RESEARCH ARTICLE

Alternative ensemble averages in molecular dynamics simulation of hard spheres

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We consider application to the hard sphere (HS) model of the mapped-averaging framework for generating alternative ensemble averages for thermodynamic properties. Specifically we develop and examine new formulas for the pressure, the singlet and pair densities, and the cavity-correlation function inside the HS core; the pressure formula in particular is constructed such that it gives an ensemble average that exactly corrects the second-order virial equation of state. The force plays a central role in mapped-averaging expressions, and we write them in a way that accounts for the impulsive, event-driven nature of the HS dynamics. Comparison between results obtained conventionally versus mapped averaging finds that the latter has some advantage at low density, while both perform equally well (in terms of uncertainties for a given amount of sampling) at higher densities.

Keywords: Hard-sphere fluid; computer simulations, event driven molecular dynamics; radial distribution function; cavity correlation function; mapped averaging

1. Introduction

High-precision data from molecular simulation are typically acquired by increasing the amount of sampling that contributes to the relevant ensemble average, until its estimated uncertainty is reduced to the desired level. Alternatively, it is sometimes possible to reduce the uncertainty for a given amount of sampling by using an ensemble average that is different from the one conventionally written for the property, but which still represents an exact formula for it [1]. Previously, we proposed mapped averaging as a general framework for deriving such averages [2]. Properties from mapped averaging are obtained as free-energy derivatives, which are formulated in new ways via the targeted-perturbation idea [3] for evaluation of free-energy differences, but applied for a differential-change limit. Yielding an expression from mapped averaging that is effective at reducing uncertainty is crucially dependent on the mapping, which may be different for each state condition and even each property.

Basically, the mapping defines a phase-space “flow field” that would move the atoms toward new positions, ones that in a specific sense leave the system in an equivalent configuration upon a differential change of state (i.e., as when performing a derivative) [1]; the movement is virtual, not actual, and is invoked only conceptually to define the free-energy derivative. In principle there exists a perfect mapping that would yield an ensemble average that gives the exact value for the property with just a single sample. Realizing such a mapping is not possible in practice,
but approximate mappings can be developed with guidance from simple theoretical treatments—even the ideal-gas law can provide useful guidance. The theory provides an estimate for the probability of a configuration, which can be input to a differential equation that when solved yields an expression for the mapping velocity field \[2\]. Having then the mapping, new expressions for the reformulated ensemble averages are obtained via direct formulas for the mapped free-energy derivatives. Despite the use of an approximate theory to help formulate the mapping, the alternative ensemble average obtained from the process is an exact expression for the property of interest—it is not itself an approximation. Although the expression is rigorous, its ability to provide a higher-precision estimate of the property does depend on how well the approximate theory describes the behavior of the system being simulated and, as usual, balancing tractability and effectiveness can be difficult. Yet in favorable cases a property can be evaluated to a given precision with several orders of magnitude less computational effort; in other cases the mapped average provides no advantage over the conventional formulation.

Presently we consider mapped-average expressions in application to the properties of the hard-sphere (HS) model. Especially interesting in this context is the impulsive nature of the HS forces—which are applied over a sequence of pairwise collisions—because the interatomic forces play a central role in the mapped-averaging formulas. Typical to HS applications, the high-contrast nature of the behavior (with energetics that are zero or infinite and nothing in between) allows us to write the averages in a unique form, distilling their features in a way that can provide insight to their structure. Essential formulas are provided in Section 2, where we review both the conventional and mapped-averaging expressions for the pressure, the singlet and pair densities, and the cavity correlation function, with specific forms presented for the HS model. Results from molecular simulation for these properties and the performance of mapped versus conventional averaging are reported in Section 3, and we finish in Section 4 with a summary and concluding remarks.

2. Model and mapped averaging formulas

The HS pair interaction is given by

\[ u_2(r_{ij}) = \begin{cases} \infty, & r_{ij} < \sigma \\ 0, & r_{ij} \geq \sigma \end{cases} \]  

(1)

where \( r_{ij} = |\mathbf{r}_j - \mathbf{r}_i| \) is the distance between spheres \( i \) and \( j \). Unless explicitly stated, we assume that there are no external forces acting on the system.

The HS model can be studied using either molecular dynamics (MD) or Monte Carlo (MC) simulation. However, in the present context the interatomic forces play a central role, and without specialized sampling methods these are not easily treated in MC simulations. Accordingly, we will proceed in our development assuming the formulas are applied in MD calculations.

2.1. Bulk pressure

The well-established virial formula \[4, 5\] is the standard expression for evaluation of the bulk pressure \( P \) in a molecular simulation. In the case of a pairwise-additive
potential, this can be written:

$$Z \equiv \frac{\beta P}{\rho} = 1 + \frac{\beta}{3} \left( \frac{1}{N} \sum_{j=1}^{N} \sum_{i>j}^{N} r_{ij} \cdot f_{ij} \right)$$  \hspace{1cm} (2)$$

where $\rho = N/V$ represents the number density, with $N$ is the number of molecules and $V$ the volume, $\beta$ is the reciprocal temperature $1/k_B T$ with $k_B$ Boltzmann’s constant, $f_{ij}$ is the force on atom $j$ due to its interaction with $i$, and $r_{ij} = r_j - r_i$ is the separation vector for atoms $i$ and $j$; Eq. (2) also defines the compressibility factor $Z$. The ensemble average may be expressed as a time average, and for HS the forces are zero except at the instant of collision, when an impulsive contribution is made to the average. This force, integrated through a time instant $dt$, is:

$$f_{ij} dt = -m (v_{ij} \cdot \hat{r}_{ij}) \hat{r}_{ij}$$  \hspace{1cm} (3)$$

where $m$ is the atom mass, $v_{ij} \equiv v_j - v_i$ is the difference of the velocities of the colliders prior to the collision, and $\hat{r}_{ij} = r_{ij}/|r_{ij}|$ with $r_{ij} = |r_{ij}|$. Hence, the time average may be expressed as a sum over collisions $c$ occurring over a time interval $\tau$, thus:

$$\frac{\beta P}{\rho} = 1 - \frac{\beta m}{3N\tau} \sum_{c(i,j)} r_{ij} \cdot v_{ij}; \hspace{1cm} (4)$$

we use the notation $c(i,j)$ to indicate that at each collision we label the colliders $i$ and $j$.

The relative velocity $v_{ij}$ for a colliding pair will be a sample from a distribution that is derived from the Maxwell-Boltzmann distribution for the individual velocities, weighted by their relative velocity to account for the increased collision rate of pairs moving faster relative to each other. Rather than sample from this distribution stochastically in the course of the molecular dynamics, we can simply average over the distribution at each collision. Then the contribution from each collision is identical, and is given by the distribution mean:

$$\langle r_{ij} \cdot v_{ij} \rangle = -\frac{1}{2} \beta m \sigma \int_{0}^{\infty} dv v^2 \exp \left( -\frac{1}{4} \beta m v^2 \right)$$

$$= - \left( \frac{\pi \sigma^2}{\beta m} \right)^{1/2}, \hspace{1cm} (5)$$

and Eq. (4) becomes [6, 7]:

$$\frac{\beta P}{\rho} = 1 + \left( \beta m \pi \sigma^2 \right)^{1/2} \frac{n_c}{3N\tau}, \hspace{1cm} (6)$$

where $n_c$ is the number of collisions in time $\tau$.

An alternative to this expression can be derived using the mapped-averaging framework. We apply the version that maps based on a simple Boltzmann-factor estimate of pair correlations, which yields [1, 2]:

$$\frac{\beta P}{\rho} = 1 + B_2 \rho + \frac{1}{2} \left( \frac{1}{N} \sum_{i}^{N} \sum_{j<i}^{N} \hat{r}_{ij}^V (r_{ij}) \beta (f_j - f_i)^* \cdot \hat{r}_{ij} \right), \hspace{1cm} (7a)$$
where \( f_i \) and \( f_j \) are the total forces on atoms \( i \) and \( j \), respectively, and \( B_2 \) is
the second virial coefficient [4] (equal to \( 2\pi\sigma^3/3 \) for hard spheres); also, the pair-distance mapping velocity is (for spheres in three dimensions):

\[
\dot{r}_{ij}(r_{ij}) = \int_0^{r_{ij}} \left( \frac{\tilde{r}}{r_{ij}} \right)^2 \left( e^{-\beta(u_2(\tilde{r})-u_2(r_{ij}))} - 1 \right) d\tilde{r}
\]

\[
\dot{r}_{ij}(r_{ij}) = -\frac{\sigma^3}{3r_{ij}^2},
\]

(7b)

where the latter equality applies to hard spheres for \( r_{ij} \geq \sigma \). Details of the derivation of Eq. (7) are provided in the Appendices.

The asterisk on the force difference in Eq. (7a) means that the forces are computed exclusive of that due to the direct \( ij \) interaction. Again, for the impulsive HS force, contributions to the average are made only when a collision takes place. The exclusion of direct \( ij \) interactions means that the forces on \( i \) or \( j \) are due to collision with another sphere \( k \), and at most one force \( f_j \) or \( f_i \) will be non-zero for a given term in the sum; we will assign the label \( j \) to \( k \)'s collider, and note then that \( f_j = -f_k \). Bringing these various details together, the mapped-average formula for the pressure of HS may be written (see Appendices):

\[
\frac{\beta P}{\rho} = 1 + \frac{2\pi}{3} \rho \sigma^3 - \frac{\beta m \sigma^3}{6N \tau} \sum_{c(j,k)} (v_{jk} \cdot \hat{r}_{jk}) \sum_{i \neq j,k} \hat{r}_{jk} \cdot \left( \frac{\hat{r}_{ij}}{r_{ij}^2} - \frac{\hat{r}_{ik}}{r_{ik}^2} \right),
\]

(8)

where the \( c \)-sum is over all collisions in time \( \tau \), with each sphere in the colliding pair labeled \( j \) and \( k \), respectively; the inner sum is over all other spheres, and is performed at each collision. As with the conventional formula, the magnitude of the relative velocities of the colliders can be integrated analytically according to Eq. (5), leaving:

\[
\frac{\beta P}{\rho} = 1 + \frac{2\pi}{3} \rho \sigma^3 + (\beta m \pi)^{1/2} \frac{\sigma^3}{6N \tau} \sum_{c(j,k)} \sum_{i \neq j,k} \hat{r}_{jk} \cdot \left( \frac{\hat{r}_{ij}}{r_{ij}^2} - \frac{\hat{r}_{ik}}{r_{ik}^2} \right).
\]

(9)

This expression is really quite curious. The contribution to the pressure depends on the collision virial (Eq. (8)), but this is tempered by a term that captures the local density anisotropy around the colliding pair, specifically:

\[
\sum_{i \neq j,k} \hat{r}_{jk} \cdot \left( \frac{\hat{r}_{ij}}{r_{ij}^2} - \frac{\hat{r}_{ik}}{r_{ik}^2} \right)
\]

(10)

The form of this term, as a function of the placement of a sphere \( i \) relative to colliders \( j \) and \( k \), is depicted in Fig. 1. Positive contributions to it (and thereby the pressure) are made by spheres \( i \) located in the region aligned with the colliders, while negative contributions are made by spheres in the region perpendicular to the colliders. In a given direction, the contribution decays as \( r_i^{-3} \) (where \( r_i = |r_i| \)), which is not fast enough to cause the contribution from all spheres to remain finite when summed to infinite distance. However, the positive and negative terms cancel exactly when integrated over the surface of a sphere for fixed \( r_i \). Hence, contributions to the pressure beyond that from the second virial coefficient depend on anisotropy in the distribution around the colliding pair. Given that the HS
pressure is consistently larger than the values from the second-order virial equation, the anisotropy in the vicinity of the colliders must be such that there is an excess of spheres in the line of their collision. It would be reasonable to expect this, given that the $jk$ collision likely results following recoil from a previous collision of $j$ or $k$ with a sphere $i$ near this line. Regardless, it is very interesting to see that the pressure may be expressed in terms of the structure of the spheres surrounding a colliding pair.

