11]. It is very important to emphasise that in common with other perturbative techniques these are nonpermanent (ghost) trial volume deformations which have no influence on the ensemble averages or particle trajectories. The methodology of Eppenga and Frenkel and others [8, 9, 11, 22] is generalised so that it is now also applicable to molecules which are non-convex in shape. In addition, the components of the pressure tensor for such molecules can be computed through anisotropic volume perturbations which involve the scaling of the particle positions along the appropriate axis (axes); in this case we show that both compressive and expansive volume deformations are required to capture all of the contributions to the tensorial components of the pressure. The latter methodology will turn out to be invaluable in calculations of the interfacial tension (surface free energy) for inhomogeneous systems of hard particles of any shape or size polydispersity. The interfacial tension can be obtained simply as the difference between the normal and tangential components of the pressure tensor relative to the interface; note that, by using such a technique, there is no need for an analysis of the density profile in the vicinity of the interface [25].

This paper is set out as follows: in section 2 we consider the virial and thermodynamic volume-perturbation methods specific to hard-body molecules which are of non-convex shape. We extend this method in section 3 so that it may be applied to systems of hard-body molecules of any shape (an alternative derivation is given in an appendix). Details of how the new method may be modified for the calculation of the components of the pressure tensor are given in section 4. We present sample results for carefully selected systems in section 5 for the purposes of validating our method and demonstrating its accuracy. Finally, in section 6, we highlight the implications on future work in this area and suggest possible systems which are suitable for analysis.

2. Isotropic volume perturbations for systems of convex hard-body particles

The perturbation method used in this work is a thermodynamic route to evaluate the pressure. The other approach, which is commonly used, is based on a virial (mechanical) route. Both of these methods can be applied in a straightforward manner to estimate, to a high degree of precision, the system pressure of hard spherical particles, although the virial route turns out in some cases to be the more accurate [22]. It is however important to mention that a mechanical approach can be inappropriate in the case of nanoscale systems such as small liquid drops due to contributions from fluctuation terms, so that a thermodynamic route is sometimes preferable [26]. In the current work we focus on the use of a thermodynamic perturbation approach for anisotropic hard-core molecules, i.e., those described by discontinuous potentials. The reader is referred to other papers [9, 11] for detailed discussions on the application of volume-perturbation methods for systems with continuous potentials.

2.1. The virial route

Though not used in our current work, we first give a brief description of the traditional virial route for the calculation of the pressure of hard particles, in order to set our thermodynamic approach in context. The pressure p may be expressed in the virial form of Clausius [4] in terms of an average over the pair contributions to the virial $\mathbf{r}_{ij} \cdot \mathbf{f}_{ij}$ as [5, 27]

$$p = \frac{Nk_B T}{V} + \frac{1}{3V} \left\langle \sum_i \sum_{j>i} \mathbf{r}_{ij} \cdot \mathbf{f}_{ij} \right\rangle, \quad (1)$$

where N is the number of particles, V is the volume, T is the temperature, k_B is the Boltzmann constant, \mathbf{r}_{ij} is the centre-to-centre vector between the pair of molecules i and j , and \mathbf{f}_{ij} is the force acting between those two molecules in the case of a system with no external fields. It is conceptually simpler to illustrate the virial approach with the corresponding expressions for spherical particles. For a homogeneous hard-sphere system, which is radially symmetric so that only the scalar intermolecular distance $r = |\mathbf{r}|$ is relevant, the average of the pressure virial [cf. equation 1] can be written in terms of the radial pair distribution function $g(r)$ as [5]

$$p = \frac{Nk_B T}{V} - \frac{2\pi}{3} \left(\frac{N}{V} \right)^2 \int_0^\infty g(r) \{ru'(r)\} r^2 dr, \quad (2)$$

where $u(r)$ is the pair potential, and $u'(r) = \partial u(r)/\partial r$. Expressing the pair distribution function in terms of the cavity function $y(r)$,

$$g(r) = \exp \left[\frac{-u(r)}{k_B T} \right] y(r) \equiv e(r)y(r), \quad (3)$$

one can write equation 2 as

$$p = \frac{Nk_B T}{V} - \frac{2\pi}{3} \left(\frac{N}{V} \right)^2 \int_0^\infty u'(r)e(r)y(r)r^3 dr \quad (4)$$

$$= \frac{Nk_B T}{V} + \frac{2\pi k_B T}{3} \left(\frac{N}{V} \right)^2 \int_0^\infty e'(r)y(r)r^3 dr, \quad (5)$$

where

$$e'(r) = \frac{\partial e(r)}{\partial r} = \frac{-u'(r)e(r)}{k_B T}. \quad (6)$$

In the case of hard spheres of diameter σ , the Boltzmann factor of the potential is a Heaviside (unit-step) function, $e(r) = \mathbb{H}(r - \sigma)$, the derivative of which is a delta function, $e'(r) = \delta(r - \sigma)$. Since the force $f(r) = -u'(r)$, from equation 6 it follows that

$$e'(r) = \delta(r - \sigma) = \frac{f(r)e(r)}{k_B T}. \quad (7)$$

In the case of a collision between hard spheres from a non-overlapping configuration, r is infinitesimally greater than σ , for which $u(r) = 0$ and $e(r) = 1$, so that

equation 7 can be expressed as

$$\delta(r - \sigma) = \frac{f(r)}{k_B T} \quad \text{or} \quad f(r) = k_B T \delta(r - \sigma). \quad (8)$$

The components of the force for a pair of molecules i and j (which in this case acts along the centre-to-centre unit vector $\hat{\mathbf{r}}_{ij}$) can thus be written as

$$\mathbf{f}_{ij} = k_B T \delta(r_{ij} - \sigma) \hat{\mathbf{r}}_{ij}. \quad (9)$$

The delta function is an infinite spike when the molecules are in contact ($r_{ij} = \sigma$). Note that in the more general case of convex hard-core molecule with a non-spherical shape, the force is parallel to the surface normal but need not lie along the centre-to-centre vector. Upon substitution of equation 9 into equation 1 one arrives at the following expression:

$$p = \frac{Nk_B T}{V} + \frac{k_B T}{3V} \left\langle \sum_i \sum_{j>i} r_{ij} \cdot \delta(r_{ij} - \sigma) \right\rangle. \quad (10)$$

Following prior work [11], one can approximate the delta function using Heaviside functions:

$$\sum_i \sum_{j>i} r_{ij} \cdot \delta(r_{ij} - \sigma) \approx \sum_i \sum_{j>i} r_{ij} \left[\frac{\mathbb{H}(r_{ij} - \sigma) - \mathbb{H}(r_{ij} - (\sigma + \Delta r))}{\Delta r} \right]. \quad (11)$$

Here, Δr represents a small increment in the centre-to-centre distance of closest approach; this is equivalent to a small increment in molecular size. The sum of the Heaviside functions is unity when $\sigma < r_{ij} < (\sigma + \Delta r)$ and zero for all other values. Therefore, in the limit of an infinitesimal Δr , this relation is exact:

$$\sum_i \sum_{j>i} r_{ij} \cdot \delta(r_{ij} - \sigma) = \lim_{\Delta r \rightarrow 0} \sum_i \sum_{j>i} r_{ij} \frac{\mathbb{H}_{ij}}{\Delta r}, \quad (12)$$

where $\mathbb{H}_{ij} = \mathbb{H}(r_{ij} - \sigma) - \mathbb{H}(r_{ij} - (\sigma + \Delta r))$. When a perturbation is made so that the system volume is scaled isotropically, we may write $r'_{ij} = r_{ij} (1 + (\Delta V/V))^{1/3}$ which, for small values of the volume-change ratio, can be approximated by $r'_{ij} \approx r_{ij} (1 + (\Delta V/3V))$. Such an isotropic volume scaling is equivalent to shrinking or increasing of the molecular size while keeping the system volume constant. The perturbation Δr in equation 12, becomes $\Delta r \approx -(\Delta V/3V) r_{ij}$, which is exact in the limit of $\Delta V \rightarrow 0$. Thereby, substitution of equation 12 into equation 10 yields

$$p = \frac{Nk_B T}{V} - \lim_{\Delta V \rightarrow 0} \frac{k_B T}{\Delta V} \left\langle \sum_i \sum_{j>i} \mathbb{H}_{ij} \right\rangle. \quad (13)$$

When summed over all pairs of molecules within the system, the Heaviside function represents simply the number of overlaps resulting from a given perturbation. Over the course of a simulation the average of the number of overlaps, denoted by n_{ov} , and the pressure can be expressed as

$$p = \frac{Nk_B T}{V} - \lim_{\Delta V \rightarrow 0} \frac{k_B T n_{ov}}{\Delta V}. \quad (14)$$

This type of virial methodology can be extended to systems of convex, anisotropic hard-core particles (see the work of Allen [21]) although, in general, it becomes more difficult to apply.

2.2. The thermodynamic route

For molecules with continuous potentials one can average the virial (the product of the intermolecular separation and force) for every possible pair combination of molecules within the system and, from this, determine the system pressure [1]. However, the presence of a discontinuity in the intermolecular potential makes the direct application of such a method problematic and an alternative approach is highly desirable; hard-body systems represent an obvious example where this is the case. Eppenga and Frenkel [8] showed that by making volume perturbations in the form of very small trial volume compressions, an estimate of the derivative of the Helmholtz free energy (A) with respect to the system volume may be found. The pressure at constant T and N can then be obtained from the usual thermodynamic relation, in the limit of an infinitesimal volume change:

$$p = - \left(\frac{\partial A}{\partial V} \right)_{N,T} = - \lim_{\Delta V \rightarrow 0} \frac{\Delta A}{\Delta V}. \quad (15)$$

The Helmholtz free energy can be written as

$$A = -k_B T \ln Q, \quad (16)$$

where Q is the canonical partition function of the system [5]. For a change in the system volume from V to $V' = V + \Delta V$,

$$\Delta A = - (k_B T \ln Q_{V'} - k_B T \ln Q_V) = -k_B T \ln \frac{Q_{V'}}{Q_V}. \quad (17)$$

The partition functions in equation 17 are expressed as

$$Q_V = \int d\vec{r}^N \int d\vec{\omega}^N \frac{1}{\mathcal{V}^N N!} \exp \left(-\frac{U_V}{k_B T} \right);$$

$$Q_{V'} = \int d\vec{r}'^N \int d\vec{\omega}^N \frac{1}{\mathcal{V}'^N N!} \exp \left(-\frac{U_{V'}}{k_B T} \right), \quad (18)$$

where \mathcal{V} is the modified thermal de Broglie volume for non-spherical molecules and U is the internal energy of the system. The molecule centre-of-mass positions are given by the vector \vec{r} and the molecular orientations are given by $\vec{\omega}$. When a volume perturbation is made, the box dimensions and molecule positions are scaled as $\vec{r} \rightarrow \vec{r}'$. If $V'/V = 1 + (\Delta V/V)$, and the system volume is scaled isotropically, then the molecule positions are scaled as follows:

$$\vec{r}'(x', y', z') = \vec{r} \left(x \left(1 + \frac{\Delta V}{V} \right)^{1/3}, y \left(1 + \frac{\Delta V}{V} \right)^{1/3}, z \left(1 + \frac{\Delta V}{V} \right)^{1/3} \right). \quad (19)$$

Upon substitution of $d\vec{r}'^N = (dx' dy' dz')^N = d\vec{r} (1 + (\Delta V/V))^N$ and $U_{V'} = U_V + \Delta U$ into the partition function of the new volume, $Q_{V'}$, from equation

18:

$$Q_{V'} = \int d\vec{r}^N \left(1 + \frac{\Delta V}{V}\right)^N \int d\vec{\omega}^N \frac{1}{\mathcal{V}^N N!} \exp\left(-\frac{U_V}{k_B T}\right) \exp\left(-\frac{\Delta U}{k_B T}\right). \quad (20)$$

In terms of the partition functions of the unperturbed and perturbed states, Q_V and $Q_{V'}$ one has

$$\begin{aligned} \Delta A &= -k_B T \ln \left(\frac{\int d\vec{r}^N \left(1 + \frac{\Delta V}{V}\right)^N \int d\vec{\omega}^N \exp\left(-\frac{U_V}{k_B T}\right) \exp\left(-\frac{\Delta U}{k_B T}\right)}{\int d\vec{r}^N \int d\vec{\omega}^N \exp\left(-\frac{U_V}{k_B T}\right)} \right) \\ &= -Nk_B T \ln \left(1 + \frac{\Delta V}{V}\right) - k_B T \ln \left\langle \exp\left(-\frac{\Delta U}{k_B T}\right) \right\rangle, \end{aligned} \quad (21)$$

where ΔU is the change in configurational energy associated with the trial volume change ΔV . The angled brackets indicate that the variables within are averaged over unperturbed states of the system. Employing the further approximation $\ln(1 + (\Delta V/V)) \approx \Delta V/V$, for very small values of the relative volume change $\Delta V/V$, it is then possible to write equation 21 as

$$\Delta A = \lim_{\Delta V \rightarrow 0} \left(-\frac{Nk_B T \Delta V}{V} - k_B T \ln \left\langle \exp\left(-\frac{\Delta U}{k_B T}\right) \right\rangle \right). \quad (22)$$

