

Supplemental Information for
Reformulation of ensemble averages via coordinate mapping

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I. A NOTE ABOUT NOTATION

Subscripts on variables in this document (and the main text) have interpretations that should be understood as follows:

- The traditional integer variables i, j, k are indices that identify a particular molecule.
- Coordinate variables (x, y, z, r, θ, ϕ , or more generally α, γ) appearing as subscripts indicate the component of a vector.
- State (or Hamiltonian) variables (e.g., β, V, E , or more generally μ, ν) indicate a derivative with respect to the subscript variable. Such variables appearing as superscripts on \mathbf{v} (or v , if \mathbf{v} consists of a single variable) indicate the state variable whose perturbation “drives” the mapping specified by \mathbf{v} .

As in the main text, λ represents a set of state or Hamiltonian parameters, and we use ν and/or μ to represent particular elements of λ , when for example specifying derivatives; λ appears as a function argument, but not as a subscript or superscript.

We continue the convention used in the main text of including an implicit multiplication by β as part of the symbols for \mathcal{A} (free energy), and for \mathcal{U} and u (configuration energies) and their coordinate derivatives \mathbf{f} and ϕ . All other symbols used for similar quantities (e.g., $U, \mathbf{F}, \boldsymbol{\tau}, u_2$, etc.) do not follow this convention.

II. DERIVATION OF MAPPING FIELD EQUATIONS

In this section we reinforce and expand on some of the results stated in the main text, regarding the field equations and in particular their treatment in the Eulerian vs. Lagrangian specifications.

A. Derivation of Field Equations for Conserved Quantity

Consider an arbitrary volume $V(\lambda)$ whose shape changes with the set of parameters, $\lambda = (\mu, \nu)$, such that $V(\lambda) \in \mathcal{D}$, where \mathcal{D} is a larger fixed volume. The boundary of the surface is denoted as $\partial V(\lambda)$ may naturally be parameterized by a function F as:

$$F(\mathbf{x}, \lambda) = 0 \tag{1}$$

where \mathbf{x} is a vector of coordinates. Let us assume that the quantity $\psi(\mathbf{x}, \lambda)$ is conserved in every volume $V(\lambda)$ that may be prescribed regardless of how it deforms with λ . This may be expressed as the following volume integral expression:

$$\frac{d}{d\nu} \int_{V(\lambda)} \psi(\mathbf{x}, \lambda) d\mathbf{x} = 0. \quad (2)$$

Note that the limits of the volume integral change in accordance with the parameterization of its bounding surface described by (1). The general transport theorem [1] may be applied to (2) to yield:

$$\int_{V(\lambda)} \frac{\partial \psi}{\partial \nu} d\mathbf{x} + \int_{\partial V(\lambda)} \psi \mathbf{v}^\nu \cdot \hat{n} d\mathbf{x} = 0, \quad (3)$$

where $\mathbf{v}^\nu(\mathbf{x}, \lambda)$ is the “velocity field” along that surface, and \hat{n} is the unit outward normal to the surface. The application of the Divergence Theorem to the 2nd integral in (3) allows it to be rewritten as:

$$\int_{V(\lambda)} \left[\frac{\partial \psi}{\partial \nu} + \nabla \cdot (\psi \mathbf{v}^\nu) \right] d\mathbf{x} = 0. \quad (4)$$

Since the equation (4) must hold for every volume $V(\lambda)$, the integrand in (4) must be zero, and thus:

$$\frac{\partial \psi}{\partial \nu} + \nabla \cdot (\psi \mathbf{v}^\nu) = 0. \quad (5)$$

The result (5) is a field equation that assures that the quantity $\psi(\mathbf{x}, \lambda)$ is conserved for all regions lying within the original domain \mathcal{D} . Equation (9) of the main text is obtained by identifying $\psi = p/q$.

B. Equation for the Evolution of the Jacobian

We consider the same domain and assumptions as in Section II A, and set out to obtain an alternative expression to equation (5) that is equivalent in content and that explicitly tracks the evolution of the Jacobian. We focus on a prescribed but arbitrary volume $V(\lambda)$ at $\lambda = \lambda_0$, denoted as $V(\lambda_0)$. At this condition, we can evaluate the integral in (2) as:

$$\int_{V(\lambda_0)} \psi(\mathbf{x}, \lambda_0) d\mathbf{x} = C, \quad (6)$$

where C is a constant. Since the volume $V(\lambda)$ is bounded by the surface parameterization (1), and we have assumed that the value of the integral in (6) is constant regardless of λ , we can write:

$$\int_{V(\lambda)} \psi(\mathbf{x}, \lambda) d\mathbf{x} = C. \quad (7)$$

The integral in (7) may be rewritten so that it has the same limits of integration in (6) through the introduction of the Jacobian, $j^{(\lambda, \lambda_0)}$, as:

$$\int_{V(\lambda_0)} \psi(\mathbf{x}, \lambda) j^{(\lambda, \lambda_0)}(\mathbf{x}, \lambda) d\mathbf{x} = C \quad (8)$$

In (8), the superscript on the Jacobian denotes that its derivatives of the coordinates at λ are taken with respect to those at the initial value $\lambda = \lambda_0$. Comparison of equation (8) and (6) reveals that:

$$j^{(\lambda, \lambda_0)} = 1 \text{ at } \lambda = \lambda_0 \quad (9)$$

Since equation (8) is valid for all λ , and $V(\lambda_0)$ is constant, we can differentiate equation (8) as:

$$\int_{V(\lambda_0)} \frac{\partial}{\partial \nu} (\psi(\mathbf{x}, \lambda) j^{(\lambda, \lambda_0)}(\mathbf{x}, \lambda)) d\mathbf{x} = 0 \quad (10)$$

Note that the integral equation (10) is equivalent in content to integral equation (2).