### 2.2. Singlet density

Arguably the simplest nontrivial case to study for the singlet density for HS model is spheres confined to a slit pore formed by two hard walls, separated by a distance $L + \sigma$ (such that $L$ is the width of the accessible region). Formally, this introduces a $z$-dependent sphere-wall potential as follows:

$$u_1(z_i) = \begin{cases} \infty, & |z_i| > L/2 \\ 0, & -L/2 \leq z_i \leq L/2 \end{cases} \quad (11)$$

In this system, the density distribution is inhomogeneous in only the $z$ dimension, and the system is periodic in other two dimensions, such that each wall is of area $A$.

We consider two formulas for the density distribution. The first is the conven-
tional approach, which prescribes collecting histograms of the sphere positions:

$$\rho(z) = \left\langle \sum_i^N \delta(z - z_i) \right\rangle.$$  \hspace{1cm} (12)

The second formula is a mapped average based on a uniform-density reference. The general equation is [8–10] (see Appendices):

$$\rho(z) = \frac{N}{AL} - \left\langle \frac{1}{A} \sum_{i=1}^N \left( H(z_i - z) - \frac{1}{2} - z_i L \right) \beta f_{z,i} \right\rangle,$$  \hspace{1cm} (13)

where $f_{z,i}$ is the $z$-component of the force on molecule $i$, and $H(.)$ denotes the Heaviside function; the term in parentheses is the mapping $\dot{z}(z_i; z)$. Equation (13) differs slightly from the one presented in Ref. 10, which was developed for a system with periodic boundaries in $z$; the mapping for the present case imposes $\dot{z}_i = 0$ at $z_i = \pm L/2$. This is illustrated for $z = -2$ in Fig. 2.

As done for the pressure in the previous section, we write the average for the HS system as a sum over collisions $c$, using $j$ and $k$ as the labels for the colliders:

$$\rho(z) = \frac{N}{AL} + \frac{\beta m}{\sigma A \tau} \sum_{c(j,k)} \left( H(z_j - z) - H(z_k - z) - \frac{z_j - z_k}{L} \right) (z_j - z_k) \left( \mathbf{v}_{jk} \cdot \mathbf{r}_{jk} \right).$$  \hspace{1cm} (14)

Then we perform the Maxwell-Boltzmann average of the velocities of the colliders as in Eq. (5):

$$\rho(z) = \frac{N}{AL} - \frac{(\beta m \pi)^{1/2}}{\sigma A \tau} \sum_{c(j,k)} \left( H(z_j - z) - H(z_k - z) - \frac{z_j - z_k}{L} \right) (z_j - z_k).$$  \hspace{1cm} (15)
The Heaviside functions cancel each other, except for \( z \) values between the centers of the colliders, i.e., \( z_j < z < z_k \), or \( z_k < z < z_j \). Specifically, they make no contribution for \( z \) at the walls, so we have

\[
\rho(\pm L/2) = \frac{N}{AL} \left( 1 + \frac{(\beta m \pi)^{1/2}}{\sigma N \tau} \sum_{c(j,k)} (z_j - z_k)^2 \right).
\]

This result can be applied in the inaccessible region as well, \( |z| > L/2 \), except that in going from Eq. (13) to (14), we must include the forces due to the collisions with the walls, because \( \dot{z}_i(z_i = \pm L/2) \neq 0 \) for \( z \) in this region; instead it is equal to \(-\text{sgn}(z_i)\). Thus,

\[
\rho(|z| > L/2) = \frac{N}{AL} \left( 1 + \frac{(\beta m \pi)^{1/2}}{\sigma N \tau} \sum_{c(j,k)} (z_j - z_k)^2 \right) + \frac{1}{A \tau} \sum_{c(j,\text{wall})} \text{sgn}(z_j) \beta f_{z,j}
\]

\[
= \rho(\pm L/2) - \beta P_{zz},
\]

which uses (16) and recognizes the force average per unit area as the \( zz \) component of the pressure tensor, \( P_{zz} \) (which for this geometry will equal the bulk pressure obtained between walls having large separation). Given that \( \rho(z) = 0 \) in the inaccessible region, we immediately obtain the well established [4] result \( \beta P_{\text{bulk}} = \rho_{\text{wall}} \).

We can alternatively develop a mapped average using a reference based on the wall potential [10], with the result (see Appendices):

\[
\rho(z) = e^{-\beta u_1(z)} \left[ \frac{N}{AL} - \frac{1}{A} \sum_{i=1}^{N} \left( H(z_i - z) - \frac{1}{2} - \frac{z_i}{L} \right) \beta \left( f_{z,i} - f_{z,\text{wall}} \right) \right] (18)
\]

Practically, this formulation is equivalent to Eq. (13), except that it explicitly enforces \( \rho(z) = 0 \) in the inaccessible region (rather than obtaining it as an average), and it explicitly removes contributions from sphere-wall collisions (rather than discounting them only by having \( \dot{z}(\pm L/2) = 0 \)).

### 2.3. Pair density of the bulk fluid

Two mapped-averaging formulas are available to develop expressions for the radial distribution function \( g(r) \) of a bulk fluid composed of molecules interacting via a spherically-symmetric pair potential energy \( u_2(r) \) [1]. The first is based on an ideal-gas reference, and can be expressed (see Appendices):

\[
g(r) = \frac{\beta}{\rho N} \left( \sum_{j=1}^{N} f_j \sum_{i \neq j} \tilde{r}_{ij} \frac{H(r_{ij} - r)}{4\pi r_{ij}^2} \right),
\]

where \( H(x) \equiv 1 - H(x) \). This formula is based on the assertion that \( g(r) = 0 \) for \( r < \sigma \), which yields an \( i \) sum that includes only pairs having separations \( r_{ij} < r \). As done for the pressure in the previous section, we can write the formula in terms of a sum over collisions. Assuming \( r > \sigma \), there is always a contribution from the colliding pair \( (jk) \), which we can separate from the other terms (the same...
contribution is counted twice, once for \( f_j \) and again for \( f_k \):

\[
g(r) = -\frac{\beta m}{2\pi \rho \sigma^2 N_T} \sum_{c(j,k)} \mathbf{v}_{jk} \cdot \hat{r}_{jk}
\]

\[
-\frac{\beta m}{\rho N_T} \sum_{c(j,k)} (\mathbf{v}_{jk} \cdot \hat{r}_{jk}) \sum_{i \neq j,k} \hat{r}_{jk} \cdot \left( \frac{\hat{r}_{ij}}{r_{ij}^2} \bar{H}(r_{ij} - r) - \frac{\hat{r}_{ik}}{r_{ik}^2} \bar{H}(r_{ik} - r) \right)
\]  \(20\)

Applying the collision-velocity average, Eq. (5), we have:

\[
g(r) = \left( \frac{\beta m}{\pi} \right)^{1/2} \frac{n_c}{2\rho \sigma^2 N_T} + \frac{(\beta m \pi)^{1/2}}{4\pi \rho N_T} \sum_{c(j,k)} \sum_{i \neq j,k} \hat{r}_{jk} \cdot \left( \frac{\hat{r}_{ij}}{r_{ij}^2} \bar{H}(r_{ij} - r) - \frac{\hat{r}_{ik}}{r_{ik}^2} \bar{H}(r_{ik} - r) \right)
\]  \(21\)

The second mapped-average formulation we consider uses the pair interaction as a reference for the mapping, and yields (see Appendices):

\[
e^{+\beta u_2(r)} g(r) = 1 - \frac{1}{\rho} \left\langle \frac{1}{N} \sum_{i < j} H(r_{ij} - r) \right\rangle e^{+\beta u_2(r_{ij})} \beta (f_j - f_i)^* \cdot \hat{r}_{ij}
\]  \(22\)

Presently, we are interested in this function for HS for separations \( r \geq \sigma \), where \( u_2(r) = 0 \), so we will omit the \( e^{\beta u_2} \) terms in what follows; they will be re-introduced in the next section, where we consider the cavity function for \( r < \sigma \). Again, writing in terms of collisions:

\[
g(r) = 1 - \frac{\beta m}{4\pi \rho N_T} \sum_{c(j,k)} (\mathbf{v}_{jk} \cdot \hat{r}_{jk}) \sum_{i \neq j,k} \hat{r}_{jk} \cdot \left( \frac{\hat{r}_{ij}}{r_{ij}^2} \bar{H}(r_{ij} - r) - \frac{\hat{r}_{ik}}{r_{ik}^2} \bar{H}(r_{ik} - r) \right)
\]  \(23\)

For HS, the pressure is related to the value of \( g(r) \) at contact, \( r = \sigma \) [4]:

\[
\frac{\beta P}{\rho} = 1 + \frac{2\pi}{3} \rho \sigma^3 g(\sigma).
\]  \(24\)

When \( g(r) \) from Eq. (23) is used in this formula, Eq. (8) results.

Finally, with the velocity average from Eq. (5) we have:

\[
g(r) = 1 + \frac{(\beta m \pi)^{1/2}}{4\pi \rho N_T} \sum_{c(j,k)} \sum_{i \neq j,k} \hat{r}_{jk} \cdot \left( \frac{\hat{r}_{ij}}{r_{ij}^2} \bar{H}(r_{ij} - r) - \frac{\hat{r}_{ik}}{r_{ik}^2} \bar{H}(r_{ik} - r) \right)
\]  \(25\)

We note that Eq. (21) can be obtained by using (25) to express \( g(r) - g(\sigma) \), so the two formulations are not fundamentally different for the application to HS.