Substituting equation 22 into equation 15 yields the pressure:

$$p = - \lim_{\Delta V \rightarrow 0} \frac{\Delta A}{\Delta V} = \frac{Nk_B T}{V} + \lim_{\Delta V \rightarrow 0} \frac{k_B T \ln \left\langle \exp\left(-\frac{\Delta U}{k_B T}\right) \right\rangle}{\Delta V}. \quad (23)$$

As discussed by Eppenga and Frenkel, [8] for the case of hard-body molecules (with no attractive term in the potential), $\exp(-\Delta U/k_B T)$ can take one of two values: unity for states with no overlapping molecules; zero for states where molecules are overlapping. When averaged over many states for a fixed relative volume change, $\langle \exp(-\Delta U/k_B T) \rangle$ becomes \mathcal{P}_{nov} , the probability of no overlaps occurring, which is a function of $\Delta V/V$. Equation 23 is rewritten as

$$p = \frac{Nk_B T}{V} + \lim_{\Delta V \rightarrow 0} \frac{k_B T \ln \mathcal{P}_{nov}}{\Delta V}. \quad (24)$$

The practical implementation of equations 24 and 14 for the determination of the system pressure from simulations requires a series of test system-volume perturbations, collecting data averaged over many states of the unperturbed reference system. To obtain the pressure of the unperturbed state, the residual pressures (the second term in equation 24 or 14, depending on the route utilised) are plotted against the relative volume change and, the residual pressure at a volume change of zero is found by extrapolation. To determine the system pressure all that remains is the simple addition of the ideal term.

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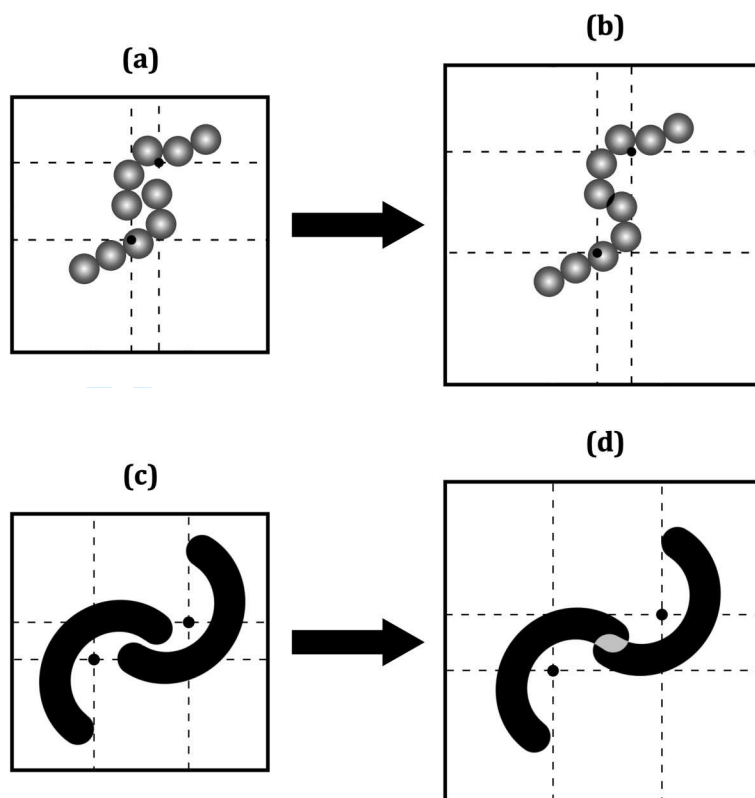
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Figure 1. The occurrence of a molecule-molecule overlap for pair of flexible hard-sphere chains or hard crescent-shaped molecules upon an isotropic expansion of the system volume. The systems labelled (a) and (c) are unperturbed, while in (b) and (d) the same systems are depicted following an isotropic volume increase in which all axes are scaled in proportion to each other. The filled dots represent the centre of mass of each molecule. The shaded area highlights the overlap of the molecules due to the perturbation.

3. Isotropic volume perturbations for non-convex hard-body molecules

The methods for the calculation of the system pressure covered in section 2 are appropriate for hard-body convex molecules. However the aforementioned methods are not suitable for molecules which are non-convex in shape. If one considers, for example, systems of flexible hard-sphere chains (see references [28, 29] for work with their linear counterparts), or of crescent-shaped / banana-shaped (bent-core) molecules, [30–32] a more-general method will be required that is able to correctly capture all of the repulsive interactions that such molecules exert upon their surroundings.

In figure 1 we illustrate the situation for a system of two hard-sphere chains or crescent-shaped molecules which undergoes an isotropic increase in the system volume (with a corresponding change in the scaled particle positions). Here, though the centres of mass of the particles are moved away from each other, the nature of the shape and the scaling (in proportion to the system volume) brings them into contact. One may therefore suppose that to correctly estimate the pressure of such a system, with a perturbation method of the type described in Section 2, one must sample the repulsive interactions from both compressive and expansive volume changes.

With this point in mind, we now present a general thermodynamic method for the pressure and pressure tensor applicable to systems of hard-body molecules of any shape and size polydispersity. The basis of the method can be developed and

understood from the condition of detailed balance for a system at equilibrium at the centre of the acceptance criterion used during Monte Carlo simulations in the isothermal-isobaric ensemble [1–3, 33–35].

We start with the partition function for the isothermal-isobaric NpT ensemble, which can be expressed as [2]

$$\Delta_{NpT} = \frac{1}{\mathcal{V}^N \Omega^N N! V_0} \int dV \int d\vec{r}^N \int d\vec{\omega}^N \exp\left(-\frac{U + pV}{k_B T}\right); \quad (25)$$

here V_0 is an arbitrary reference volume so as to make the partition function dimensionless and $\Omega = \int d\vec{\omega}$ (e.g., $\Omega = 8\pi^2$ for non-linear molecules; $\Omega = 4\pi$ for molecules with cylindrical symmetry). One can scale the particle positions to dimensionless quantities in terms of the system box lengths L_x , L_y and L_z where the product of all three is the system volume, V . We write the molecule positions relative to these axes, so $x = x^* L_x$, $y = y^* L_y$ and $z = z^* L_z$ such that $d\vec{r}^N = (L_x L_y L_z)^N d\vec{r}^{*N} = V^N d\vec{r}^{*N}$, and thus

$$\Delta_{NpT} = \frac{1}{\mathcal{V}^N \Omega^N N! V_0} \int dV \int V^N d\vec{r}^{*N} \int d\vec{\omega}^N \exp\left(-\frac{U + pV}{k_B T}\right). \quad (26)$$

Bringing the volume term inside the exponential allows us to write the partition function in terms of the Boltzmann factor which is appropriate for states sampled in terms of the scaled coordinates as

$$\Delta_{NpT} = \frac{1}{\mathcal{V}^N \Omega^N N! V_0} \int dV \int d\vec{r}^{*N} \int d\vec{\omega}^N \exp\left(\frac{-U + pV - Nk_B T \ln V}{k_B T}\right). \quad (27)$$

The probability of finding the system in a given state is thus given by

$$\Pi = \frac{1}{\mathcal{V}^N \Omega^N N! V_0} \frac{\exp\left(-\frac{U + pV - Nk_B T \ln V}{k_B T}\right)}{\Delta_{NpT}} d\vec{r}^{*N} d\vec{\omega}^N dV. \quad (28)$$

3.1. Detailed balance and acceptance criteria

Invoking the condition of detailed balance (or microscopic reversibility) allows one to evaluate the acceptance criterion for moves to less favourable states in importance sampling schemes, such as the Metropolis Monte Carlo algorithm [36]. Although this is described in detail in standard texts (e.g., see references [1, 2]) it is helpful to review briefly the important ideas.

The condition of detailed balance requires that the probability of finding a state i and moving to state j must be equal to the probability of finding a state j and making the reverse move to state i . We can write and rearrange this in the following form:

$$\Pi_i P_{i \rightarrow j} = \Pi_j P_{j \rightarrow i} \Rightarrow \frac{P_{i \rightarrow j}}{P_{j \rightarrow i}} = \frac{\Pi_j}{\Pi_i}, \quad (29)$$

where Π_i and Π_j denote the probabilities of the system being in state i and j respectively; $P_{i \rightarrow j}$ and $P_{j \rightarrow i}$ are the transition probabilities of moves between states i and j with the direction of the move indicated by the subscript. In the case of Monte Carlo simulations in the isothermal-isobaric ensemble the ratio Π_j/Π_i on

right-hand side of equation 29 can be written explicitly with the use of equation 28:

$$\begin{aligned} \frac{\Pi_j}{\Pi_i} &= \frac{\exp\left(-\frac{U_j + pV_j - Nk_B T \ln V_j}{k_B T}\right)}{\exp\left(-\frac{U_i + pV_i - Nk_B T \ln V_i}{k_B T}\right)} \\ &= \exp\left(-\frac{\Delta U_{i \rightarrow j} + p\Delta V_{i \rightarrow j} - Nk_B T \ln\left(\frac{V_j}{V_i}\right)}{k_B T}\right). \end{aligned} \quad (30)$$

Writing like this allows us to express the relative probability in terms of an enthalpic contribution of a given state H , where $H = U + pV - Nk_B T \ln V$ (note that the additional term $-Nk_B T \ln V$ here is due to the volume scaling employed in the simulation):

$$\frac{P_{i \rightarrow j}}{P_{j \rightarrow i}} = \frac{\Pi_j}{\Pi_i} = \exp\left(-\frac{\Delta H_{i \rightarrow j}}{k_B T}\right). \quad (31)$$

Before continuing it is useful first to consider the standard Metropolis Monte Carlo algorithm[36] for systems in the canonical ensemble. In this case equation 30 is much simpler as $\Delta V_{i \rightarrow j} = 0$ and $V_j/V_i = 1$. For constant NVT ensembles we now have:

$$\left(\frac{P_{i \rightarrow j}}{P_{j \rightarrow i}}\right)_{NVT} = \left(\frac{\Pi_j}{\Pi_i}\right)_{NVT} = \exp\left(-\frac{\Delta U_{i \rightarrow j}}{k_B T}\right)_{NVT}. \quad (32)$$

When a move is attempted to a state with a lower energy than the current state, it is accepted. Moves to states which have a higher energy are accepted with a prescribed probability of acceptance. In mathematical terms, if $\Delta U_{i \rightarrow j} < 0$, then since $\Delta U_{i \rightarrow j} = U_j - U_i = -\Delta U_{j \rightarrow i}$ it is clear that for the reverse move $\Delta U_{j \rightarrow i} > 0$. Since moves to lower-energy states are always accepted, $(P_{i \rightarrow j})_{NVT} = 1$. From equation 32 one obtains

$$(P_{j \rightarrow i})_{NVT} = \exp\left(-\frac{\Delta U_{j \rightarrow i}}{k_B T}\right)_{NVT}. \quad (33)$$

Equation 33 represents, of course, the well-known Metropolis acceptance criterion for moves to higher-energy states; this criterion is thus seen to be a consequence of the condition of detailed balance.

We now turn our attention back to the isothermal-isobaric ensemble. This time the change in the ‘‘instantaneous’’ enthalpy, rather than the energy, has to be considered. Correspondingly, if the enthalpy change $\Delta H_{i \rightarrow j}$ from equation 31 is less than zero, then a move from state i to state j must be accepted [34]. The analogy with the NVT scheme is that now we choose always to accept a move if $\Delta H_{i \rightarrow j}$ (instead of $\Delta U_{i \rightarrow j}$) is less than zero, *i.e.*, we take the transition probability of this move to be unity:

$$[P_{i \rightarrow j} = 1]_{\Delta H_{i \rightarrow j} < 0}. \quad (34)$$

If we make the reverse move from j to i then the enthalpy change $\Delta H_{j \rightarrow i}$ must now

be positive, since $\Delta H_{j \rightarrow i} = H_j - H_i = -\Delta H_{i \rightarrow j}$. Using this relation and $P_{i \rightarrow j} = 1$ in equation 31, we find that the corresponding condition of detailed balance is

$$\left[P_{j \rightarrow i} = \exp\left(-\frac{\Delta H_{j \rightarrow i}}{k_B T}\right) \right]_{\Delta H_{j \rightarrow i} > 0}. \quad (35)$$

Equations 34 and 35 are the sufficient transition probabilities for the isothermal-isobaric ensemble; these two expressions define the acceptance criteria for moves made during a MC- NpT simulation, based upon the requirement of detailed balance. In the next section we will examine how these relations can be used to determine the general form of the system pressure.