2.4. Cavity correlation function

The cavity correlation function \( y(r) = e^{+\beta u_2(r)} g(r) \) extends the radial distribution function into separations where the spheres overlap [4]. It eliminates the direct interaction between two spheres, so that in effect they behave as a pair of cavities.
that each exclude all the other spheres, but can mutually overlap. Clearly \( y(r) = g(r) \) for HS for \( r \geq \sigma \), and moreover the function is continuous through the contact value \( r = \sigma \). The cavity function plays an important role in the formulation and understanding of integral-equation theories \([11, 12]\). Also, the value at \( r = 0, g(0) \), is closely related to the chemical potential \([12–15]\).

2.4.1. Conventional formulation

The cavity function may be written as a conventional ensemble average:

\[
y(r) = 2 \rho N \sum_{i=1}^{N} \sum_{j<i} \left\langle \frac{\delta(r - r_{ij})}{4\pi r_{ij}^2} e^{\beta u_2(r_{ij})} \right\rangle.
\]

(26)

This formula prescribes the use of histograms for evaluation of \( y(r) \). Each term in the sum is equivalent, but not all can be evaluated at once if treated as typical ensemble average. The ensemble sampling weight prohibits any sphere overlaps, but the contribution to \( y(r) \) for \( r < \sigma \) is made when a pair overlaps, where it is given infinite weight due to the \( e^{\beta u} \) term. A remedy is to use an ensemble weight where this term for a single pair is included, allowing that pair to sample overlap configurations. We indicate this with the notation \( \left\langle \ldots \right\rangle_{ij} \), to specify an ensemble average with \( e^{\beta u_2(r_{ij})} \) included in the sampling weight. Then

\[
y(r) = 2 \rho N \sum_{i=1}^{N} \sum_{j<i} \left\langle \frac{\delta(r - r_{ij})}{4\pi r_{ij}^2} \right\rangle_{ij} = V \left\langle \frac{\delta(r - r_{12})}{4\pi r_{12}^2} \right\rangle_{12},
\]

(27)

where we arbitrarily select the 12 pair as getting this special treatment, representing all \( N(N - 1)/2 \) equivalent pairs (also, assuming large \( N \) we have approximated \( N - 1 \approx N \)).

Equation (27) is problematic in that the signal for measuring \( y(r) \) at a specific \( r \) comes only when the special pair is at that separation. The probability for this decreases as \( 1/V \), an effect that is compensated by the multiplication of the average by \( V \), making \( y(r) \) properly \( V \)-independent for a given \( \rho \). A remedy is to introduce a sampling bias that forces or encourages the special pair to sample the separations of interest (in particular \( r < \sigma \)). This can be done in several ways, for example by tethering the 12 pair so they cannot separate further than \( r = \sigma \), or by performing biased test-particle insertions \([11]\); the latter is one approach we examine here.

Additionally, we perform standard MD while allowing a single pair to overlap, and when the natural dynamics causes that pair to separate, the next colliding pair is then allowed to overlap, effectively relabeling them as the 12 pair. For \( r < \sigma \), this opportunistic approach yields a cavity function (labeled \( y^*(r) \)) that is biased. This bias is removed by multiplying by the ratio \( n_{\sigma^+}/n_{\sigma^-} \), where \( n_{\sigma^-} \) is the number of collision events that occur coming from \( r < \sigma \) and \( n_{\sigma^+} \) is the number of collision events (considering all atom pairs) that occur coming from \( r > \sigma \), hence:

\[
y(r)_{r<\sigma} = y^*(r) \frac{n_{\sigma^+}}{n_{\sigma^-}}.
\]

(28)

If the spheres were free to move in and out of the hard core, then \( n_{\sigma^-} = n_{\sigma^+} \) and their ratio indicates how biased the probabilities are, due to artificially allowing only one pair to overlap at a time. This approach requires that “separation” events
occur with sufficient frequency to allow evaluation of $n_\sigma$—with useful precision; hence, at high density this biasing method will fail.

Having obtained $y(r)$, we can obtain $y(0)$ by fitting $\ln y(r)$ to a polynomial in $r$.

2.4.2. Mapped average

Equation (22) is directly a mapped-average expression for $y(r)$. The right-hand side includes a term $e^{\beta u_{ij}(r_{ij})}$, which as in Eq. (26) has the effect of turning off the interaction of the $ij$ pair in the ensemble average, allowing them to sample configurations where they overlap. Such configurations are where information about $y(r)$ in the core is obtained.

As with the conventional formulation of $y(r)$, we represent the $N(N - 1)/2$ identical averages in Eq. (22) in terms of a pair labeled $12$.

$$y(r) = 1 - \frac{V}{2} \left\langle \frac{H(r_{12} - r)}{4\pi r_{12}^2} \beta (f_2 - f_1)^* \cdot \hat{r}_{12} \right\rangle_2.$$  \hspace{1cm} (29)

Further, it is convenient to express the cavity function in excess of its value at contact:

$$y(r) - y(\sigma) = -\frac{V}{2} \left\langle \frac{H(r_{12} - r)}{4\pi r_{12}^2} - \frac{H(r_{12} - \sigma)}{4\pi r_{12}^2} \right\rangle \beta (f_2 - f_1)^* \cdot \hat{r}_{12}.$$  \hspace{1cm} (30)

Non-zero force contributions occur only at collision with a third sphere, labeled $k$, which we say collides with sphere $2$, such that $f_2 = m(v_{2k} \cdot \hat{r}_{2k})\hat{r}_{2k}$, $f_1 = 0$, and integrating over velocities we have:

$$y(r) - y(\sigma) = \left( \beta m \right)^{1/2} V \sum_{c(2,k)} \left[ \frac{H(r_{12} - r)}{r_{12}^2} - \frac{H(r_{12} - \sigma)}{r_{12}^2} \right].$$  \hspace{1cm} (31)

The resulting Heaviside difference is 1 for $r < r_{12}$, but only if $r_{12} < \sigma$.

When generating pairs for $r < \sigma$ using the opportunistic algorithm described in the previous subsection (2.4.1), Eq. (31) yields $y^*(r) - y^*(\sigma)$. Before rescaling according to Eq. (28), we first shift the function up by adding $y^*(\sigma)$. We can estimate this shift by considering how much time the system has had an overlap:

$$\frac{t_{\text{overlapping}}}{t} = \frac{4\pi N \rho}{2} \int_0^\sigma \tilde{r}^2 y^*(\tilde{r}) d\tilde{r}$$

$$= \frac{4\pi N \rho}{2} \int_0^\sigma \tilde{r}^2 (\Delta y^* + y^*(\sigma)) d\tilde{r}$$

$$= \frac{4\pi N \rho}{2} \left( \frac{\sigma^3 y^*(\sigma)}{3} + \int_0^\sigma \tilde{r}^2 \Delta y^* d\tilde{r} \right)$$  \hspace{1cm} (32)

where $\Delta y^*$ is the quantity measured in Eq. (31) using the opportunistic overlap sampling algorithm. Solving for $y^*(\sigma)$,

$$y^*(\sigma) = \frac{3}{\sigma^3} \left( \frac{t_{\text{overlapping}}}{t} \frac{1}{2\pi N \rho} - \int_0^\sigma \tilde{r}^2 \Delta y^* d\tilde{r} \right)$$  \hspace{1cm} (33)

The integral is evaluated using the trapezoid rule.
3. Results and discussion

To evaluate the properties reviewed in Sec. 2 we conducted molecular dynamics (MD) simulations for hard spheres by employing the event driven techniques [5]. Our aim is not to generate state-of-the-art data, but instead to demonstrate the new mapped-averaging formulas and to examine their performance. Therefore, the main body of simulations were performed for a system of \( N = 1000 \) particles although in some cases systems with smaller/larger number of particles were considered as well to probe the sensitivity of results on system size. Except for the singlet-density calculations, all simulations were performed in cubic simulation volumes, with sizes selected to give the desired density for the specified \( N \). In all cases the averages, collected by using mapped-averaging formulas, were compared against the commonly used approaches, i.e., histogram technique for distribution functions and virial equation for the pressure.

To calculate uncertainties, the block average method is used [5] with each block being an independent run. The length of the blocks was varied depending on the system size and the property of interest.

3.1. Pressure

To discuss the case of pressure, we conducted simulations at five densities: \( \rho \sigma^3 = 0.05, 0.20, 0.40, 0.60, \) and 0.80, respectively. These values match some of those examined in a recent study by Pieprzyk et al. [16], who reported high-precision MD data of the HS equation of state (compressibility factor) using collision formula, Eq. (6), and very large systems (as much as \( N = 1098500 \) atoms). At each density we conducted simulations for \( N = 500, 1000, \) and 2000 atoms, respectively, and computed the compressibility factor using: (a) conventional virial, Eq. (4); (b) collision rate, Eq. (6) and (c) mapped averaging, Eq. (9), with no truncation of the \( i \) sum. For each system size, 40 independent runs (blocks) were performed. The duration of each run (in terms of the number of collisions \( n_c \) within the same system size was kept constant; specifically, \( n_c = 10000 \) for \( N = 500 \) and 1000, and \( n_c = 2000 \) for \( N = 2000 \). To confirm that the block length is sufficient for yielding uncorrelated samples for the uncertainties, for the basic system \( N = 1000 \) shorter runs with \( n_c = 1000 \) were performed as well, although these results are not presented.

As can be seen from Table 1, all methods demonstrate smaller relative uncertainties in low density region, although this may have something to do with how the length of the simulations (in simulated time) varies with density. Perhaps surprisingly, the treatment of Maxwell-Boltzmann averaging (stochastic, Eq. (4), versus analytic, Eq. (6)) does not have any effect on the precision of the results. On the other hand, the mapped-averaging approach shows a clear advantage at lower densities, \( \rho \sigma^3 < 0.60 \), yielding results with an uncertainty that 2 to 6 times smaller than that given by conventional methods.

The advantage presented by mapped averaging is offset to a degree by the added computation it requires, introducing at each collision a sum of the colliders with all the other atoms. We accommodate this tradeoff by reference to the difficulty, \( D \), defined [17]

\[
D = t^{1/2}u
\]  

(34)

where \( t \) is the CPU time applied to evaluate a property with uncertainty \( u \). For large samples, this group is asymptotically independent of the amount of sampling, and it
Table 1. MD results for compressibility factor of hard spheres, as given by several averaging formulas

<table>
<thead>
<tr>
<th>( \rho \sigma^3 )</th>
<th>( N )</th>
<th>Conv., Eq. (4)</th>
<th>Collision, Eq. (6)</th>
<th>Mapped, Eq. (9)</th>
<th>Ref. [16]*</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>500</td>
<td>1.11183(17)</td>
<td>1.11192(16)</td>
<td>1.11191(4)</td>
<td>1.11192</td>
</tr>
<tr>
<td>0.05</td>
<td>1000</td>
<td>1.11192(19)</td>
<td>1.11188(16)</td>
<td>1.11193(4)</td>
<td>1.11192</td>
</tr>
<tr>
<td>0.05</td>
<td>2000</td>
<td>1.11234(49)</td>
<td>1.11231(42)</td>
<td>1.11203(7)</td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>500</td>
<td>1.5528(9)</td>
<td>1.5532(7)</td>
<td>1.5533(3)</td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>1000</td>
<td>1.5528(9)</td>
<td>1.5529(7)</td>
<td>1.5533(3)</td>
<td>1.5536</td>
</tr>
<tr>
<td>0.2</td>
<td>2000</td>
<td>1.5518(25)</td>
<td>1.5510(21)</td>
<td>1.5521(8)</td>
<td></td>
</tr>
<tr>
<td>0.4</td>
<td>500</td>
<td>2.5221(29)</td>
<td>2.5236(24)</td>
<td>2.5222(15)</td>
<td></td>
</tr>
<tr>
<td>0.4</td>
<td>1000</td>
<td>2.5216(26)</td>
<td>2.5208(21)</td>
<td>2.5211(14)</td>
<td>2.5216</td>
</tr>
<tr>
<td>0.4</td>
<td>2000</td>
<td>2.5244(49)</td>
<td>2.5213(46)</td>
<td>2.5214(26)</td>
<td></td>
</tr>
<tr>
<td>0.6</td>
<td>500</td>
<td>4.290(5)</td>
<td>4.290(5)</td>
<td>4.292(4)</td>
<td></td>
</tr>
<tr>
<td>0.6</td>
<td>1000</td>
<td>4.297(6)</td>
<td>4.296(4)</td>
<td>4.297(4)</td>
<td>4.295</td>
</tr>
<tr>
<td>0.6</td>
<td>2000</td>
<td>4.282(13)</td>
<td>4.285(13)</td>
<td>4.291(10)</td>
<td></td>
</tr>
<tr>
<td>0.8</td>
<td>500</td>
<td>7.804(15)</td>
<td>7.801(13)</td>
<td>7.800(12)</td>
<td></td>
</tr>
<tr>
<td>0.8</td>
<td>1000</td>
<td>7.768(11)</td>
<td>7.770(12)</td>
<td>7.772(12)</td>
<td>7.770</td>
</tr>
<tr>
<td>0.8</td>
<td>2000</td>
<td>7.780(36)</td>
<td>7.775(29)</td>
<td>7.770(24)</td>
<td></td>
</tr>
</tbody>
</table>

Numbers in parentheses show standard uncertainty (68% confidence) in the last digit(s) of the given value
*Uncertainty is smaller than digits displayed

allows comparison of methods that require different computational effort to achieve a result. Accordingly, conventional and mapped-average properties were computed in independent simulations, to allow proper evaluation of the computational effort required by each. Using this measure, we find that the extra computational effort in mapped averaging lowers the break-even density to about \( \rho \sigma^3 = 0.20 \), although this is slightly system-size dependent.

We can reduce the added effort of mapped averaging by choosing to contribute to the average not with every collision, but instead at some interval. This of course yields less data, but it could be helpful if the data it eliminates is highly correlated with the data that is kept. However, we find that doing this does not yield improved efficiency, as quantified by the difficulty. Alternatively, computational effort could be reduced by truncating the \( i \)-sum Eq. (6) to pairs within a specified cutoff distance from the center of the colliding pair. Potentially this could introduce inaccuracy in the calculation, but it is likely worthwhile, particularly for larger systems; however, we did not investigate this option in the present work.

3.2. Singlet density – parallel hard walls

To examine the formula (15) for the singlet density, we consider the system of HS between parallel hard walls, each of area \( A \). The walls are separated in \( z \)-direction by a distance \( L_z = L + \sigma \), so the volume accessible to the sphere centers is \( LA \). Periodic boundary conditions in \( x \) and \( y \) directions are preserved. We examine singlet density distribution \( \rho(z) \) for a system of \( N = 1000 \) hard spheres under fixed wall separations of \( L = 10\sigma \) and various values of squared area \( A = L_x \times L_y \). In particular, Figs. 3 and 4 present results for \( A/\sigma^2 = 12 \times 12 \) and \( 20 \times 20 \), respectively. The averages were collected from \( 5 \times 10^6 \) collisions using Eq. (15) as well as conventional histograms. Since walls are identical, we present data for one
wall only, showing half of the pore. The figures show that the mapped-averaging formula provides correct results, in comparison to conventional histograms.

Increasing the wall area results in a lower nominal density \(N/(LA)\) of the system. Therefore, the singlet density distribution \(\rho(z)\) in Fig. 4 becomes constant at value \(\rho(z) \approx 0.2426\) already around distances \(z \geq 2\sigma\) from the wall. Following the so-called contact theorem, \(\beta P_{\text{bulk}} = \rho_{\text{wall}}\), and using for the HS pressure, for example, an improved Carnahan-Starling expression \([18, 19]\), \(\beta P/\rho = (1 + \eta + \eta^2 - (2/3)\eta^3 - (2/3)\eta^4)/(1 - \eta)^3\) we obtain that \(\rho_{\text{wall}} = 0.41630\) that agrees well with simulation data in Fig. 4 (result of Eq. (15)) is 0.41628).

As wall area becomes smaller, the nominal density of HS in the system is increasing and singlet density \(\rho(z)\) exhibits oscillating behavior, reflecting stratification of HS imposed by hard walls. In such a case, bulk conditions in the system could not be established and the contact theorem could not be applied. Following Eq. (17), the bulk region could be determined by the distances at which hard spheres are not experiencing collisions with confining walls, i.e., when \(f_{z,j} = 0\).

As for uncertainties in the case of singlet density \(\rho(z)\sigma^3\), at low density, they fluctuate around \(1 \times 10^{-3}\) for mapped averaging, and are about three times that for conventional. At high density, the uncertainties for both methods are about the same, fluctuating in a range around 0.015. The uncertainties do not show appreciable dependence on distance from the wall.

In this regard, it should be noted that the uncertainties for histogram-based methods are strongly dependent on the bin width, and that any straightforward application of histogramming must trade off high resolution (narrower bins) against high precision (wider bins). We handle this in a different way when studying the pair density in the next section.

![Figure 3. Singlet density distribution \(\rho(z)\) for \(N = 1000\) hard spheres between parallel hard walls each of area \(A/\sigma^2 = 12 \times 12\). Results are presented for one wall only, with the rest of the profile being a reflection about \(z/\sigma = 5\). The red (smoother) line describes the results using the mapped-averaging formula, and the blue (pummier) line shows the results from conventional histogramming.](image-url)
3.3. Pair density and cavity distribution function

Averages for the cavity distribution function \( y(r) \) (representing also \( g(r) \) where \( r > \sigma \)) are displayed in Figs. 5 and 6, for densities \( \rho \sigma^3 = 0.20 \) and \( 0.80 \), respectively. Results are presented for simulations of \( N = 1000 \) particles, and are not significantly different from data obtained for \( N = 500 \) or \( 2000 \). Averages represent results from \( 1 \times 10^6 \) time steps of size \( \Delta t = 0.005\sigma/\sqrt{\beta m} \). The methods represented in the plots include: (a) Eq. (25); (b) Eq. (21); (c) fitting of a histogram as described in Sec. 2.4.1; (d) Eq. (31); (e) Eq. (25), scaled as specified by Eq. (28) when the pair separation \( r < \sigma \); (f) conventional histogram, fit to a discrete function as described in the Appendix; (g) trial insertions at preset distances from one atom in an \( N \)-atom simulation. Here, the cavity function is constructed as \( y(r) = (p(r)/p(\sigma))g(\sigma) \), where \( g(\sigma) \) comes from Eq. (24) and the virial pressure as given by Eq. (6), and \( p(r) \) is the fraction of trial insertions at \( r \) that encountered no overlap with another sphere \( y(0) \) is obtained by taking \( p(0) = 1 \).

While there are slight differences that may be observed in the plotted results, the discrepancies are fully within the uncertainties in the data, and therefore all methods provide results that are mutually consistent. All of the curves look very smooth, but the degree of visible noise should not be used to gauge the uncertainty: for mapped averages, different values of \( r \) will be strongly correlated; for conventional histogramming, a smoothing fit has been applied to the results (see Appendix).

The uncertainties are better understood when plotted explicitly, as done in Figs. 7 and 8 for the same densities and methods presented in Figs. 5 and 6. Again we reference the precision in relation to the computational effort via the difficulty (Eq. (34)). The comparisons in Figs. 7 and 8 show the clear advantage of mapped averaging for calculation of \( g(r) \) at lower density, relative to conventional histogramming. At higher densities, the advantage disappears, and both approaches perform equally well. For both densities, particle insertion does best for \( r < \sigma \).
Figure 5. Cavity distribution $y(r)$ for hard spheres at density $\rho \sigma^3 = 0.20$. Results are presented for several methods, as described in Sec. 3.3.

4. Conclusion

Mapped averaging is a very versatile framework for formulating alternative ensemble averages. It can be applied to many thermodynamic properties, including distribution functions, and it can generate many different forms of an ensemble average for a given property. The different forms are obtained from the choice of a different approximate reference model, which enters into the derivation of the mapping that leads to the formulas for the properties [1, 2]. Several such formulas have been presented and examined here, and still more can be derived using other choices for a reference system.

As observed in previous applications, we find that mapped-averaging formulas provide their greatest advantage when applied at conditions where the underlying reference has greatest validity. The formulas examined in this work are based on either the ideal-gas law, or on a pairwise approximation to the fluid structure, and accordingly they are most effective at low density; nevertheless, when applied at other conditions they provide results that are as accurate and precise as conventional methods (but perhaps with added computational cost).

Apart from consideration of performance of molecular simulations, the alternative ensemble averages are interesting in themselves. It is often instructive to derive new rigorous expressions for properties, with nontrivial differences from long-standing representations. Whether this development leads to an improved understanding of the hard-sphere model, or fluids in general, remains to be seen.

Acknowledgments

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Figure 6. Same as Fig. 5, but for density $\rho \sigma^3 = 0.80$.

gineering of the University at Buffalo, SUNY for hosting him as Fulbright Visiting Scholar 2018–2019, when the present studies were accomplished.