3.2. Computing the pressure at equilibrium

Now we consider an MC- NpT simulation at thermal and mechanical equilibrium. At equilibrium we may say that, on average, moves to a larger volume must be balanced by moves to a smaller volume. If this were not the case then the system would tend systematically to larger or smaller volumes and would clearly not be at equilibrium. We take i to be a representative state at equilibrium. If $\Delta V_{i \rightarrow j+}$ represents the change in volume for an attempted move to a larger volume and $P_{i \rightarrow j+}$ the corresponding transition probability, then the total positive change of volume that is actually made during a simulation is given by

$$\sum_{\mathcal{N}^+} \Delta V_{i \rightarrow j+} P_{i \rightarrow j+}, \quad (36)$$

where \mathcal{N}^+ is the number of moves attempted to a larger volume. Equation 36 must be balanced by that for the total negative change in volume if the system is at equilibrium:

$$\sum_{\mathcal{N}^+} \Delta V_{i \rightarrow j+} P_{i \rightarrow j+} = - \sum_{\mathcal{N}^-} \Delta V_{i \rightarrow j-} P_{i \rightarrow j-}, \quad (37)$$

where \mathcal{N}^- is the number of moves attempted to a smaller volume, $\Delta V_{i \rightarrow j-}$ is the volume change of those moves, and $P_{i \rightarrow j-}$ the corresponding transition probability. Since the sign of each attempted volume change is random, then to very good approximation we can write:

$$\mathcal{N}^+ = \mathcal{N}^- = \frac{\mathcal{N}}{2}, \quad (38)$$

where \mathcal{N} is the total number of attempted volume changes. This relation is exact in the limit of an infinite number of volume changes. Clearly:

$$\frac{2}{\mathcal{N}} \sum_{\mathcal{N}^+} \Delta V_{i \rightarrow j+} P_{i \rightarrow j+} = \frac{2}{\mathcal{N}} \sum_{\mathcal{N}^-} -\Delta V_{i \rightarrow j-} P_{i \rightarrow j-}, \quad (39)$$

i.e.,

$$\langle \Delta V_{i \rightarrow j+} P_{i \rightarrow j+} \rangle_{\text{eq}} = - \langle \Delta V_{i \rightarrow j-} P_{i \rightarrow j-} \rangle_{\text{eq}}. \quad (40)$$

The subscripts here signify that this relation is valid only at equilibrium.

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We now restrict ourselves to purely repulsive (hard-body) interactions and examine the implications of equations 34, 35 and 40. With this notation the enthalpy change from an increase in volume is given by

$$\Delta H_{i \rightarrow j+} = \Delta U_{i \rightarrow j+} + p \Delta V_{i \rightarrow j+} - N k_B T \ln \left(\frac{V_{j+}}{V_i} \right). \quad (41)$$

Here, V_{j+}/V_i is replaced by $(V_i + \Delta V_{i \rightarrow j+})/V_i = 1 + (\Delta V_{i \rightarrow j+}/V_i)$. Assuming that $\Delta V_{i \rightarrow j+}/V_i$ is small, we can make the following approximation: $\ln(1 + (\Delta V_{i \rightarrow j+}/V_i)) \approx \Delta V_{i \rightarrow j+}/V_i$. This gives

$$\begin{aligned} \Delta H_{i \rightarrow j+} &= \Delta U_{i \rightarrow j+} + p \Delta V_{i \rightarrow j+} - N k_B T \frac{\Delta V_{i \rightarrow j+}}{V_i} \\ &= \Delta U_{i \rightarrow j+} + \Delta V_{i \rightarrow j+} \left(p - \frac{N k_B T}{V_i} \right). \end{aligned} \quad (42)$$

This relation is valid in the limit of $\Delta V_{i \rightarrow j+} \rightarrow 0$. For the sake of compactness this limit will be omitted from the derivation for the moment. In equation 42, $N k_B T/V_i$, which is the pressure of an ideal gas, must by definition be less than that of the a hard-body system. Therefore for a small positive volume change (expansion) the second term in equation 42 will always be positive. Meanwhile for hard-body systems $\Delta U_{i \rightarrow j+}$ will take one of two values, either zero (for configurations with no overlaps) or infinity (when an overlap between a pair of molecules occurs). Hence, for hard-body systems, the right-hand side of equation 42 and therefore the enthalpy change (associated with a small positive volume change), will always be positive. Recalling equation 35 for positive enthalpy changes we can see that the transition probability for an increase in volume for a hard-body system can be written as

$$P_{i \rightarrow j+} = \exp \left(- \frac{\Delta U_{i \rightarrow j+} + p \Delta V_{i \rightarrow j+} - N k_B T \ln \left(1 + \frac{\Delta V_{i \rightarrow j+}}{V_i} \right)}{k_B T} \right). \quad (43)$$

We now apply the same reasoning to a volume reduction (compression) from an equilibrium state. Here a form of equation 42 is used with the subscripts altered to indicate the reduction in volume:

$$\Delta H_{i \rightarrow j-} = \Delta U_{i \rightarrow j-} + \Delta V_{i \rightarrow j-} \left(p - \frac{N k_B T}{V_i} \right). \quad (44)$$

In this case we have that the volume change is negative so (for small volume changes) the second term of equation 44 is always less than zero. Here one must consider the two possible values of $\Delta U_{i \rightarrow j-}$ separately. For the case when there are no overlapping molecules $\Delta U_{i \rightarrow j-} = 0$, and so $\Delta H_{i \rightarrow j-} < 0$. From equation 34 it is evident that the transition probability for a negative enthalpy change is equal to one

$$[P_{i \rightarrow j-} = 1]_{\Delta U_{i \rightarrow j-} = 0}. \quad (45)$$

For the case when there are overlapping molecules $\Delta U_{i \rightarrow j-} = \infty$ and clearly now $\Delta H_{i \rightarrow j-} = \infty$. The enthalpy change is now irrefutably larger than zero so from

equation 35 we can say that the transition probability is given as

$$\left[P_{i \rightarrow j-} = \exp \left(- \frac{\Delta U_{i \rightarrow j-} + \Delta V_{i \rightarrow j-} \left(p - \frac{Nk_B T}{V_i} \right)}{k_B T} \right) = 0 \right]_{\Delta U_{i \rightarrow j-} = \infty} \quad (46)$$

Equations 45 and 46 give us the forms of the transition probability for the two possible values of $\Delta U_{i \rightarrow j-}$. It would be very convenient for us to be able to write a single expression that is valid in both cases. An expression that satisfies these conditions is $P_{i \rightarrow j-} = \exp(-\Delta U_{i \rightarrow j-}/k_B T)$:

$$P_{i \rightarrow j-} = \exp \left(- \frac{\Delta U_{i \rightarrow j-}}{k_B T} \right) \begin{cases} = 1; & \text{if } \Delta U_{i \rightarrow j-} = 0 \\ = 0; & \text{if } \Delta U_{i \rightarrow j-} = \infty \end{cases} \quad (47)$$

Both of the transition-probability terms in equation 40 have now been derived. The substitution of equations 43 and 47 into equation 40 gives:

$$\begin{aligned} & \left\langle -\Delta V_{i \rightarrow j-} \exp \left(- \frac{\Delta U_{i \rightarrow j-}}{k_B T} \right) \right\rangle_{\text{eq}} = \\ & \left\langle \Delta V_{i \rightarrow j+} \exp \left(- \frac{\Delta U_{i \rightarrow j+} + p\Delta V_{i \rightarrow j+} - Nk_B T \ln \left(1 + \frac{\Delta V_{i \rightarrow j+}}{V_i} \right)}{k_B T} \right) \right\rangle_{\text{eq}} \quad (48) \end{aligned}$$

Equation 48 is valid in the NpT ensemble (and could be used to independently estimate the pressure), however it is not especially useful in its current form. To proceed, it is instructive to consider first the case where the magnitudes of the attempted volume changes are constant, *i.e.*, $\Delta V_{i \rightarrow j+} = -\Delta V_{i \rightarrow j-}$. These prefactors now come out of the averaging brackets and cancel:

$$\begin{aligned} & \left\langle \exp \left(- \frac{\Delta U_{i \rightarrow j-}}{k_B T} \right) \right\rangle_{\text{eq}} = \\ & \exp \left(- \frac{p\Delta V_{i \rightarrow j+}}{k_B T} \right) \left\langle \exp \left(- \frac{\Delta U_{i \rightarrow j+} - Nk_B T \ln \left(1 + \frac{\Delta V_{i \rightarrow j+}}{V_i} \right)}{k_B T} \right) \right\rangle_{\text{eq}} \quad (49) \end{aligned}$$

Rearranging and taking logarithms:

$$\begin{aligned} \frac{p\Delta V_{i \rightarrow j+}}{k_B T} &= \ln \left\langle \exp \left(- \frac{\Delta U_{i \rightarrow j+} - Nk_B T \ln \left(1 + \frac{\Delta V_{i \rightarrow j+}}{V_i} \right)}{k_B T} \right) \right\rangle_{\text{eq}} \\ &\quad - \ln \left\langle \exp \left(- \frac{\Delta U_{i \rightarrow j-}}{k_B T} \right) \right\rangle_{\text{eq}} \quad (50) \end{aligned}$$

We now go on to illustrate how equation 50 contains the information we require for the calculation of the pressure in the NVT ensemble. One way to calculate

the pressure in the NVT ensemble is to employ a volume perturbation scheme. Each perturbation effectively corresponds to a ghost volume deformation in the NpT ensemble. This has the very convenient benefit that p is constant during each perturbation. In an NVT simulation V_i will always be constant and is unaltered by the perturbation (since this represents the volume of the unperturbed simulation cell). Assuming that the magnitudes of the attempted volume changes are constant, the ratio $\Delta V_{i \rightarrow j+}/V_i$ is a constant and may be taken outside of the averaging brackets:

$$\frac{p\Delta V_{i \rightarrow j+}}{k_B T} = N \ln \left(1 + \frac{\Delta V_{i \rightarrow j+}}{V_i} \right) + \ln \left\langle \exp \left(-\frac{\Delta U_{i \rightarrow j+}}{k_B T} \right) \right\rangle_{\text{eq}} - \ln \left\langle \exp \left(-\frac{\Delta U_{i \rightarrow j-}}{k_B T} \right) \right\rangle_{\text{eq}}. \quad (51)$$

Once more we make use of the approximation $\ln(1 + (\Delta V_{i \rightarrow j+}/V_i)) \approx \Delta V_{i \rightarrow j+}/V_i$, which is valid in the limit of $\Delta V_{i \rightarrow j+} \rightarrow 0$. We also divide both sides of equation 50 by $\Delta V_{i \rightarrow j+}/k_B T$ and recall that $\Delta V_{i \rightarrow j+} = -\Delta V_{i \rightarrow j-}$ to give an expression for the pressure as (with the correct limits of validity now shown explicitly)

$$p = \frac{Nk_B T}{V_i} + \lim_{\Delta V_{i \rightarrow j+} \rightarrow 0} \frac{k_B T}{\Delta V_{i \rightarrow j+}} \ln \left\langle \exp \left(-\frac{\Delta U_{i \rightarrow j+}}{k_B T} \right) \right\rangle_{\text{eq}} + \lim_{\Delta V_{i \rightarrow j-} \rightarrow 0} \frac{k_B T}{\Delta V_{i \rightarrow j-}} \ln \left\langle \exp \left(-\frac{\Delta U_{i \rightarrow j-}}{k_B T} \right) \right\rangle_{\text{eq}}. \quad (52)$$

There are clearly three contributions to the pressure: the first term in equation 52 represents the ideal contribution; the second term is the contribution to the residual (in excess of ideal) pressure from ghost volume expansions; similarly, the final term is the contribution to the residual pressure from ghost volume compressions. One should note that though expression 52 strictly should be used only in the NVT ensemble, although it is in practice also appropriate for an independent computation of the equilibrium pressure in the NpT ensemble for small volume perturbations; in the latter case one should strictly retain the volume of each state inside the average and use an expression of the form of equation 48, but the volume will remain very close to its equilibrium value $V_i \approx V_{\text{eq}}$ for systems of moderate to large size.