References

Figure 7. Comparison of difficulty (Eq. (34)) for several methods of calculation of cavity and radial distribution function of hard-sphere fluid at $\rho \sigma^3 = 0.20$. Methods are as follows: “pair mapping,” Eq. (25); “pair mapping (from $\sigma$),” Eq. (21); “2-atom histogram fit,” as described in Sec. 2.4.1; “2-atom mapping,” Eq. (31); “pair mapping (cavity),” Eq. (25) but multiplied by $n_{\sigma=\sigma_-}$ when the pair separation $r < \sigma$ “histogram discrete fit,” conventional histogram, fit to a discrete function to offset the effect on uncertainty of the arbitrary choice of bin width, as described in the text; “insertion” is based on trial insertions at preset distances from one atom in an $N$-atom simulation, with cavity function constructed as described in Sec. 3.3; filled symbols are based on insertions for $r/\sigma$ from 0.1 to 1.0, while the open symbol is from a simulation focused on obtaining $y(0)$ (using only insertions at $r = \sigma$).

Appendix A. Piecewise fit

The bin width within the conventional approach can be varied; with small bins, each bin will have high uncertainty while with large bins, each bin has a low uncertainty, but the overall description of the function is poor because of low resolution. One remedy is to fit the histogrammed data to a function, but this may fail if the data are not well described by any function. While spline interpolation can (in principle) describe the function, most interpolation schemes ignore the uncertainties and simply connect the points, which may be noisy if the bins are small.

We have taken a different approach, which is to take the function to be defined by linear interpolation between discrete points $y_i$, which are optimized with least-squares regression. We begin by defining the range of independent-variable ($r$) values and the number of $r$ values ($n_r$). The $r$ values are then $r_i = r_{\text{min}} + i\Delta r$ with $\Delta r = (r_{\text{max}} - r_{\text{min}})/n_r$. For $r = r_i$, $y(r) = y_i$, while for $r_i < r < r_{i+1}$,

$$y(r) = y_i + (y_{i+1} - y_i)f_i(r)$$

(A1)

where $f_i(r) = (r - r_i)/\Delta r$. The fitting function $y(r)$ is then continuous and piecewise linear.

The binned histogram values will be denoted $Y_j$ with uncertainties $\sigma_j$, and which are evaluated for the set of $r$ values labeled as $R_j$. Our objective function is the
same as in any weighted least-squares regression,

\[ \Omega = \sum_j \left( \frac{Y_j - y(R_j)}{\sigma_j} \right)^2 \]  

(A2)

The derivative with \( y_i \) is then

\[ \frac{\partial \Omega}{\partial y_i} = -\sum_{j^+} \frac{2}{\sigma_j^2} (Y_j - y_i - (y_{i+1} - y_i)f_{ij})(1 - f_{ij}) \]

\[ -\sum_{j^-} \frac{2}{\sigma_j^2} [Y_j - y_{i-1} - (y_i - y_{i-1})f_{(i-1)j}] f_{(i-1)j} \]  

(A3)

where the first sum is taken over those \( j \) where \( r_i \leq R_j \leq r_{i+1} \) and then second sum is taken over those \( j \) where \( r_{i-1} \leq R_j \leq r_i \). We set \( \partial \Omega/\partial y_i = 0 \) and rearrange to yield

\[ \sum_{j^+} \frac{1}{\sigma_j^2} \left[ (1 - f_{ij})^2 y_i + f_{ij}(1 - f_{ij})y_{i+1} \right] \]

\[ + \sum_{j^-} \frac{1}{\sigma_j^2} \left[ f_{(i-1)j}(1 - f_{(i-1)j})y_{i-1} + f_{(i-1)j}^2 \right] \]

\[ = \sum_{j^+} \frac{1}{\sigma_j^2} (1 - f_{ij})Y_j + \sum_{j^-} \frac{1}{\sigma_j^2} f_{(i-1)j}Y_j \]  

(A4)

where we define \( f_{ij} \equiv f_i(R_j) \). Having constructed such an equation for each \( i \), the system of equations can be solved together for all \( y_i \). The number of \( y_i \) values
is determined by a $\chi^2$ statistic to avoid over- or under-fitting. Uncertainties in the $y_i$ are propagated from the uncertainties in the $Y_j$, which are assumed to be uncorrelated. We find that the uncertainties in the $y_i$ are insensitive to the size of the bins used to accumulate the $Y_j$, which was the primary aim of this analysis.

![Figure A1. Illustration of the piecewise-linear fit of the histogram data. The (red) $y_i$ points are determined by the fit, which is made for the given set of (black) $Y_j$ points. Only a small range of the total set of points are shown.](image)

Appendix B. Mapped-Averaging Formulas

The remainder of the Appendix provides details about the derivations of the mapped-averaging formulas used in this paper. Although the resulting formulas are often concise and easy to implement, sometimes their development is lengthy, and examples showing the details can be instructive. We begin with a summary of the general mapped-averaging formulas, and in following sections we derive expressions for specific properties.

Mapped averages are obtained via derivatives of the free energy $A$ with respect to some parameter designated $\lambda$ or $\mu$, via the formulas [2]:

\[
(\beta A)_\lambda \equiv \frac{\partial (\beta A)}{\partial \lambda} = - \langle J_\lambda \rangle + \langle (\beta U)_\lambda \rangle
\]  

(B1a)

\[
(\beta A)_{\lambda\mu} \equiv \frac{\partial^2 (\beta A)}{\partial \lambda \partial \mu} = - \langle J_{\lambda\mu} - J_\lambda J_\mu \rangle + \langle (\beta U)_{\lambda\mu} \rangle
\]  

(B1b)

\[ - \text{Cov} \left[ J_\lambda - (\beta U)_\lambda, J_\mu - (\beta U)_\mu \right]. \]

These are expressed in terms of averages of the Jacobian and energy derivatives,
given as:

\[ J_\lambda = \nabla_x \cdot \dot{x}^\lambda \]  

(B2a)

\[ J_{\lambda\mu} - J_\lambda J_\mu = \nabla_x \cdot \dot{x}_\mu^\lambda + \dot{x}_\mu^\lambda \cdot \nabla_x (\nabla_x \cdot \dot{x}^\lambda) \]

(B2b)

\[ (\beta U)_\lambda = (\beta u)_\lambda - \beta f \cdot \dot{x}^\lambda \]  

(B2c)

\[ (\beta U)_{\lambda\mu} = (\beta u)_{\lambda\mu} - \left( \dot{x}_\mu^\lambda + \dot{x}_\mu^\lambda \cdot \nabla_x \dot{x}^\lambda \right) \cdot \beta f 
+ \dot{x}_\mu^\lambda \cdot \beta \phi \cdot \dot{x}^\lambda 
- \left( \dot{x}_\lambda^\mu \cdot (\beta f)_\mu + \dot{x}_\mu^\lambda \cdot (\beta f)_\lambda \right) . \]

(B2d)

Here, \( x \) represents a vector of all atomic coordinates (e.g., for \( N \) atoms in 3D, \( x \) is of length \( 3N \)), \( f \equiv -\nabla_x u \) is the force vector and \( \phi \equiv \nabla_x \nabla_x u \) is the force-constant matrix (Hessian) for a given configuration.

The key to the effectiveness of a mapped average is the mapping velocity, \( \dot{x}^\lambda \), which is formulated to satisfy the master equation:

\[ \frac{\partial}{\partial \lambda} \left( \frac{p}{q} \right) + \nabla_x \cdot \left( \frac{p}{q} \dot{x}^\lambda \right) = 0, \]

(B3a)

or

\[ \nabla_x \cdot \left( \frac{p}{q} \dot{x}^\lambda \right) = -\frac{\partial p}{\partial \lambda} + p \frac{\partial \ln q}{\partial \lambda}, \]

(B3b)

where \( q = \int dx \ p(x) \) is the normalization constant for the unnormalized probability \( p(x) \), which is chosen to make the mathematics tractable while providing a good approximation to the true probability of a configuration. Making a good selection for \( p(x) \) is the “art” of developing a mapped average formula.

We may combine Equations (B1a), (B3), (B2a), and (B2c) to obtain:

\[ (\beta A)_\lambda = -\left( \ln q \right)_\lambda \]

(B4)

\[ + \left( (\ln p)_\lambda + (\beta u)_\lambda + \dot{x}_\lambda \cdot (\nabla_x \ln p - \beta f) \right) . \]

Whereas Equations (B1) and (B2) are true in general—for any choice of \( \dot{x}^\lambda \)—Equation (B4) is correct only if \( \dot{x}^\lambda \) is given according to Equation (B3).

We use \( r \) to represent a spatial-coordinate vector, so \( r_i \) is a component of \( x \) that represents the position of atom \( i \).

Appendix C. Derivation of Eqs. (7) and (8)

In this section we consider volume derivatives to yield the pressure, so \( \lambda \equiv V \) and we want:

\[ \beta P = -(\beta A)_V . \]

(C1)
C.1. Single-pair mapping

We derive the mapping for a weighting function that accounts for the interaction of a single pair:

\[ p(x) = \exp(-\beta u_2(r_i, r_j)) \equiv e_{ij} \]  \hspace{1cm} (C2a)

\[ q(V) = \int_V dxe_{ij} = V^{N-1} \int d\mathbf{r}_{ij} e_{ij} = V^{N} \left(1 - \frac{2B_2}{V}\right), \]  \hspace{1cm} (C2b)

where \( B_2 \) is the second virial coefficient:

\[ B_2 = -\frac{1}{2} \int d\mathbf{r}_{ij} f_{ij} = -\frac{1}{2} \int d\mathbf{r}_{ij} (e_{ij} - 1). \]  \hspace{1cm} (C3)

With (C2) in the mapping equation (B3b)

\[ \nabla_x \cdot (e_{ij} \dot{\mathbf{x}}^V) = e_{ij} \left(\frac{N}{V} + \frac{2B_2}{V^2} + O(V^{-3})\right). \]  \hspace{1cm} (C4)

We write out the divergence explicitly

\[ e_{ij} \sum_{k \neq i,j} \nabla_{\mathbf{r}_k} \cdot \dot{\mathbf{r}}_k^V + e_{ij} \nabla_{\mathbf{R}_{ij}} \cdot \dot{\mathbf{R}}_{ij}^V + \nabla_{\mathbf{r}_{ij}} \cdot (e_{ij} \dot{\mathbf{r}}_{ij}^V) = e_{ij} \left(\frac{N}{V} + \frac{2B_2}{V^2}\right). \]  \hspace{1cm} (C5)