As shown by Eppenga and Frenkel[8] for hard-body molecules a further notational simplification may be made for the exponential terms. As discussed previously, for such molecules the exponential terms in equation 52 can take one of only two values: unity for perturbations leading to states with no overlapping molecules or zero for perturbations which would lead to states where molecules overlap. When averaged over many states for a fixed volume change, $\langle \exp(-\Delta U_{i \rightarrow j+}/k_B T) \rangle_{\text{eq}}$ and $\langle \exp(-\Delta U_{i \rightarrow j-}/k_B T) \rangle_{\text{eq}}$ become the probabilities of no overlaps occurring for the particular volume perturbation, which are denoted by $P_{\text{nov}+}$ and $P_{\text{nov}-}$. Our equation for the pressure is now given as

$$p = \frac{Nk_B T}{V} + \lim_{\Delta V_{i \rightarrow j+} \rightarrow 0} \frac{k_B T}{\Delta V_{i \rightarrow j+}} \ln P_{\text{nov}+} + \lim_{\Delta V_{i \rightarrow j-} \rightarrow 0} \frac{k_B T}{\Delta V_{i \rightarrow j-}} \ln P_{\text{nov}-}. \quad (53)$$

The contributions to the residual pressure from the volume expansions and compression are now cast in terms of the probabilities $P_{\text{nov}+}$ and $P_{\text{nov}-}$; note that in this expression V_i has been replaced by V as there is no change in volume in this

ensemble.

This expression can be used to calculate the pressure from simulations of hard-body molecules performed in the NVT ensemble through a series of ‘ghost’ volume perturbations. The pressure may be found by the determination of P_{nov+} and P_{nov-} in the limit of the change in volume approaching zero. These terms are easily obtained and so this method offers an attractive route for the pressure calculation of hard-body systems. Volume perturbations are also made naturally in the NpT ensemble and thus during each perturbation the pressure is constant; this offers an independent route to the calculation of the probabilities P_{nov+} and P_{nov-} and an independent check of expression 53 for the pressure.

4. Calculating components of the pressure tensor with anisotropic volume perturbations

The pressure of a homogeneous system is a scalar quantity, however with inhomogeneous systems the pressure is a tensor. A slightly different approach is required when one employs volume perturbations approaches in such systems.

If, instead of isotropically, the volume scaling during the perturbations is performed anisotropically by changing the length of one of the simulation cell axes only, one can determine these tensorial components of the pressure. Using the methods outlined in section 2 one can obtain the tensorial components of the pressure for hard-sphere systems with only a slight adjustment to the equations as detailed in previous work. [11] However for non-spherical (anisometric) hard particles a different method is required.

In Figure 2 it is demonstrated how for hard convex molecules (in this example hard spherocylinders) undergoing an anisotropic volume change overlaps may occur upon an increase in volume. This part of the repulsive interaction that a convex molecule exerts upon its surroundings needs to be taken into account. This is an important point to remember not only for the calculation of the pressure tensor in constant-volume simulations, but also in maintaining the pressure in constant-tensorial-pressure (constant stress) simulations of inhomogeneous systems. Constant stress simulations of this type are almost invariably carried out within a molecular dynamics (MD) framework [37–39]. Though their use within a Monte Carlo simulation is less common (see, e.g., references [40–43]) it is straightforward and somewhat simpler to implement in MC than in MD.

For convex hard-body molecules one could employ the method presented by Allen [21] to estimate the components of the pressure tensor with isotropic perturbative volume compressions. This requires the calculation of the vector normal to the common tangent plane at the point of contact between two overlapping molecules. This vector is used to apportion the correct contribution of the residual pressure to each of the cartesian axes from each overlapping pair of molecules. While this is a straightforward check to perform for convex bodies such as hard ellipsoids [44], the procedure is more complicated for molecules (and mixtures of molecules) of general shape or even for deceptively simple models such hard spherocylinders and hard disks.

The method we suggest here can be employed for the calculation of the components of the pressure tensor for molecules of general shape and interactions, and there is the added advantage that no more knowledge is required than the molecule-molecule overlap check, which is in any case necessary for the implementation of the Monte Carlo algorithm. By making the appropriate modifications to the derivations illustrated in section 3, we show how the tensorial components of the pressure can be formulated in an equivalent manner. One needs only to prove

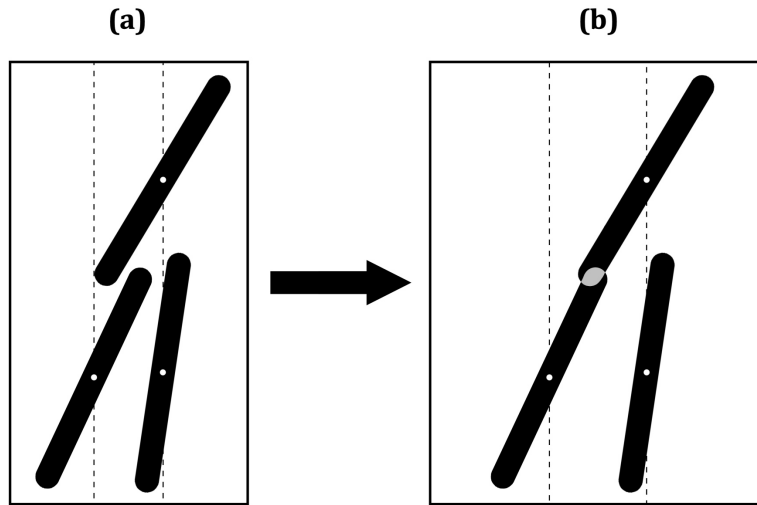


Figure 2. The occurrence of a molecule-molecule overlap in a system of hard spherocylinders. The system in (a) is unperturbed, while in (b) the same system is shown following an anisotropic expansion in the volume in which only the horizontal axis is scaled. Each molecules centre of mass is indicated by white dots. The presence of an overlap is indicated by the area shaded in grey.

that the first part of the derivation provides an almost identical expression for the transitional probability. It is then apparent that following the remaining steps will lead to an equivalent final expression.

The partition function of a system with a constant tensorial component of pressure (labelled here as $p_{\alpha\alpha}$ to denote the generic Cartesian axis α), number of molecules, temperature and area (in this case $A = L_\beta L_\gamma$ in the $\beta - \gamma$ plane perpendicular to α axis) may be written as

$$\Delta_{Np_{\alpha\alpha}TA} = \frac{1}{\mathcal{V}^N \Omega^N N! V_0} \int dV \int d\vec{r}^N \int d\vec{\omega}^N \exp\left(-\frac{U + p_{\alpha\alpha}V}{k_B T}\right). \quad (54)$$

The subscript $Np_{\alpha\alpha}TA$ here indicates the parameters that are constant in this ensemble. From equation 54 we can scale the molecular coordinates in the usual way to dimensionless quantities in terms of the system box lengths L_α , L_β , and L_γ with the positions defined relative to these axes such that if $\alpha = x$, $\beta = y$ and $\gamma = z$ then $x = x^*L_x$, $y = y^*L_y$ and $z = z^*L_z$. In this case $d\vec{r}^N = (L_\alpha L_\beta L_\gamma)^N d\vec{r}^{*N}$, and thus we write:

$$\Delta_{Np_{\alpha\alpha}TA} = \frac{1}{\mathcal{V}^N \Omega^N N! V_0} \int d(L_\alpha L_\beta L_\gamma) (L_\alpha L_\beta L_\gamma)^N \int d\vec{r}^{*N} \int d\vec{\omega}^N \exp\left(-\frac{U + p_{\alpha\alpha}V}{k_B T}\right). \quad (55)$$

Since the volume perturbations in this ensemble are made by scaling only the α axis, L_β and L_γ will remain constant during the perturbations. Equation 55 can then be expressed as rearranged as

$$\Delta_{Np_{\alpha\alpha}TA} = \frac{L_\beta^{N+1} L_\gamma^{N+1}}{\mathcal{V}^N \Omega^N N! V_0} \int dL_\alpha L_\alpha^N \int d\vec{r}^{*N} \int d\vec{\omega}^N \exp\left(-\frac{U + p_{\alpha\alpha}V}{k_B T}\right). \quad (56)$$

One can express this relation as an effective Boltzmann factor by including the

perturbed system box length, L_α^N , in of the exponential function:

$$\Delta_{Np_{\alpha\alpha}TA} = \frac{L_\beta^{N+1} L_\gamma^{N+1}}{\mathcal{V}^N \Omega^N N! V_0} \int dL \int d\vec{r}^{*N} \int d\vec{\omega}^N \exp\left(-\frac{U + p_{\alpha\alpha}V - Nk_B T \ln L_\alpha}{k_B T}\right). \quad (57)$$

In this ensemble the probability of finding the system in a given state is:

$$\Pi = \frac{L_\beta^{N+1} L_\gamma^{N+1} \exp\left(-\frac{U + p_{\alpha\alpha}V - Nk_B T \ln L_\alpha}{k_B T}\right)}{\mathcal{V}^N \Omega^N N! V_0 \Delta_{Np_{\alpha\alpha}TA}} d\vec{r}^{*N} d\vec{\omega}^N dL_\alpha. \quad (58)$$

The ratio of the probabilities of two different states, i and j , is now given by

$$\begin{aligned} \frac{\Pi_j}{\Pi_i} &= \frac{\exp\left(-\frac{U_j + p_{\alpha\alpha}V_j - Nk_B T \ln L_j}{k_B T}\right)}{\exp\left(-\frac{U_i + p_{\alpha\alpha}V_i - Nk_B T \ln L_i}{k_B T}\right)} \\ &= \exp\left(-\frac{\Delta U_{i \rightarrow j} + p_{\alpha\alpha} \Delta V_{i \rightarrow j}^\alpha - Nk_B T \ln\left(\frac{L_j}{L_i}\right)}{k_B T}\right). \end{aligned} \quad (59)$$

Here the superscript α is used to denote that the volume is changed by perturbing the box length in the α direction only. The ratio L_j/L_i is of course equivalent to the ratio of the volumes of the two states V_j/V_i , and we can write

$$\frac{\Pi_j}{\Pi_i} = \exp\left(-\frac{\Delta U_{i \rightarrow j} + p_{\alpha\alpha} \Delta V_{i \rightarrow j}^\alpha - Nk_B T \ln\left(\frac{V_j}{V_i}\right)}{k_B T}\right). \quad (60)$$

This is of the same form as equation 30. Following the rest of the derivation from equations 30 to 53 leads to our final equivalent expression for the component of the pressure tensor:

$$p_{\alpha\alpha} = \frac{Nk_B T}{V} + \lim_{\Delta V_{i \rightarrow j}^+ \rightarrow 0} \frac{k_B T}{\Delta V_{i \rightarrow j}^+} \ln P_{nov+} + \lim_{\Delta V_{i \rightarrow j}^- \rightarrow 0} \frac{k_B T}{\Delta V_{i \rightarrow j}^-} \ln P_{nov-}; \quad (61)$$

note that as previously (in equation 53) V_i has been replaced by V in this expression.

Though deceptively equation 61 appears to be identical to equation 53 for the scalar pressure of the isotropic system, it is important to recall that the ghost volume perturbations and the corresponding overlap probabilities are now for anisotropic deformations along a single direction (here denoted by α).

5. Results

A detailed analysis of the approach outlined in the previous sections is made here for a number of carefully selected systems to demonstrate the accuracy of the perturbation method in evaluations of the pressure and pressure tensor. Starting with

a very simple test of Monte Carlo simulations of hard spheres in the isothermal-isobaric ensemble, where the pressure is known exactly, we then examine the adequacy of the technique when applied to systems in the canonical ensemble. A comparison is made with published simulation data and theoretical predictions. The results from Monte Carlo simulations of hard spherocylinders are then shown in both of these ensembles. Finally, we briefly examine the applicability of the approach for the determination of the interfacial tension of inhomogeneous systems of hard spherocylinders confined between two parallel structureless hard walls. In the following the numerical values of pressure are expressed in dimensionless units: $p^* = pV_m/k_B T$ where V_m is the volume of a molecule.

5.1. Systems of hard spheres

A simple and straightforward assessment of the perturbation method can be made by applying it to systems of hard spheres in the constant NpT isothermal-isobaric ensemble over a range of pressures in the fluid state. Here, we have the advantage of being able to set the value for the pressure and therefore know precisely what to expect from the estimates of the pressure obtained with the perturbation scheme.