Here we have recast the atom coordinates \( \mathbf{r}_i \) and \( \mathbf{r}_j \) in terms of their geometric center \( \mathbf{R}_{ij} \equiv (\mathbf{r}_i + \mathbf{r}_j)/2 \) and their separation vector \( \mathbf{r}_{ij} \equiv \mathbf{r}_j - \mathbf{r}_i \):

\[ \mathbf{r}_i = \mathbf{R}_{ij} - \frac{1}{2} \mathbf{r}_{ij}, \]  \hspace{1cm} (C6a)

\[ \mathbf{r}_j = \mathbf{R}_{ij} + \frac{1}{2} \mathbf{r}_{ij}; \]  \hspace{1cm} (C6b)

note that \( e_{ij} \) depends only on \( \mathbf{r}_{ij} \). This single equation for all the components of \( \dot{\mathbf{x}}^V \) can be satisfied by the following equations:

\[ \nabla_{\mathbf{r}_k} \cdot \dot{\mathbf{r}}_k^V = \frac{1}{V} \]  \hspace{1cm} (C7a)

\[ \nabla_{\mathbf{R}_{ij}} \cdot \dot{\mathbf{R}}_{ij}^V = \frac{1}{V} \]  \hspace{1cm} (C7b)

\[ \nabla_{\mathbf{r}_{ij}} \cdot (e_{ij} \dot{\mathbf{r}}_{ij}^V) = e_{ij} \left(\frac{1}{V} + \frac{2B_2}{V^2}\right). \]  \hspace{1cm} (C7c)

The first two equations are solved to yield the usual affine-expansion mapping:

\[ \dot{\mathbf{r}}_k^V = \frac{\mathbf{r}_k}{3V} \]  \hspace{1cm} (C8a)

\[ \dot{\mathbf{R}}_{ij}^V = \frac{\mathbf{R}_{ij}}{3V}. \]  \hspace{1cm} (C8b)

We treat the third equation as follows. Consider that the \( \mathbf{r}_{ij} \) scaling is in the direction of their separation, so it depends only on \( r_{ij} = |\mathbf{r}_{ij}| \): \( \dot{\mathbf{r}}_{ij}^V = \frac{\dot{r}_{ij}^V}{r_{ij}} \mathbf{r}_{ij} \). Write
\[ \dot{r}_{ij}^V = r_{ij}/3V + \Delta \dot{r}_{ij}^V, \] defining the excess \( \Delta \dot{r}_{ij}^V \) above the base scaling. Then
\[
\frac{1}{r_{ij}^2} \frac{d}{dr_{ij}} \left[ r_{ij}^2 (f_{ij} + 1) \left( \frac{r_{ij}^2}{3V} + \Delta \dot{r}_{ij}^V \right) \right] = (f_{ij} + 1) \left( \frac{1}{V} + \frac{2B_2}{V^2} \right). \tag{C9}
\]

The terms not involving \( f_{ij}, \Delta \dot{r}_{ij}^V \) or \( 1/V^2 \) cancel, leaving
\[
\frac{1}{r_{ij}^2} d \left[ \left( \frac{f_{ij} r_{ij}^3}{3V} + r_{ij}^2 e_{ij} \Delta \dot{r}_{ij}^V \right) \right] = \frac{f_{ij} V}{V} + e_{ij} 2B_2 \frac{V}{V^2}. \tag{C10}
\]

Integrating:
\[
\Delta \dot{r}_{ij}^V (r_{ij}) = \int_{r_{ij}}^{r_{ij}} d \tilde{r}_{ij} \left[ \frac{\tilde{r}_{ij}^2 f(\tilde{r}_{ij}) - f(r_{ij})}{r_{ij}^2} e_{ij} \frac{2B_2}{V^2} \right], \tag{C11a}
\]

or
\[
\Delta \dot{r}_{ij}^V (r_{ij}) = \frac{1}{V} \int_{r_{ij}}^{r_{ij}} d \tilde{r}_{ij} \left[ \tilde{r}_{ij}^2 \left( \frac{e(\tilde{r}_{ij})}{e(r_{ij})} - 1 \right) + \frac{\tilde{r}_{ij}^2 e(\tilde{r}_{ij})}{r_{ij}^2 e(r_{ij})} 2B_2 \right], \tag{C11b}
\]

or
\[
\Delta \dot{r}_{ij}^V (r_{ij}) = \frac{2B_2}{3V^2} r_{ij} + \frac{1}{V} \left( 1 + \frac{2B_2}{V} \right) \int_{r_{ij}}^{r_{ij}} d \tilde{r}_{ij} \frac{\tilde{r}_{ij}^2}{r_{ij}^2} \left( \frac{e(\tilde{r}_{ij})}{e(r_{ij})} - 1 \right). \tag{C11c}
\]

The integral appearing in this expression is plotted in Fig. C1 for the Lennard-Jones model at several temperatures. Interestingly, it shows negative mapping velocities at close range (pulling the atoms closer) and positive velocities at larger separations (pushing them further apart). This shows that the aim of the mapping is not necessarily to lower the energy, but to keep the relative importance of the configuration constant (an unfavorable overlap is to some extent restored by the pair mapping after it is relieved by the baseline affine mapping).

Putting it together, for atoms \( i \) and \( j \) the total mapping is
\[
\dot{r}_i^V = \frac{r_i}{3V} - \frac{1}{2} \Delta \dot{r}_{ij}^V \dot{r}_{ij} \tag{C12a}
\]
\[
\dot{r}_j^V = \frac{r_j}{3V} + \frac{1}{2} \Delta \dot{r}_{ij}^V \dot{r}_{ij}. \tag{C12b}
\]

For all other atoms \( k \neq i, j \), the mapping is given by Eq. (C8a).

### C.2. Multi-pair mapped average

A mapped average that involves just a single pair will not lead to a new ensemble average that is significantly different from the standard formula for the pressure, which is based on an ideal-gas starting point; hence we do not yet go on to derive a pressure expression from the mapping developed above. We have not found a formulation of an approximate weight \( p(x) \) that handles multiple pairs in a way that does not reduce to something similarly ineffective in the limit of \( N \to \infty \). For
Figure C1. The integral in Eq. (C11c), the primary component of $\Delta V^r_i$. Calculations are performed for the Lennard-Jones model at four temperatures (solid lines, from top to bottom): 0.7, 1.0, 1.3, and 2.0. Thick solid red line is corresponding quantity for the hard-sphere model with $\sigma = 1$, as given by Eq. (7b), while the thick solid black line (visible only because it is thicker than the lines on top of it) is the integral evaluated by treating the hard-sphere model as the $n \to \infty$ limit of a $1/r^n$ potential. Dashed line shows the Lennard-Jones potential.

$(\ln q)_V$ to yield $\rho + B_2 \rho^2$ in Eq. (B4) requires

$$q = V^N \left( 1 - \frac{2B_2}{V} \right)^{N(N-1)/2},$$

and we do not know of a tractable choice for $p(x)$ that yields this $q$.

Instead, we take the results from the previous section and introduce an *ad hoc* extension, with an “excess mapping” for molecule $i$ given as a sum of its pairwise mapping with all other molecules $j$:

$$\dot{r}^V_i = \frac{r_i}{3V} + \frac{1}{2} \sum_{j \neq i} \Delta \dot{r}^V_{ij} \hat{r}_{ji};$$

(C14)

note that $\hat{r}_{ji}$ is the unit vector from $j$ to $i$. This mapping does not satisfy the balance equation, Eq. (B3), for a known $p/q$, so to derive properties we must use Eqs. (B1) and (B2). For the Jacobian derivative we have

$$J_V = \sum_i \nabla_{r_i} \cdot \dot{r}^V_i$$

$$= \left( \sum_i \nabla_{r_i} \cdot \frac{r_i}{3V} \right) + \frac{1}{2} \sum_i \sum_{j \neq i} \nabla_{r_i} \cdot (\Delta \dot{r}^V_{ij} \hat{r}_{ji})$$

$$= \frac{N}{V} + \frac{1}{2} \sum_i \sum_{j \neq i} \frac{1}{r_{ij}^2} \frac{d}{dr_{ij}} (r_{ij}^2 \Delta \dot{r}^V_{ij}),$$

(C15)
With \( \Delta f_{ij}^V \) from Eq. (C11c) this becomes

\[
J_V = \rho + \frac{1}{2} \sum_i \sum_{j \neq i} \frac{1}{2} \frac{d}{dr_{ij}} \left[ \frac{2B_2}{3V^2} r_{ij}^3 + \frac{1}{V} \left( 1 + \frac{2B_2}{V} \right) \int_0^{r_{ij}} d\tilde{r}_{ij} \tilde{r}_{ij}^2 \left( \frac{e(\tilde{r}_{ij})}{e(r_{ij})} - 1 \right) \right]
\]

\[
= \rho + \frac{N(N-1)}{V^2} B_2 + \frac{1}{2V} \left( 1 + \frac{2B_2}{V} \right) \sum_i \sum_{j \neq i} \beta u'(r_{ij}) \int_0^{r_{ij}} d\tilde{r}_{ij} \tilde{r}_{ij}^2 \frac{e(\tilde{r}_{ij})}{e(r_{ij})}
\]

\[
= \rho + B_2 \left( \rho^2 - \frac{\rho}{V} \right) - \frac{\rho}{2} \left( 1 + \frac{2B_2}{V} \right) \frac{1}{N} \sum_i \sum_{j \neq i} \beta f_{ji} \int_0^{r_{ij}} d\tilde{r}_{ij} \tilde{r}_{ij}^2 \left( \frac{e(\tilde{r}_{ij})}{e(r_{ij})} - 1 \right)
\]

\[
= \rho + B_2 \rho^2 \left( 1 - \frac{1}{N} \right) - \frac{\rho}{2} \left( 1 + \frac{2B_2\rho}{N} \right) \frac{1}{3N} \sum_i \sum_{j \neq i} \beta f_{ji} \cdot r_{ji}
\]

\[
- \frac{\rho}{2} \left( 1 + \frac{2B_2\rho}{N} \right) \frac{1}{N} \sum_i \sum_{j \neq i} \beta f_{ji} \cdot \tilde{r}_{ji} \int_0^{r_{ij}} d\tilde{r}_{ij} \tilde{r}_{ij}^2 \left( \frac{e(\tilde{r}_{ij})}{e(r_{ij})} - 1 \right)
\]

The energy derivative is, from Eq. (B2c),

\[
-(\beta U)_V = -\beta u_V + \sum_i \beta f_i \cdot \dot{r}_i^V
\]

\[
= -\beta u_V + \frac{1}{3V} \sum_i \beta f_i \cdot \dot{r}_i + \frac{1}{2} \sum_i \beta f_i \cdot \sum_{j \neq i} \dot{r}_{ji} \Delta r_{ij}^V
\]

\[
= -\beta u_V + \frac{\rho}{3N} \sum_i \beta f_i \cdot r_i
\]

\[
+ \frac{1}{2} \sum_i \beta f_i \cdot \sum_{j \neq i} \dot{r}_{ji} \left[ \frac{2B_2}{3V^2} r_{ij}^3 + \frac{1}{V} \left( 1 + \frac{2B_2}{V} \right) \int_0^{r_{ij}} d\tilde{r}_{ij} \tilde{r}_{ij}^2 \frac{e(\tilde{r}_{ij})}{e(r_{ij})} - 1 \right]
\]

\[
= -\beta u_V + \frac{\rho}{3N} \sum_i \beta f_i \cdot r_i - \frac{B_2\rho^2}{3N} \sum_i \beta f_i \cdot \dot{r}_{ij}
\]

\[
+ \frac{\rho}{2} \left( 1 + \frac{2B_2\rho}{N} \right) \frac{1}{N} \sum_i \beta f_i \cdot \sum_{j \neq i} \dot{r}_{ji} \int_0^{r_{ij}} d\tilde{r}_{ij} \tilde{r}_{ij}^2 \left( \frac{e(\tilde{r}_{ij})}{e(r_{ij})} - 1 \right),
\]
where \( \bar{r}_{ij} \equiv \frac{1}{N} \sum_{j \neq i}^N r_{ij} \). Here we include \( u_V \), which is \( (\partial u/\partial V)_x \), describing how the energy changes with volume while keeping the coordinates fixed. This contribution captures effects of the boundary, including the molecules in the periodic boundaries, which move away from the central-image atoms as the volume is increased [20, 21].