Each of our simulated systems comprises $N = 256$ hard spheres in a perfect cubic cell with standard periodic boundaries. The isothermal-isobaric Monte Carlo simulations (MC- NpT) are carried out in the standard manner with isotropic changes in the volume of the simulation cell with equivalent isotropic changes in the scaled particle positions in the three Cartesian axes [1, 2]. The initial configuration is a face-centred cubic lattice, and the simulations are performed for pressures ranging from a dilute gas to the dense fluid. Once equilibrium is achieved after $\sim 2 \times 10^7$ cycles we begin a run of 8×10^7 cycles, each cycle comprising N trial molecule displacements, and one trial volume change (perturbation) is made every 20 cycles. To maintain microscopic reversibility for each move, the molecule to be displaced or the volume change is randomly selected at each step. The average density (packing fraction $\eta = NV_m/V$) of the cell corresponding to the pressure that is set is obtained as a configurational average. As a test of our methodology we also carry out a separate set of standard Metropolis Monte Carlo (MC- NVT) for systems with densities corresponding to the equilibrium densities of the MC- NpT simulations. In this case we run 2×10^7 cycles for equilibration and 1.5×10^8 cycles to accumulate the averages, with a cycle again corresponding to N trial particle displacement.

Volume perturbations are made once every 20 cycles in both the NVT and NpT ensembles: the simulation is temporarily paused and volume perturbations are made to the current state before the simulation is allowed to resume once more from the point at which it was paused. During each perturbation the system cell volume is scaled, at first isotropically so that all box lengths are changed in proportion to each other and all molecule positions scale such that their positions relative to each axis remain the same. Subsequently, anisotropic volume perturbations are made, in which only one axis is scaled at a time; the molecule coordinates are scaled only in the cartesian axis to which the perturbation is made. In the case of the MC- NpT simulations the perturbations can give rise to new states with different system volumes, while for MC- NVT simulations the only “ghost” perturbations are made enabling one to estimate the bulk pressure and its tensorial components. During each volume perturbation, data are collected and recorded detailing how many overlapping pairs of molecules would be brought about by that perturbation. Twenty evenly spaced values of the relative volume change $\Delta V/V$ (ranging from 0.00300 to 0.00015) are tested during the perturbations and the overlaps recorded; this is to allow extrapolation to find the contribution to the residual pressure at

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Table 1. The pressure and pressure tensor for systems of $N = 256$ hard spheres obtained from Monte Carlo simulations in the isothermal-isobaric ensemble (MC- NpT), using isotropic (indicated by the subscript xyz) and anisotropic (with the subscripts xx , yy and zz to indicate the perturbed axis) volume perturbations. The pressure is given in the non-dimensional form of $p^* = pV_m/k_B T$ where V_m is the volume of a molecule. The average packing fraction η of each system and also corresponds to the ideal contribution to the reduced pressure. The columns denoted by p^{*+} and p^{*-} represent the contributions to the residual pressure from an expansion and a compression, respectively. The calculated pressure, p^* , is the sum of the ideal (η) and the residual (p^{*+} and p^{*-}) contributions. The pressure at which each system is simulated during the period of averaging is denoted by p_{input}^* . AAD% is the absolute average deviation of the pressure obtained with the volume perturbation approach with respect to the input pressure.

η	p_{xyz}^{*-}	p_{xyz}^{*+}	p_{xyz}^*	p_{input}^*	AAD%
0.2498 ± 0.0003	0.5172 ± 0.0049	0	0.7670 ± 0.0052	0.7685	0.20
0.3001 ± 0.0002	0.9029 ± 0.0157	0	1.2029 ± 0.0159	1.1921	0.90
0.3496 ± 0.0002	1.4752 ± 0.0194	0	1.8248 ± 0.0196	1.8220	0.15
0.3996 ± 0.0002	2.3563 ± 0.0237	0	2.7559 ± 0.0239	2.7704	0.52
η	p_{xx}^{*-}	p_{xx}^{*+}	p_{xx}^*	p_{input}^*	AAD%
0.2498 ± 0.0003	0.5172 ± 0.0049	0	0.7669 ± 0.0052	0.7685	0.21
0.3001 ± 0.0002	0.9027 ± 0.0155	0	1.2027 ± 0.0157	1.1921	0.89
0.3496 ± 0.0002	1.4725 ± 0.0191	0	1.8221 ± 0.0193	1.8220	0.00
0.3996 ± 0.0002	2.3552 ± 0.0213	0	2.7547 ± 0.0215	2.7704	0.56
η	p_{yy}^{*-}	p_{yy}^{*+}	p_{yy}^*	p_{input}^*	AAD%
0.2498 ± 0.0003	0.5172 ± 0.0050	0	0.7670 ± 0.0053	0.7685	0.20
0.3001 ± 0.0002	0.9011 ± 0.0157	0	1.2012 ± 0.0159	1.1921	0.76
0.3496 ± 0.0002	1.4754 ± 0.0199	0	1.8250 ± 0.0201	1.8220	0.16
0.3996 ± 0.0002	2.3524 ± 0.0238	0	2.7520 ± 0.0240	2.7704	0.66
η	p_{zz}^{*-}	p_{zz}^{*+}	p_{zz}^*	p_{input}^*	AAD%
0.2498 ± 0.0003	0.5174 ± 0.0049	0	0.7672 ± 0.0052	0.7685	0.18
0.3001 ± 0.0002	0.9026 ± 0.0161	0	1.2027 ± 0.0163	1.1921	0.88
0.3496 ± 0.0002	1.4743 ± 0.0198	0	1.8239 ± 0.0200	1.8220	0.10
0.3996 ± 0.0002	2.3557 ± 0.0269	0	2.7553 ± 0.0271	2.7704	0.54

$\Delta V/V = 0$. The actual range of values for the ghost relative volume changes are similar to those employed in previous work [11, 22], though in general one performs exploratory simulations to find the range that will give the best numerical estimates of the pressure. Volume perturbations are made for both expansions and compressions in the system volume with separate isotropic and anisotropic volume scaling.

For the case of hard spheres we already know that there will be no overlaps brought about by an increase in volume, either for isotropic or anisotropic volume scaling, thus these perturbations, if performed, would not contribute to the residual part of the pressure and pressure tensors. However as described in section 3 this is not generally the case for non-spherical molecules.

The results from the four isothermal-isobaric simulations of hard-spheres are presented in table 1. The system pressure is calculated from perturbations using equation 53, and the x , y and z tensorial pressure components are calculated using equation 61. As can be clearly seen the perturbation method gives results within a 1% deviation for the set NpT system pressures that are investigated; one could use the more formal expression (48) which is in the most appropriate form for the NpT ensemble but we did not find this to be necessary in practice.

For our analysis with the canonical ensemble a comparison is made with previously calculated pressures for hard-sphere systems from volume perturbations [11], as well as theoretical predictions. The accuracy of the Carnahan and Starling equation [45] in predicting the pressure of hard-sphere systems is now well established (e.g., see the recent work of Mulero *et al.* [46]); the early molecular-dynamics simulation data of Erpenbeck and Wood [47] show very close agreement with this

Table 2. The pressure and pressure tensor for systems of $N = 256$ hard spheres obtained from Monte Carlo simulations for a range of packing fractions in the canonical ensemble (MC- NVT), using isotropic (indicated by the subscript xyz) and anisotropic (the subscripts xx , yy and zz indicate the perturbed axis) volume perturbations. The pressure is given in the non-dimensional form of $p^* = pV_m/k_B T$ where V_m is the volume of a molecule. The columns denoted by p^{*+} and p^{*-} represent the contributions to the residual pressure from an expansion and a compression, respectively. The calculated pressure is the sum of the ideal (η) and the residual (p^{*+} and p^{*-}) contributions. p_{DMJ}^* is the pressure calculated from isotropic volume perturbations in previous work [11], while p_{CS}^* is the predicted pressure obtained from the Carnahan and Starling equation for hard spheres [45]. $AAD_{DMJ}\%$ and $AAD_{cs}\%$ are the corresponding absolute average deviation of the perturbations results from the DMJ and CS values.

η	p_{xyz}^{*-}	p_{xyz}^{*+}	p_{xyz}^*	p_{DMJ}^*	$AAD_{DMJ}\%$	p_{CS}^*	$AAD_{CS}\%$
0.25	0.5195 ± 0.0003	0	0.7695 ± 0.0003	0.7707	0.16	0.7685	0.13
0.30	0.8947 ± 0.0007	0	1.1947 ± 0.0007	1.1964	0.14	1.1921	0.22
0.35	1.4765 ± 0.0015	0	1.8265 ± 0.0015	1.8300	0.19	1.8220	0.25
0.40	2.3775 ± 0.0022	0	2.7775 ± 0.0022	2.7766	0.03	2.7704	0.26
η	p_{xx}^{*-}	p_{xx}^{*+}	p_{xx}^*	p_{DMJ}^*	$AAD_{DMJ}\%$	p_{CS}^*	$AAD_{CS}\%$
0.25	0.5189 ± 0.0003	0	0.7689 ± 0.0003	0.7707	0.24	0.7685	0.05
0.30	0.8939 ± 0.0013	0	1.1939 ± 0.0013	1.1964	0.21	1.1921	0.15
0.35	1.4746 ± 0.0009	0	1.8246 ± 0.0009	1.8300	0.30	1.8220	0.14
0.40	2.3744 ± 0.0020	0	2.7744 ± 0.0020	2.7766	0.08	2.7704	0.15
η	p_{yy}^{*-}	p_{yy}^{*+}	p_{yy}^*	p_{DMJ}^*	$AAD_{DMJ}\%$	p_{CS}^*	$AAD_{CS}\%$
0.25	0.5188 ± 0.0004	0	0.7688 ± 0.0004	0.7707	0.25	0.7685	0.03
0.30	0.8935 ± 0.0003	0	1.1935 ± 0.0003	1.1964	0.24	1.1921	0.12
0.35	1.4762 ± 0.0003	0	1.8262 ± 0.0003	1.8300	0.21	1.8220	0.23
0.40	2.3754 ± 0.0026	0	2.7754 ± 0.0026	2.7766	0.05	2.7704	0.18
η	p_{zz}^{*-}	p_{zz}^{*+}	p_{zz}^*	p_{DMJ}^*	$AAD_{DMJ}\%$	p_{CS}^*	$AAD_{CS}\%$
0.25	0.5191 ± 0.0002	0	0.7691 ± 0.0002	0.7707	0.22	0.7685	0.07
0.30	0.8946 ± 0.0008	0	1.1946 ± 0.0008	1.1964	0.15	1.1921	0.21
0.35	1.4732 ± 0.0011	0	1.8232 ± 0.0011	1.8300	0.37	1.8220	0.07
0.40	2.3732 ± 0.0016	0	2.7732 ± 0.0016	2.7766	0.12	2.7704	0.10

equation of state in the density region of interest. Hence the Carnahan and Starling relation provides both a straightforward and an excellent benchmark to assess our results.

Four separate systems are now examined in the canonical ensemble for values of the packing fraction which correspond to the pressures set in the isothermal-isobaric with Carnahan and Starling relation: $\eta = 0.25, 0.30, 0.35$ or 0.40 . The results from these MC- NVT simulations are presented in table 2. One may observe that the results obtained with the perturbation approach lie within 0.40% deviation of the previous data [11], which is to be expected as the method is essentially the same for hard spheres. When compared to the Carnahan and Starling equation of state [45] we see close agreement with no more than 0.30% deviation.

5.2. Systems of hard spherocylinders

Having confirmed the accuracy of the proposed perturbation method for systems of hard spheres in both the NpT and NVT ensembles, we shift our focus towards the more interesting and challenging systems of non-spherical molecules. We examine systems of $N = 256$ hard spherocylinders (hard cylinders of length L with hemispherical caps of diameter D on each end) with an aspect ratio characterised by $L/D = 5$, for states in the dense isotropic liquid and in the anisotropic nematic liquid-crystalline phase [48, 49]. The systems are first simulated in the isothermal-isobaric ensemble for 2×10^7 cycles (with volume perturbations every 20 cycles), at reduced pressures of $p^* = 3$ and 6 , until the equilibrium is reached, and a further 9×10^7 cycles are performed to obtain averages of the equilibrium packing fractions. Perturbations are made increasing and decreasing the system volume isotropically, and also anisotropically in each of the three cartesian axes. Details of

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Table 3. Simulation results for two systems of 256 hard spherocylinders, with a length to diameter ratio 5:1, in the isothermal-isobaric ensemble undergoing isotropic (indicated by a subscript xyz) and anisotropic (subscripts xx , yy and zz indicate the perturbed axis) volume perturbations. Pressures in a non-dimensional form of $p^* = pV_{\text{mol}}/k_B T$ where V_{mol} is the molecule volume. η is the average packing fraction and ideal contribution to the pressure. p^{*+} and p^{*-} are the contributions to the residual pressure from volume increases and reductions respectively. The calculated pressure, p^* , is the sum of the residual (p^{*+} and p^{*-}) and ideal (η) contributions. p_{input}^* is the inputted pressure of each system during the period of averaging. AAD% is the absolute average deviation of the perturbation results from the input pressure.

η	p_{xyz}^{*-}	p_{xyz}^{*+}	p_{xyz}^*	p_{input}^*	AAD%
0.3291 ± 0.0001	2.6581 ± 0.0355	0	2.9871 ± 0.0356	3.0000	0.43
0.4438 ± 0.0002	5.5628 ± 0.0808	0	6.0066 ± 0.0808	6.0000	0.11
η	p_{xx}^{*-}	p_{xx}^{*+}	p_{xx}^*	p_{input}^*	AAD%
0.3291 ± 0.0001	3.0149 ± 0.0378	-0.3591 ± 0.0068	2.9849 ± 0.0321	3.0000	0.50
0.4438 ± 0.0002	6.3088 ± 0.2766	-0.7533 ± 0.2809	5.9993 ± 0.0821	6.0000	0.01
η	p_{yy}^{*-}	p_{yy}^{*+}	p_{yy}^*	p_{input}^*	AAD%
0.3291 ± 0.0001	3.0189 ± 0.0396	-0.3586 ± 0.0051	2.9893 ± 0.0354	3.0000	0.36
0.4438 ± 0.0002	6.2051 ± 0.3347	-0.6399 ± 0.3241	6.0090 ± 0.0827	6.0000	0.15
η	p_{zz}^{*-}	p_{zz}^{*+}	p_{zz}^*	p_{input}^*	AAD%
0.3291 ± 0.0001	3.0152 ± 0.0388	-0.3597 ± 0.0061	2.9845 ± 0.0345	3.0000	0.52
0.4438 ± 0.0002	6.2701 ± 0.3352	-0.7081 ± 0.3146	6.0058 ± 0.0764	6.0000	0.10

these results are provided in table 3. The data obtained with the perturbation approach are all within a deviation of 0.6% from our input pressure. It is particularly pleasing that the methodology works just as well in the $p^* = 3$ liquid state as the $p^* = 6$ nematic state where one would expect some instantaneous anisotropies in the pressure (long equilibration runs are required). It is also interesting to note, for the tensorial pressure components, that the relative contributions to the pressure resulting from increases to the volume are relatively small and negative (tensile) compared with the larger positive (compressive) contributions from decreases in the volume.

Next the simulations are halted and the density fixed at the equilibrium packing fractions recorded from the preceding runs, before being resumed from this point onwards in the canonical ensemble. Averages are then taken over 6×10^7 Monte Carlo cycles with perturbations again being made to the system every 20 cycles. The results for the MC-NVT are shown in table 4. Here we see no more than 0.6% deviation from the original pressures in the corresponding MC-NpT simulations. As one would have hoped the results from table 3 and table 4 are gratifyingly similar.

5.3. Volume perturbations for inhomogeneous systems of hard particles and the calculation of interfacial tension

In this section we illustrate the simplicity with which our method may be adapted to the calculation of the interfacial tension of inhomogeneous hard-core systems. We briefly give details of the equations used and present a preliminary study of hard spherocylinders confined between two hard structureless walls. Note that this and further work relating to calculation of surface tensions will be presented in greater detail in a forthcoming publication.

There are three main routes for the determination the interfacial tension from molecular simulations [7]; the usual virial and thermodynamic relations and, in addition, methods based on finite-size scaling, such as the Landau free energy approach of Binder [50]. The results we present here are obtained using the pressure tensor relation for the surface tension, originating from the expression given by

Table 4. The pressure and pressure tensor for systems of $N = 256$ hard spherocylinders with an aspect ratio characterised by $L/D = 5$ obtained from Monte Carlo simulations in the canonical ensemble (MC- NVT) for packing fractions in isotropic ($\eta = 0.3291$) and nematic ($\eta = 0.4438$) states. These correspond to the average packing fractions at equilibrium pressures $p_{\text{input}}^* = 3$ and 6, respectively (data taken from MC- NpT simulations of the same system, cf. Table III). The pressure is given in the non-dimensional form of $p^* = pV_m/k_B T$ where V_m is the volume of a molecule. The pressures are determined from isotropic (indicated by the subscript xyz) and anisotropic (with the subscripts xx , yy and zz to indicate the perturbed axis) volume perturbations. The columns denoted by p^{*+} and p^{*-} represent the contribution to the residual pressure determined from expansions and compressions in the volume, respectively. The calculated pressure, p^* , is the sum of the ideal (η) and residual (p^{*+} and p^{*-}) contributions. AAD% is the absolute average deviation of the pressure obtained with the volume perturbation approach with respect to the pressure set in the MC- NpT simulations.

η	p_{xyz}^{*-}	p_{xyz}^{*+}	p_{xyz}^*	p_{NpT}^*	AAD%
0.3291	2.6729 ± 0.0078	0	3.0019 ± 0.0078	3.0000	0.06
0.4438	5.5691 ± 0.0218	0	6.0129 ± 0.0218	6.0000	0.21
η	p_{xx}^{*-}	p_{xx}^{*+}	p_{xx}^*	p_{NpT}^*	AAD%
0.3291	3.0291 ± 0.0101	-0.3624 ± 0.0023	2.9958 ± 0.0075	3.0000	0.14
0.4438	6.4124 ± 0.3260	-0.8307 ± 0.3040	6.0255 ± 0.0314	6.0000	0.42
η	p_{yy}^{*-}	p_{yy}^{*+}	p_{yy}^*	p_{NpT}^*	AAD%
0.3291	3.0350 ± 0.0086	-0.3606 ± 0.0032	3.0034 ± 0.0075	3.0000	0.11
0.4438	6.2457 ± 0.2586	-0.6633 ± 0.2835	6.0262 ± 0.0336	6.0000	0.44
η	p_{zz}^{*-}	p_{zz}^{*+}	p_{zz}^*	p_{NpT}^*	AAD%
0.3291	3.0309 ± 0.0085	-0.3626 ± 0.0030	2.9973 ± 0.0082	3.0000	0.09
0.4438	6.3594 ± 0.3604	-0.7679 ± 0.3570	6.0352 ± 0.0237	6.0000	0.59

Kirkwood and Buff [51] for planar interfaces [52]:

$$\gamma = \int_{-\infty}^{\infty} dz (p_N(z) - p_T(z)). \quad (62)$$

Here, we assume that the surface is in the $x-y$ plane so p_N is the tensorial pressure normal to the surface (in our case taken as $p_N = p_{zz}$) and p_T the tensorial pressure transverse to the surface ($p_T = p_{xx} = p_{yy}$). For systems with planar interfaces one can employ the mean-value theorem and write the expression in terms of the average values of the tensorial components $\int dz p_{\alpha\beta}(z) = L_z p_{\alpha\beta}$. [11] This allows the interfacial tension of our systems to be expressed conveniently in the form:

$$\gamma = L_z (p_N - p_T). \quad (63)$$

Two systems of hard spherocylinders with an aspect ratio of $L/D = 10$ are examined, one comprising $N = 100$ molecules and the other 200. There are standard periodic boundaries in two axes (x and y) while the third axis (z) is confined by two smooth impenetrable planar walls at $z = 0$ and $z = L_z$. The axes lengths are $L_x \approx 39.89D$, $L_y \approx 39.23D$ and $L_z \approx 43D$ in units of molecular diameters. The simulations are performed in the canonical ensemble for selected packing fractions in the isotropic and nematic liquid-crystalline states. A full examination of the fluid phase and interfacial behaviour of the system in the higher-density region will be explored in greater depth in a forthcoming publication. Values of the normal and tangential components of the pressure tensor of the confined system are obtained using the thermodynamic anisotropic test-volume equation 61 and the interfacial tension is then obtained from equation 63. However, note that as in our case the simulation cell comprises two walls (surfaces), the surface tension calculated using equation 63 must be divided by two to give the tension corresponding to a sin-

Table 5. The pressure tensor and surface tension for systems of hard spherocylinders characterised by an aspect ratio of $L/D = 10$ confined by two hard structureless walls ($L_z^* = L_z/D$ apart) obtained from Monte Carlo simulations in the canonical ensemble (MC-NVT) for overall packing fractions of $\eta = 0.0127, 0.0255, 0.1020$ and 0.2804 . The packing fractions in the bulk fluid (obtained as averages of the density profiles for the middle third of the system) are $\eta_{\text{bulk}} = 0.0141, 0.0277, 0.1047$ and 0.2742 . The tensorial components of the pressure are given in the non-dimensional form of $p_{\alpha\alpha}^* = p_{\alpha\alpha} V_m / k_B T$ where V_m is the volume of a molecule and $\alpha\alpha$ is the corresponding axis in which that component of the pressure acts. The pressure tensor is obtained from anisotropic volume perturbations in the xx , yy and zz axes. The columns denoted by $p_{\alpha\alpha}^{*+}$ and $p_{\alpha\alpha}^{*-}$ are the contribution to the residual tensorial pressure from expansions and compressions in the volume, respectively. The calculated tensorial pressure, $p_{\alpha\alpha}^*$, is the sum of the ideal (η_{bulk}) and residual ($p_{\alpha\alpha}^{*+}$ and $p_{\alpha\alpha}^{*-}$) contributions. The wall-particle interfacial tension of the systems is found from the relation: $\gamma^* = \gamma D^2 / k_B T = (1/2) (L_z D^2 / V_m) (p_{zz}^* - (1/2) [p_{xx}^* + p_{yy}^*])$. The systems with overall packing fractions of $\eta = 0.0127, 0.0255$, and 0.1020 corresponding to bulk isotropic states, while the system with $\eta = 0.2804$ corresponds to a bulk nematic state.

N	η	η_{bulk}	Phase	L_z	$\alpha\alpha$	$p_{\alpha\alpha}^{*+}$	$p_{\alpha\alpha}^{*-}$	$p_{\alpha\alpha}^*$	γ^*
100	0.0127	0.0141	Isotropic	43	xx	-0.0007 ± 0.0000	0.0031 ± 0.0000	0.0151 ± 0.0000	0.0057 ± 0.0001
					yy	-0.0007 ± 0.0000	0.0031 ± 0.0000	0.0151 ± 0.0000	
					zz	-0.0007 ± 0.0000	0.0053 ± 0.0000	0.0173 ± 0.0000	
200	0.0255	0.0277	Isotropic	43	xx	-0.0030 ± 0.0000	0.0129 ± 0.0001	0.0354 ± 0.0001	0.0121 ± 0.0001
					yy	-0.0030 ± 0.0000	0.0129 ± 0.0001	0.0354 ± 0.0000	
					zz	-0.0030 ± 0.0000	0.0176 ± 0.0001	0.0401 ± 0.0000	
800	0.1020	0.1047	Isotropic	43	xx	-0.0636 ± 0.0002	0.2629 ± 0.0003	0.3012 ± 0.0005	0.0590 ± 0.0018
					yy	-0.0637 ± 0.0004	0.2629 ± 0.0004	0.3012 ± 0.0008	
					zz	-0.0617 ± 0.0003	0.2840 ± 0.0003	0.3242 ± 0.0003	
2200	0.2804	0.2742	Nematic	43	xx	-0.6740 ± 0.0442	2.3642 ± 0.0032	1.9706 ± 0.0045	0.1280 ± 0.0098
					yy	-0.5251 ± 0.0573	2.2169 ± 0.0509	1.9722 ± 0.0034	
					zz	-0.2645 ± 0.0021	2.0054 ± 0.0032	2.0213 ± 0.0028	

gle surface; the results are presented in table 5. Here we examine two low-density isotropic liquid states, a high-density isotropic liquid state, and a high-density anisotropic nematic state. It is clear from table 5 that our method provides an accurate estimate of the tension (the error bars estimated over 10 blocks of 2×10^7 cycles are at most 8%).