We add (C17) and (C18) to obtain the mapped-average expression for the pressure:

\[
\frac{\beta P}{\rho} = \frac{1}{\rho} \left( J_V - (\beta U)_V \right)
\]

\[
= \left[ 1 + B_2 \rho \left( 1 - \frac{1}{N} \right) - \frac{1}{2} \left( 1 + \frac{2B_2\rho}{N} \right) \right] \left( \frac{1}{3N} \sum_i \sum_{j \neq i}^N \beta f_{ij} \cdot r_{ij} \right)
\]

\[
- \frac{1}{2} \left( 1 + \frac{2B_2\rho}{N} \right) \left( \frac{1}{N} \sum_i \sum_{j \neq i}^N \beta f_{ij} \cdot \bar{r}_{ij} \int_0^r d\tilde{r}_{ij} \frac{r_{ij}^2}{\bar{r}_{ij}^2} \left( \frac{e(\tilde{r}_{ij})}{e(r_{ij})} - 1 \right) \right)
\]

\[
+ \left[ -\beta u_V + \frac{1}{3N} \sum_i^N \beta f_i \cdot r_i - \frac{1}{6N} \sum_i \sum_{j \neq i}^N \beta f_{ij} \cdot r_{ij} \right] - B_2 \rho \left( \frac{1}{3N} \sum_i^N \beta f_i \cdot \bar{r}_{ij} \right)
\]

\[
+ \frac{1}{2} \left( 1 + \frac{2B_2\rho}{N} \right) \left( \frac{1}{N} \sum_i \sum_{j \neq i}^N \beta f_i^* \cdot \bar{r}_{ij} \int_0^r d\tilde{r}_{ij} \frac{r_{ij}^2}{\bar{r}_{ij}^2} \left( \frac{e(\tilde{r}_{ij})}{e(r_{ij})} - 1 \right) \right) . \quad \text{(C19)}
\]

Rearranging:

\[
\frac{\beta P}{\rho} = 1 + B_2 \rho \left( 1 - \frac{1}{N} \right) - \frac{B_2\rho}{N} \left( \frac{1}{3N} \sum_i \sum_{j \neq i}^N \beta f_{ij} \cdot r_{ij} \right)
\]

\[
+ \left[ -\beta u_V + \frac{1}{3N} \sum_i^N \beta f_i \cdot r_i - \frac{1}{6N} \sum_i \sum_{j \neq i}^N \beta f_{ij} \cdot r_{ij} \right] - B_2 \rho \left( \frac{1}{3N} \sum_i^N \beta f_i \cdot \bar{r}_{ij} \right)
\]

\[
+ \frac{1}{2} \left( 1 + \frac{2B_2\rho}{N} \right) \left( \frac{1}{N} \sum_i \sum_{j \neq i}^N \beta f_i^* \cdot \bar{r}_{ij} \int_0^r d\tilde{r}_{ij} \frac{r_{ij}^2}{\bar{r}_{ij}^2} \left( \frac{e(\tilde{r}_{ij})}{e(r_{ij})} - 1 \right) \right) . \quad \text{(C20)}
\]

where the \( f_i^* \equiv f_i - f_{ji} \) is the force on \( i \) exclusive of the contribution due to molecule \( j \). Eliminating terms of order \( 1/N \):

\[
\frac{\beta P}{\rho} = 1 + B_2 \rho + \left\{ -\beta u_V + \frac{1}{3N} \sum_i^N \beta f_i \cdot r_i - \frac{1}{6N} \sum_i \sum_{j \neq i}^N \beta f_{ij} \cdot r_{ij} \right\}
\]

\[
- B_2 \rho \left( \frac{1}{3N} \sum_i \beta f_i \cdot \bar{r}_{ij} \right)
\]

\[
+ \frac{1}{2} \left( \frac{1}{N} \sum_i \sum_{j \neq i}^N \beta f_i^* \cdot \bar{r}_{ij} \int_0^r d\tilde{r}_{ij} \frac{r_{ij}^2}{\bar{r}_{ij}^2} \left( \frac{e(\tilde{r}_{ij})}{e(r_{ij})} - 1 \right) \right) . \quad \text{(C21)}
\]

The first term in angle-brackets on the right-hand side will be zero for pairwise additive potentials in periodic boundaries. The term following that should be small, as the vector sum from \( i \) to every \( j \) should tend to cancel; still, fluctuations may
correlate with \( f_i \) and prevent the term from being identically zero. Neglecting these two contributions, we have:

\[
\frac{\beta P}{\rho} = 1 + B_2 \rho + \frac{1}{2} \left( \frac{1}{N} \sum_{i} \sum_{j \neq i} \beta f_i^* \cdot \hat{r}_{ji} \int_0^{r_{ij}} d\tilde{r}_{ij} \frac{\tilde{r}_{ij}^2}{r_{ij}^2} \left( \frac{e(\tilde{r}_{ij})}{e(r_{ij})} - 1 \right) \right). \tag{C22}
\]

Alternatively,

\[
\frac{\beta P}{\rho} = 1 + B_2 \rho + \frac{1}{2} \left( \frac{1}{N} \sum_{i} \sum_{j < i} \beta (f_i - f_j)^* \cdot \hat{r}_{ji} \int_0^{r_{ij}} d\tilde{r}_{ij} \frac{\tilde{r}_{ij}^2}{r_{ij}^2} \left( \frac{e(\tilde{r}_{ij})}{e(r_{ij})} - 1 \right) \right). \tag{C23}
\]

This is the formula given as Eq. (7) in the main part of the paper.

We now write this as a sum over collisions involving colliders labeled \( j, k \), and introduce Eq. (7b) for the integral:

\[
\frac{\beta P}{\rho} = 1 + B_2 \rho - \frac{1}{6} \frac{\sigma^3}{N^7} \sum_{c(j,k)} \sum_{i} \sum_{j < i} \beta (f_i - f_j)^* \cdot \hat{r}_{ji}. \tag{C24}
\]

If \( i \) and \( j \) appearing in the difference \( (f_i - f_j)^* \) were the two colliders, the whole term would be zero because it is defined to exclude forces due to \( i \) and \( j \). Hence, only one force \( f_i \) or \( f_j \) in \( (f_i - f_j)^* \) will be nonzero, as it is the one colliding with another sphere, \( k \). Thus, once the sum over pairs is completed, there will be two force terms to consider, one for each collider, with terms collected as follows:

\[
\frac{\beta P}{\rho} = 1 + B_2 \rho - \frac{\beta \sigma^3}{6N^7} \sum_{c(j,k)} \left[ f_j \cdot \sum_{i \neq (j,k)} \frac{\hat{r}_{ij}}{r_{ij}^2} + f_k \cdot \sum_{i \neq (j,k)} \frac{\hat{r}_{ik}}{r_{ik}^2} \right]. \tag{C25}
\]

With the forces given via Eq. (3), this expression then yields Eq. (8).

**Appendix D. Derivation of Eqs. (13), (14), and (18)**

In this section we develop mapped-averaging expressions to yield the singlet density, which is given as the functional derivative of the free energy with respect to a contribution \( \phi_1(r) \) to the overall singlet potential [4]:

\[
\rho(r) = \frac{1}{\beta} \frac{\delta(\beta A)}{\beta \delta \phi_1(r)} = \frac{1}{\beta} (\beta A) \phi_1(r). \tag{D1}
\]

We introduce \( \phi_1(r) \) as a device to derive the singlet density via this derivative; in the end we set \( \phi_1(r) \equiv 0 \) before arriving at the final formula for \( \rho(r) \). The “real” contribution to the singlet potential, designated \( u_1(r) \), is separate from this and may or may not be zero for the system of interest.

In this development we assume the density varies in only one dimension, labeled
$z$, and accordingly for $\phi_1$; thus, we want the functional derivative

$$\rho(z) = \frac{1}{\beta} (\beta A)_{A\phi_1(z)}$$  \hspace{1cm} \text{(D2)}

$$= \frac{1}{A^\beta} (\beta A)_{\phi_1(z)}.$$  \hspace{1cm} \text{(D3)}

While (D2) and (D3) are equivalent, the choice between using the functional derivative with respect to $A\phi_1(z)$ or $\phi_1(z)$ affects a few of the intermediate results, but the final formula for $\rho(z)$ is the same either way. We will use (D3).