Other methodologies can be used to estimate the surface tension of hard-core systems of the type examined in our paper. One can simulate the system in the grand canonical ensemble (MC- μVT) [1, 2], and integrate the Gibbs adsorption equation over a range of chemical potentials μ at constant temperature to give the surface tension [52]. An excellent example of this is the work of Mao *et al.* [25] who have also determined the surface tension of hard rods of aspect ratio $L/D = 10$ confined between two hard slits. To make a rough comparison with our results, we have performed a linear interpolation of the data points of Mao *et al.* in the low-density region: for the two lowest density states that we examine, our values of the surface tension lie within 10% deviation of their values. We should mention at this point that the integration of the adsorption over chemical potential inherent in a grand canonical approach can lead to inaccuracies particularly for the high density states where particle insertion is prohibitive. Our test-volume thermodynamic approach does not suffer from a deterioration in performance at high density. Alternatively one could use the contact theorem for the particles at the wall to estimate the surface tension (e.g., see the book by Hansen and MacDonald [5]). Again however, this type of approach is difficult to implement in high-density isotropic liquid and nematic states as the density profiles become very sharply peaked near the hard-wall, and extrapolation to contact can lead to significant error.

We have shown that our method is simple and straight-forward to implement for the calculation of the interfacial tension. It can also be readily applied to a wide range of hard-body systems including colloid-polymer systems [53, 54], dipolar hard-core mesogens [48, 55–58], and liquid-crystal mixtures [59–63] which are currently being studied in confinement with this type of approach.

6. Conclusions

We have presented a robust and efficient perturbative thermodynamic approach for the calculation of the pressure and the components of the pressure tensor for systems of hard-body molecules, extending previous work [8, 9, 11]. Using the condition of detailed balance, we have derived an expression which is valid for systems of hard-body molecules of any shape and size, suitable for use in the canonical ensemble. This is particularly useful given that in general the more-realistic models are non-convex in shape. Further to this, with a slight modification to the method, we have shown how it is possible to determine the tensorial components of the pressure in an equivalent manner. We have discussed the practical use of this expression with volume perturbations and presented results for hard spheres and hard spherocylinders illustrating their accuracy and generality. One may conclude that this method is particularly convenient for the calculation of the surface energy of inhomogeneous hard-body systems. It is applicable to a wide range of hard-body systems. The only requirement is a knowledge of the overlap criteria, which of course is needed in the first instance in a general Monte Carlo scheme.

The occurrence of a repulsive contribution upon expansion of systems composed purely of hard-body molecules is also of importance to the correct implementation of constant-pressure simulations. When dealing with non-convex molecules, overlap checks need to be made in the case of isotropic volume increases (and of course decreases) to systems in such ensembles, and checks must be made for all but perfectly spherical molecules when the volume is increased or decreased anisotropically.

From our results one can see the relative contributions to the pressure made by expansive and compressive perturbations to the volume. As one might expect, these contributions are found not to be equal. The asymmetry is most apparent for the case of hard spheres; here, all of the repulsive interactions that the molecules exert on their surroundings are captured by volume compressions alone. In the case of hard spherocylinders (of aspect ratio $L/D = 5$), the contribution to the pressure from an expansion in the volume is (in magnitude) of order 10% to 13% that from a compression.

In summary, we have developed a new volume-perturbation method for the estimation of the pressure and pressure tensor of hard-body systems that, unlike existing methods, applies not only to homogeneous systems of convex molecules, but also to systems incorporating non-convex molecules or inhomogeneities. The method provides reliable estimates for the pressure, of similar accuracy (for the case of spherical molecules) as existing methods, and (for the case of spherocylindrical molecules) shows self-consistency with the specified pressure in MC- NpT simulations. Finally, as we have shown, this method has great potential for calculation of the interfacial tension of inhomogeneous hard-body systems. A alternative derivation of the expressions for the test-volume method is given for systems interacting via potentials of general (attractive/repulsive) form is given in the Appendix to emphasise the generality of the approach.

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Appendix A. Isotropic volume perturbations for non-convex molecules interacting through continuous potentials

We consider the derivation of a similar expression to equation 52 that is applicable to systems with continuous potentials and thereby reveals the generality of the concepts presented.

From equations 34 and 35 we can see how the transition probability of moving from one state to another is influenced by the sign of the change in the instantaneous enthalpy. If the enthalpy change is negative the probability of the transition is unity, while when the enthalpy change is positive this probability is given instead by its appropriate Boltzmann factor.

In section 3.2 equation 47 is introduced as a way of satisfying both the conditions of possible changes in energy for hard-body systems brought about by a reduction in volume. We will now do something similar for changes in enthalpy, this time keeping our expressions general to include continuous potentials and applicable to either expansions or compressions in volume.

We make use of Heaviside functions of the enthalpy change, $\mathbb{H}(\Delta H_{i \rightarrow j+})$ and $\mathbb{H}(\Delta H_{i \rightarrow j-})$, in order to write expressions for the transition probability that are valid for moves which increase or decrease the system volume:

$$P_{i \rightarrow j+} = 1 + \mathbb{H}(\Delta H_{i \rightarrow j+}) \left(\exp \left(-\frac{\Delta H_{i \rightarrow j+}}{k_B T} \right) - 1 \right); \quad (\text{A1})$$

$$P_{i \rightarrow j-} = 1 + \mathbb{H}(\Delta H_{i \rightarrow j-}) \left(\exp \left(-\frac{\Delta H_{i \rightarrow j-}}{k_B T} \right) - 1 \right). \quad (\text{A2})$$

Since the systems of interest are at equilibrium, equation 40 still holds, which, incorporating equations A1 and A2, becomes

$$\begin{aligned} & \left\langle \Delta V_{i \rightarrow j+} \left[1 + \mathbb{H}(\Delta H_{i \rightarrow j+}) \left(\exp \left(-\frac{\Delta H_{i \rightarrow j+}}{k_B T} \right) - 1 \right) \right] \right\rangle_{\text{eq}} = \\ & \left\langle -\Delta V_{i \rightarrow j-} \left[1 + \mathbb{H}(\Delta H_{i \rightarrow j-}) \left(\exp \left(-\frac{\Delta H_{i \rightarrow j-}}{k_B T} \right) - 1 \right) \right] \right\rangle_{\text{eq}}. \end{aligned} \quad (\text{A3})$$

If the change in volume associated with the perturbations is taken to be constant throughout a simulation, the ΔV terms may be moved outside the averaging brackets. Moreover, since $\Delta V_{i \rightarrow j+} = -\Delta V_{i \rightarrow j-}$ these terms then cancel:

$$\begin{aligned} & \left\langle \mathbb{H}(\Delta H_{i \rightarrow j+}) \left(\exp \left(-\frac{\Delta H_{i \rightarrow j+}}{k_B T} \right) - 1 \right) \right\rangle_{\text{eq}} = \\ & \left\langle \mathbb{H}(\Delta H_{i \rightarrow j-}) \left(\exp \left(-\frac{\Delta H_{i \rightarrow j-}}{k_B T} \right) - 1 \right) \right\rangle_{\text{eq}}. \end{aligned} \quad (\text{A4})$$

Inserting the definition for the change in enthalpy from equation 41 for volume

expansions and the equivalent form for volume compressions into equation A4 gives

$$\left\langle \mathbb{H}(\Delta H_{i \rightarrow j+}) \left(\exp \left(-\frac{\Delta U_{i \rightarrow j+} + p\Delta V_{i \rightarrow j+} - Nk_B T \ln \left(\frac{V_{j+}}{V_i} \right)}{k_B T} \right) - 1 \right) \right\rangle_{\text{eq}} = \left\langle \mathbb{H}(\Delta H_{i \rightarrow j-}) \left(\exp \left(-\frac{\Delta U_{i \rightarrow j-} + p\Delta V_{i \rightarrow j-} - Nk_B T \ln \left(\frac{V_{j-}}{V_i} \right)}{k_B T} \right) - 1 \right) \right\rangle_{\text{eq}}. \quad (\text{A5})$$

As before V_{j+}/V_i is replaced by $(V_i + \Delta V_{i \rightarrow j+})/V_i = 1 + (\Delta V_{i \rightarrow j+}/V_i)$ and V_{j-}/V_i is replaced by $(V_i + \Delta V_{i \rightarrow j-})/V_i = 1 + (\Delta V_{i \rightarrow j-}/V_i)$. With some rearrangement we now have

$$\left\langle \mathbb{H}(\Delta H_{i \rightarrow j+}) \left(\exp \left(-\frac{\Delta U_{i \rightarrow j+}}{k_B T} \right) \exp \left(-\frac{p\Delta V_{i \rightarrow j+}}{k_B T} \right) \left(1 + \frac{\Delta V_{i \rightarrow j+}}{V_i} \right)^N - 1 \right) \right\rangle_{\text{eq}} = \left\langle \mathbb{H}(\Delta H_{i \rightarrow j-}) \left(\exp \left(-\frac{\Delta U_{i \rightarrow j-}}{k_B T} \right) \exp \left(-\frac{p\Delta V_{i \rightarrow j-}}{k_B T} \right) \left(1 + \frac{\Delta V_{i \rightarrow j-}}{V_i} \right)^N - 1 \right) \right\rangle_{\text{eq}}, \quad (\text{A6})$$

Recalling that we have already restricted the discussion to the case in which the magnitudes of the attempted volume changes are constant, and now also recognising that p is constant, $\exp(-p\Delta V_{i \rightarrow j+}/k_B T)$ and $\exp(-p\Delta V_{i \rightarrow j-}/k_B T)$ can be taken outside of the averaging brackets:

$$\exp \left(-\frac{p\Delta V_{i \rightarrow j+}}{k_B T} \right) \left\langle \mathbb{H}(\Delta H_{i \rightarrow j+}) \exp \left(-\frac{\Delta U_{i \rightarrow j+}}{k_B T} \right) \left(1 + \frac{\Delta V_{i \rightarrow j+}}{V_i} \right)^N \right\rangle_{\text{eq}} - \langle \mathbb{H}(\Delta H_{i \rightarrow j+}) \rangle_{\text{eq}} = \exp \left(-\frac{p\Delta V_{i \rightarrow j-}}{k_B T} \right) \left\langle \mathbb{H}(\Delta H_{i \rightarrow j-}) \exp \left(-\frac{\Delta U_{i \rightarrow j-}}{k_B T} \right) \left(1 + \frac{\Delta V_{i \rightarrow j-}}{V_i} \right)^N \right\rangle_{\text{eq}} - \langle \mathbb{H}(\Delta H_{i \rightarrow j-}) \rangle_{\text{eq}}. \quad (\text{A7})$$

Although this equation can be used to extract the pressure, for example one could determine the pressure by numerical solution, it is not straightforward to isolate p in terms of the other variables. However an expression may be obtained for the case in which the distribution of ΔH is symmetric with respect to volume expansions and compressions, as may be expected for systems of particles interacting via continuous potentials. In this event, $\langle \mathbb{H}(\Delta H_{i \rightarrow j-}) \rangle_{\text{eq}} = \langle \mathbb{H}(\Delta H_{i \rightarrow j+}) \rangle_{\text{eq}}$ and these two averages will disappear from equation A7, allowing one to take logs of the equation which can then be rearranged in favour of p . It is important to stress that, although one might expect such symmetry in the distribution of ΔH in the limit of $\Delta V \rightarrow 0$, this is not true in general; in particular, it clearly will not be true in the case where the system interacts through hard potentials.

Taking logarithms as described gives

$$\begin{aligned} & -\frac{p\Delta V_{i\rightarrow j+}}{k_B T} + \ln \left\langle \mathbb{H}(\Delta H_{i\rightarrow j+}) \exp\left(-\frac{\Delta U_{i\rightarrow j+}}{k_B T}\right) \left(1 + \frac{\Delta V_{i\rightarrow j+}}{V_i}\right)^N \right\rangle_{\text{eq}} \\ & -\frac{p\Delta V_{i\rightarrow j-}}{k_B T} + \ln \left\langle \mathbb{H}(\Delta H_{i\rightarrow j-}) \exp\left(-\frac{\Delta U_{i\rightarrow j-}}{k_B T}\right) \left(1 + \frac{\Delta V_{i\rightarrow j-}}{V_i}\right)^N \right\rangle_{\text{eq}}. \end{aligned} \quad (\text{A8})$$

Note that in equation A8 two terms of the form “ $-p\Delta V/k_B T$ ” appear, whereas in the analogous equation 50 for hard particles, only one such term appears; this will give rise to a factor of 1/2 in the final expression for p for systems with continuous potentials that did not appear in the equivalent expression for systems of hard particles. Since $\Delta V_{i\rightarrow j+} = -\Delta V_{i\rightarrow j-}$, these two terms may be collected together; following a little rearrangement one obtains

$$\begin{aligned} p \approx & \frac{1}{2} \frac{k_B T}{\Delta V_{i\rightarrow j+}} \left\{ \ln \left\langle \mathbb{H}(\Delta H_{i\rightarrow j+}) \exp\left(-\frac{\Delta U_{i\rightarrow j+}}{k_B T}\right) \left(1 + \frac{\Delta V_{i\rightarrow j+}}{V_i}\right)^N \right\rangle_{\text{eq}} \right. \\ & \left. - \ln \left\langle \mathbb{H}(\Delta H_{i\rightarrow j-}) \exp\left(-\frac{\Delta U_{i\rightarrow j-}}{k_B T}\right) \left(1 + \frac{\Delta V_{i\rightarrow j-}}{V_i}\right)^N \right\rangle_{\text{eq}} \right\}. \end{aligned} \quad (\text{A9})$$

Finally, for systems at equilibrium (for which V_i is approximately constant and equal to the equilibrium value of V) one can extract the $(1 - \Delta V_{i\rightarrow j}/V_i)^N$ factors from the averaging brackets and, recognising that $\Delta V_{i\rightarrow j} \ll V_i$ (so that the logarithms may be simplified) one finally obtains

$$\begin{aligned} p \approx & \frac{Nk_B T}{V_i} + \lim_{\Delta V_{i\rightarrow j+} \rightarrow 0} \frac{1}{2} \frac{k_B T}{\Delta V_{i\rightarrow j+}} \ln \left\langle \mathbb{H}(\Delta H_{i\rightarrow j+}) \exp\left(-\frac{\Delta U_{i\rightarrow j+}}{k_B T}\right) \right\rangle_{\text{eq}} \\ & + \lim_{\Delta V_{i\rightarrow j-} \rightarrow 0} \frac{1}{2} \frac{k_B T}{\Delta V_{i\rightarrow j-}} \ln \left\langle \mathbb{H}(\Delta H_{i\rightarrow j-}) \exp\left(-\frac{\Delta U_{i\rightarrow j-}}{k_B T}\right) \right\rangle_{\text{eq}}; \end{aligned} \quad (\text{A10})$$

the implied limits have been explicitly restored in the final expression. It is interesting to compare this equation, which is true only for systems interacting through (continuous) potentials for which $\Delta H_{i\rightarrow j}$ is symmetric with respect to expansions and compressions, with its analogy for the hard-potential system. In the latter (equation 52) the second and third terms on the right-hand side appear without the factor of 1/2; this subtle difference can thus be seen to be a consequence of the asymmetry of $\Delta H_{i\rightarrow j}$ with respect to expansions and compressions.

A.1. Purely repulsive potentials

When considering hard-body interactions, for systems undergoing an increase in volume, equation 42 implies that $\Delta H_{i\rightarrow j+}$ is always greater than zero. Thus $\mathbb{H}(\Delta H_{i\rightarrow j+}) = 1$. Equation A4 now becomes:

$$\left\langle \mathbb{H}(\Delta H_{i\rightarrow j-}) \left(\exp\left(-\frac{\Delta H_{i\rightarrow j-}}{k_B T}\right) - 1 \right) \right\rangle_{\text{eq}} + 1 = \left\langle \exp\left(-\frac{\Delta H_{i\rightarrow j+}}{k_B T}\right) \right\rangle_{\text{eq}}. \quad (\text{A11})$$

As we have already covered in section 3.2, we know that for volume reductions $\Delta H_{i \rightarrow j-}$ can take either positive or negative values at equilibrium, so we must look at each of these cases separately. $\mathbb{H}(\Delta H_{i \rightarrow j-}) = 0$ when $\Delta H_{i \rightarrow j-} < 0$, while $\mathbb{H}(\Delta H_{i \rightarrow j-}) = 1$ for the case where $\Delta H_{i \rightarrow j-} > 0$. Considering equation 44, we recall that for hard-body molecules $\Delta H_{i \rightarrow j-} < 0$ for all cases where there are no overlapping molecules, and when there are overlapping molecules $\Delta H_{i \rightarrow j-} = \infty$. Thus $\mathbb{H}(\Delta H_{i \rightarrow j-}) (\exp(-\Delta H_{i \rightarrow j-}/k_B T) - 1)$ may be replaced by $\exp(-\Delta U_{i \rightarrow j-}/k_B T) - 1$ in equation A11. In writing $\Delta H_{i \rightarrow j+}$ in terms of the system pressure as given by equation 42, we obtain

$$\left\langle \exp\left(-\frac{\Delta U_{i \rightarrow j-}}{k_B T}\right) \right\rangle_{\text{eq}} = \left\langle \exp\left(-\frac{\Delta U_{i \rightarrow j+} + p\Delta V_{i \rightarrow j+} - Nk_B T \left(\frac{\Delta V_{i \rightarrow j+}}{V_i}\right)}{k_B T}\right) \right\rangle_{\text{eq}}. \quad (\text{A12})$$

Equation A12 can be evaluated for ghost volume perturbations in either the NVT or the NpT ensemble. When the change in volume $\Delta V_{i \rightarrow j+}$ and the volume of the unperturbed state V_i are kept constant, one can write

$$\left\langle \exp\left(-\frac{\Delta U_{i \rightarrow j-}}{k_B T}\right) \right\rangle_{\text{eq}} = \left\langle \exp\left(-\frac{\Delta U_{i \rightarrow j+}}{k_B T}\right) \right\rangle_{\text{eq}} \exp\left(-\frac{p\Delta V_{i \rightarrow j+}}{k_B T}\right) \exp\left(\frac{N\Delta V_{i \rightarrow j+}}{V_i}\right). \quad (\text{A13})$$

Rearranging, taking logarithms, dividing both sides by $\frac{\Delta V_{i \rightarrow j+}}{k_B T}$ and recalling that $\Delta V_{i \rightarrow j+} = -\Delta V_{i \rightarrow j-}$ allows us to write

$$p = \frac{Nk_B T}{V_i} + \frac{k_B T}{\Delta V_{i \rightarrow j+}} \ln \left\langle \exp\left(-\frac{\Delta U_{i \rightarrow j+}}{k_B T}\right) \right\rangle_{\text{eq}} + \frac{k_B T}{\Delta V_{i \rightarrow j-}} \ln \left\langle \exp\left(-\frac{\Delta U_{i \rightarrow j-}}{k_B T}\right) \right\rangle_{\text{eq}}. \quad (\text{A14})$$

As before we now reinstate the limits for which our equation is valid to give the final form as

$$p = \frac{Nk_B T}{V_i} + \lim_{\Delta V_{i \rightarrow j+} \rightarrow 0} \frac{k_B T}{\Delta V_{i \rightarrow j+}} \ln P_{\text{nov}+} + \lim_{\Delta V_{i \rightarrow j-} \rightarrow 0} \frac{k_B T}{\Delta V_{i \rightarrow j-}} \ln P_{\text{nov}-}. \quad (\text{A15})$$

Equations A15 and 53 are of course identical.

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Imperial College
London

Department of Chemical Engineering
Imperial College London

Room 415, ACE Building
South Kensington Campus
London SW7 2AZ
United Kingdom
Tel: +44 (0) 20 75945640

g.jackson@imperial.ac.uk
<http://www.imperial.ac.uk/people/gjackson>

27 September 2010

George Jackson DPhil FRSC CChem
Professor of Chemical Physics

Prof. J.-P. Hansen FRS
Editor: Molecular Physics
The University Chemical Laboratory
University of Cambridge
Lensfield Road
Cambridge CB2 1EW, UK

Dear Jean-Pierre,

RE: Manuscript submitted for publication in *Molecular Physics*

REF: TMPH-2010-0301

TITLE: *Subtleties in the calculation of the pressure and pressure tensor of anisotropic particles from volume-perturbation methods and the apparent asymmetry of the compressive and expansive contributions.*

AUTHORS: *Paul E. Brumby, Andrew J. Haslam, Enrique de Miguel, and George Jackson*

Thank you for sending us the referee report for our paper. We found the comments and suggestions most useful, and were very pleased to hear that the referee found that the paper was a “very interesting” and “well written”, and that it represents “a very useful new methodology in the simulation of hard core molecules”. We have addressed the points that are raised about the virial route, and have revised the manuscript accordingly. Our detailed response with the appropriate changes to the manuscript are listed below:

1) The derivative of the hard sphere force is not a delta function. You get a delta function as the derivative of a unit step. The hard sphere potential is an infinite step! Thus eq. 2 is wrong.

In hindsight we agree with the referee that this part of the description is problematic. The way we presented the virial expression is rather obscure and concise, and only applicable to the case of spherical particles. Equation 2 (now Equation 8) actually follows directly from the standard derivation of the virial (pressure) equation presented in, e.g., Hansen and McDonald, *Theory of Simple Liquids*, 3rd Edition. We demonstrate this by starting with the pressure equation for a system of spherical particles (Equation 2.5.22, page 32 of the monograph):

$$\frac{\beta p}{\rho} = 1 - \frac{2\pi}{3} \beta \rho \int_0^{\infty} u'(r) g(r) r^3 dr = 1 - \frac{2\pi}{3} \beta \rho \int_0^{\infty} \left\{ r \frac{\partial u(r)}{\partial r} \right\} g(r) r^2 dr, \quad (i)$$

where the variables take their usual meaning.

Expressing the pair distribution function $g(r)$ in terms of the cavity function $y(r)$,

$$g(r) = \exp[-\beta u(r)]y(r) = e(r)y(r), \quad (\text{ii})$$

one can write Equation (i) as

$$\frac{\beta p}{\rho} = 1 - \frac{2\pi}{3} \beta \rho \int_0^{\infty} u'(r)e(r)y(r)r^3 dr = 1 + \frac{2\pi}{3} \rho \int_0^{\infty} e'(r)y(r)r^3 dr, \quad (\text{iii})$$

where

$$e'(r) = \frac{\partial e(r)}{\partial r} = \frac{\partial \exp[-\beta u(r)]}{\partial r} = -\beta u'(r)e(r). \quad (\text{iv})$$

In the case of a system of hard spheres of diameter σ , the Boltzmann factor of the potential is a Heaviside (unit-step) function, $e(r) = H(r - \sigma)$, the derivative of which is a delta function, $e'(r) = \delta(r - \sigma)$. Since the force $f(r) = -u'(r)$, from Equation (iv) it follows that

$$e'(r) = \delta(r) = \beta f(r)e(r). \quad (\text{v})$$

In the case of a collision between hard spheres from a non-overlapping configuration r is infinitesimally greater than σ for which $u(r) = 0$ and $e(r) = 1$, so that Equation (v) can be expressed as

$$\delta(r - \sigma) = \beta f(r) \quad \text{or} \quad f(r) = k_B T \delta(r - \sigma), \quad (\text{vi})$$

which is the same as equation (2) (now equation (8)) in our paper for the force acting between hard spheres in a homogeneous phase with radial symmetry.

In order to make this clearer we have revised the manuscript by mentioning after equation (1) that the virial equation can be expressed in terms of the radial pair distribution function for a homogeneous phase of hard spheres with radial symmetry [cf. Equation (i)]. We then follow the description given above [Equations (ii) - (vi)] to show that in this particular case the force is proportional to the delta function as expressed in equation (2) (now equation (8)).

2) Above eq. 3 it is stated that a delta function is unity at contact. Again this is not true - a delta function is an infinitely high spike! Also the direction of the force is parallel to the surface normal at the point of contact - this, in general, is not the same direction at the centre-to-centre vector.

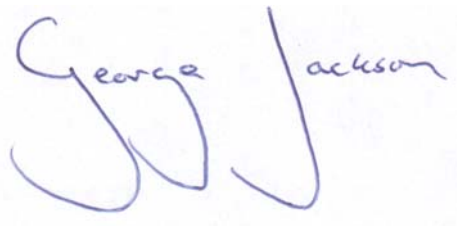
We apologise for this error; we were in fact referring to the Heaviside function (not the delta function) as approached from non-overlapping configurations. This has been corrected in the revised manuscript by stating that the delta function is an infinite spike at contact.

It is true that in the general case of molecules of non-spherical shape the force is parallel to the surface normal and not along the centre-to-centre vector. The derivation was exemplified for the case of hard spheres where this always holds. We have revised the manuscript to make this point explicitly.

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We hope that the work will now be deemed to be acceptable for publication in the *Molecular Physics*.

Please keep me informed on the progress of our manuscript, and do not hesitate to contact me if you require any further assistance in this matter.

A handwritten signature in blue ink that reads "George Jackson". The signature is written in a cursive style with a large initial "G" and "J".

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