The governing equation for the mapping velocity, Eq. (B3b), given explicitly is:

$$\sum_{i=1}^{N} \left[ \frac{\partial}{\partial x_i} (p_1(z_i)^{\phi_1(z)}) + \frac{\partial}{\partial y_i} (p_1(z_i)^{\phi_1(z)}) + \frac{\partial}{\partial z_i} (p_1(z_i)^{\phi_1(z)}) \right] = -\delta p(x) + p(x) \frac{\delta \ln q}{\delta \phi_1(z)}.$$  \hspace{1cm} \text{(D4)}

We choose to work with estimated probability densities that can be written as a product of single-body probabilities $p_1$ of the form:

$$p(x) = \prod_{i=1}^{N} p_1(z_i)$$

$$= \prod_{i=1}^{N} p_0(z_i) \exp (-\beta \phi_1(z_i)).$$  \hspace{1cm} \text{(D5)}

where $p_0$ is independent of $\phi_1$. Also,

$$q = \int dx \, p(x)$$

$$= \left[ \int dz \, p_0(z) \exp (-\beta \phi_1(z)) \right]^{N}$$

$$\equiv q_1^{N}.$$  \hspace{1cm} \text{(D6)}

This, along with the assertion that all $x$ and $y$ derivatives are zero, allows us to write Eq. (D4) as:

$$\sum_{i=1}^{N} \left( \prod_{j \neq i}^{N} p_1(z_j) \right) \frac{\partial}{\partial z_i} (p_1(z_i)^{\phi_1(z)}) = -\delta p(x) + p(x) \frac{\delta \ln q}{\delta \phi_1(z)}$$

$$= \sum_{i=1}^{N} \left( \prod_{j \neq i}^{N} p_1(z_j) \right) \left( -\frac{\delta p_1(z_i)}{\delta \phi_1(z)} + p_1(z_i) \frac{\delta \ln q_1}{\delta \phi_1(z)} \right)$$

$$= \sum_{i=1}^{N} \left( \prod_{j \neq i}^{N} p_1(z_j) \right) \left( \beta p_1(z_i) \delta(z - z_i) - \beta p_1(z_i) \frac{p_1(z)}{q_1} \right).$$  \hspace{1cm} \text{(D7)}
This equation may be solved by solving it for each \( i \) individually:

\[
\frac{\partial}{\partial z_i} \left( p_1(z_i) \dot{z}_i^\phi(z) \right) = \beta p_1(z) \left( \delta(z - z_i) - \frac{p_1(z_i)}{q_1} \right),
\tag{D8}
\]

For the uniform-reference case \( (p_0(z) \equiv 1), q_1 = L \), and while also setting \( \phi_1(z) \equiv 0 \), this becomes

\[
\frac{\partial}{\partial z_i} \dot{z}_i^\phi(z) = \beta \left( \delta(z - z_i) - \frac{1}{L} \right).
\tag{D9}
\]

Integration with the boundary condition \( \dot{z}_i^\phi(z) = 0 \) at \( z_i = -L/2 \) (hard-wall boundary) yields

\[
\dot{z}_i^\phi(z) = \beta \left( H(z_i - z) - \frac{1}{2} - \frac{z_i}{L} \right),
\tag{D10}
\]

which also satisfies \( \dot{z}_i^\phi(z) = 0 \) at \( z_i = +L/2 \).

To develop the expression for the singlet density, we turn to Eq. (B4), which for this case becomes:

\[
\rho(z) = \frac{1}{A} \beta (\beta A)_{\phi_1(z)} \\
\quad = -\frac{N}{A} (\ln q_1)_{\phi_1(z)} + \frac{1}{A \beta} \left( (\ln p)_{\phi_1(z)} + (\beta u)_{\phi_1(z)} + \sum_{i=1}^{N} \dot{z}_i^\phi(z) \left( \frac{\partial \ln p}{\partial z_i} - \beta f_{z,i} \right) \right) \\
\quad = \frac{N p_1(z)}{A q_1} + \left\langle \frac{1}{A \beta} \sum_{i=1}^{N} (-\beta \delta(z - z_i) + \beta \delta(z - z_i) + \dot{z}_i^\phi(z) \left( \frac{d \ln p_0(z_i)}{dz_i} - \beta f_{z,i} \right) \right\rangle \\
\quad = \frac{N p_0(z)}{A q_1} + \left\langle \frac{1}{A \beta} \sum_{i=1}^{N} \dot{z}_i^\phi(z) \left( \frac{d \ln p_0(z_i)}{dz_i} - \beta f_{z,i} \right) \right\rangle.
\tag{D11}
\]

where in the last line we have also set \( \phi_1(z) = 0 \). For the uniform-reference case, (D11) becomes:

\[
\rho(z) = \frac{N}{A L} - \left\langle \frac{1}{A \beta} \sum_{i=1}^{N} \dot{z}_i^\phi(z) \beta f_{z,i} \right\rangle,
\tag{D12}
\]

and with \( \dot{z}_i^\phi(z) \) given by Eq. (D10), this yields Eq. (13).

When we write the ensemble average as a sum over collisions between atoms
labeled \( j \) and \( k \), Eq. (D12) is:

\[
\rho(z) = N/A - \frac{1}{A\tau} \sum_{c(j,k)} (\dot{z}_{j}^{\phi_{1}}(z) f_{z,kj} + \dot{z}_{k}^{\phi_{1}}(z) f_{z,kj}) \\
= N/A - \frac{1}{A\tau} \sum_{c(j,k)} (\dot{z}_{j}^{\phi_{1}}(z) - \dot{z}_{k}^{\phi_{1}}(z)) f_{z,kj} \\
= N/A - \frac{\beta}{A\tau} \sum_{c(j,k)} \left( H(z_{j} - z) - H(z_{k} - z) - \frac{z_{j} - z_{k}}{L} \right) f_{z,kj},
\]

(D13)

Then, with integration through the impulsive force as in Eq. (3), using \( \hat{r}_{jk} = r_{jk}/\sigma \) at collision,

\[
\rho(z) = N/A + \frac{\beta m}{\sigma A\tau} \sum_{c(j,k)} \left( H(z_{j} - z) - H(z_{k} - z) - \frac{z_{j} - z_{k}}{L} \right) (v_{kj} \cdot \hat{r}_{kj})(r_{kj} \cdot \hat{e}_{z})
\]

(D14)

Recognizing that \( r_{kj} \cdot \hat{e}_{z} = z_{j} - z_{k} \), this yields Eq. (14).

If, rather than use a uniform reference, we define \( p_{0}(z) \) consistent with the hard-wall potential \( (p_{0}(z) = \exp(-\beta u_{1}(z)) = 0 \text{ for } |z| > L/2, \text{ and } 1 \text{ otherwise}) \), then Eq. (D10) for the mapping velocity becomes (for \( -L/2 \leq z_{i} \leq L/2 \)):

\[
\dot{z}_{i}^{\phi_{1}}(z) = \beta \frac{p_{0}(z)}{p_{0}(z_{i})} \left( H(z_{i} - z) - \frac{1}{2} - \frac{z_{i}}{L} \right);
\]

(D15)

\( \dot{z}_{i}^{\phi_{1}}(z) = 0 \) for \( |z_{i}| \geq L/2 \), because the integral that solves (D8) goes flat—remaining equal to the value at the wall—where \( p_{0}(z_{i}) \) is zero. Consequently, problems that would potentially arise from the division by \( p_{0}(z_{i}) \) in (D15) (which would require sampling with one sphere able to go inside the wall) are avoided.

Equation (18) results when this is combined with (D11) while writing

\[
\frac{d\ln p_{0}(z)}{dz} = -\beta \frac{d u_{1}(z)}{dz} = \beta f_{z,i}^{\text{wall}}.
\]

(D16)

**Appendix E. Derivation of Eqs. (19), (20), (22), and (23)**

The radial distribution function is derived in a manner similar to the singlet density. We define \( \phi_{2}(r) \) as a spherically-symmetric auxiliary contribution to the pair potential \( u_{2}(r) \), and evaluate \( g(r) \) as the functional derivative:

\[
g(r) = \frac{2}{\rho N \beta} \frac{1}{4\pi r^{2}} \left( \frac{\delta(\beta A)}{\delta \phi_{2}(r)} \right)_{\beta,V,N}.
\]

(E1)
From this point, the following mapped-average expression for $g(r)$ may be developed [10]:

$$\begin{align*}
g(r) &= \frac{(N-1)}{\rho q} p_0(r) \\
&\quad + \frac{2}{V} \left( \sum_{i=1}^{N} \sum_{j<i} \phi_{ij}(r) \left( \frac{1}{\beta} \frac{d \ln p_0(r_{ij})}{dr_{ij}} - \frac{1}{2} (f_j - f_i) \cdot \hat{r}_{ij} \right) \right),
\end{align*}$$

(E2)

This is Eq. (32) of Ref. 10 (for $V \to \infty$), and the details of its derivation are given there. Also derived there is the general expression for the mapping velocity:

$$\phi_{ij}^2(r_{ij}) = \beta \frac{p(r)}{r_{ij}^2} p(r_{ij}) \left( \frac{H(r_{ij} - r)}{4\pi} - \frac{c_r(r_{ij})}{q} \right),$$

(E3a)

where the radial-cumulative probability function is

$$c_r(r_{ij}) = \int_{0}^{r_{ij}} \tilde{r}^2 p(\tilde{r}) d\tilde{r}.$$  

(E3b)

$p(r)$ normally is short-ranged, so $q \equiv \int_V p(r) 4\pi r^2 dr$ is $O(V)$, and for $V \to \infty$ we can neglect the term $c_r/q$ in Eq. (E3a).

In (E2), $p_0(r)$ is the reference probability for the pair separation. Equation (36) of Ref. 10 presents an expression for the case where $p_0(r) \equiv 1$, which (with some rearrangements of the sum, and a stipulation that $g(r) = 0$ inside the core, as described in Ref. 10) can be written as:

$$g(r) = \frac{\beta}{\rho N} \left( \sum_{j=1}^{N} f_j \cdot \sum_{i \neq j} \hat{r}_{ij} \frac{1 - H(r_{ij} - r)}{4\pi r_{ij}^2} \right),$$

(E4)

which is Eq. (19) in the main document, above.

When written as a sum over collisions, only two terms in the $j$-sum contribute during a given collision, i.e., the terms for the colliders, now labeled $j$ and $k$:

$$g(r) = \frac{\beta}{\rho N\tau} \left( \sum_{c(j,k)} f_j \cdot \left( \sum_{i \neq j} \hat{r}_{ji} \frac{\bar{H}(r_{ij} - r)}{4\pi r_{ij}^2} \right) + f_k \cdot \left( \sum_{i \neq k} \hat{r}_{ki} \frac{\bar{H}(r_{ik} - r)}{4\pi r_{ik}^2} \right) \right),$$

(E5)

The $i$-sum in the $j$ term includes $k$, and the $i$-sum in the $k$ term includes $j$; we separate these out of each sum and, after invoking Eq. (3), this gives rise to the first term on the right-hand side of Eq. (20). The remaining part of (20) is obtained using $f_k = -f_j$ and again invoking (3).

Equation (22) is obtained from (E2) using $p_0(r) = \exp(-\beta u_2(r))$. Then $d \ln p_0(r_{ij})/dr_{ij}$ gives the force between $i$ and $j$, which removes the direct $ij$ contribution to the forces $f_i$ and $f_j$ (giving rise to the $\ast$ on the force difference in Eq. (22)). With the mapping velocity as prescribed by Eq. (E3a), (E2) is easily rearranged to yield Eq. (22).

In a manner similar to the derivation of Eq. (8) described in Appendix C, Eq. (22) is manipulated to yield the collision-sum form as given by Eq. (23).