Before proceeding further to obtain a field equation equivalent to equation (5) involving the integrand alone, it is necessary to correctly interpret the coordinate \mathbf{x} in equation (10). The Jacobian deformation in equation (10) is applied to *every* distorted volume element in the domain relative to its undistorted state at $\lambda = \lambda_0$. Thus, \mathbf{x} represents the coordinates of undistorted domain regardless of the value of λ , and is in fact a Lagrangian description of the domain. Any field equation derived from equation (10) is thus Lagrangian, and this is in contrast to the Eulerian equation (5). To formally acknowledge this difference in perspective, we shift notation in equation (10) by replacing the dummy variable \mathbf{x} with \mathbf{X} , the coordinates of each point in the undistorted volume. Note that this is part of a general Lagrangian framework in which the initial location of any point in the domain moves to other locations in the distorted domain in accordance with:

$$\mathbf{x} = \mathcal{X}(\mathbf{X}, \lambda), \text{ where } \mathbf{x} = \mathbf{X} \text{ at } \lambda = \lambda_0. \quad (11)$$

We thus rewrite (10) as

$$\int_{V(\lambda_0)} \frac{\partial}{\partial \nu} (\Psi(\mathbf{X}, \lambda) J^{(\lambda, \lambda_0)}(\mathbf{X}, \lambda)) d\mathbf{X} = 0, \quad (12)$$

where we have capitalized the dependent variables ψ and $j^{(\lambda, \lambda_0)}$ from (10) to clearly denote a Lagrangian perspective. As we did in going from equation (4) to (5) in Section II A, we now argue that since $V(\lambda_0)$ is arbitrary, the integrand in equation (12) must be zero, i.e.:

$$\frac{\partial}{\partial \nu} (\Psi(\mathbf{X}, \lambda) J(\mathbf{X}, \lambda)) = 0 \quad (13)$$

In (13), we have removed the superscript on J for notational clarity, and we rewrite equation (9) with consistent notation as:

$$J = 1 \text{ at } \lambda = \lambda_0 \quad (14)$$

Equation (13) is the Lagrangian form of the Eulerian field equation (5), which does indeed involve the Jacobian.

We desire an Eulerian form of the equation (13) so it may be used in conjunction with equation (5). To do so, the Lagrangian expression (11) may be inverted as $\mathbf{X} = \mathcal{X}^{-1}(\mathbf{x}, \lambda)$, and thus $\Psi(\mathbf{X}, \lambda) = \Psi(\mathcal{X}^{-1}(\mathbf{x}, \lambda), \lambda) = \psi(\mathbf{x}, \lambda)$, where $\psi(\mathbf{x}, \lambda)$ is Eulerian. Similarly, the Eulerian analogue of $J(\mathbf{X}, \lambda)$, denoted as $j(\mathbf{x}, \lambda)$, is obtained as $J(\mathbf{X}, \lambda) = J(\mathcal{X}^{-1}(\mathbf{x}, \lambda), \lambda) = j(\mathbf{x}, \lambda)$. Using these relations, and following standard approaches of continuum mechanics [1], it is straightforward to show that the derivative in equation (13) is in fact a substantial derivative when expressed in Eulerian form, i.e.:

$$\frac{\partial}{\partial \nu} (\Psi(\mathbf{X}, \lambda) J(\mathbf{X}, \lambda)) = \frac{\partial j \psi}{\partial \nu} + \nabla \cdot (j \psi \mathbf{v}^\nu) \quad (15)$$

where $\mathbf{v}^\nu(\mathbf{x}, \lambda)$ is the Eulerian velocity field as defined in Section II A. Using (15) in (13) and rewriting the constraint (9) in Eulerian form, we obtain:

$$\frac{\partial j \psi}{\partial \nu} + \nabla \cdot (j \psi \mathbf{v}^\nu) = 0, \text{ where } j = 1 \text{ at } \lambda = \lambda_0. \quad (16)$$

Equation (16) is equivalent to equation (5) above, but this equation explicitly includes the Jacobian. By carrying through the derivatives in (16) and inserting the relation (5), we can obtain a more useful form of equation (16):

$$j_\nu + \mathbf{v}^\nu \cdot \nabla j = j \nabla \cdot \mathbf{v}^\nu, \text{ where } j = 1 \text{ at } \lambda = \lambda_0; \quad (17)$$

this form has made use of the subscript notation for the ν derivative: $j_\nu \equiv (\partial j / \partial \nu)_{\mathbf{x}, \mu}$. This equation is intuitively pleasing as we see that the evolution of the Jacobian, which is purely kinematic, is related to the kinematic description of velocity (\mathbf{v}^ν) in the domain. Finally, we note that the left-hand side of equation (17) is the substantial derivative of $j(\mathbf{x}, \lambda)$, which in terms of its equivalent Lagrangian quantity is equal to J_ν [1], allowing (17) to be expressed:

$$J_\nu = j \nabla \cdot \mathbf{v}^\nu, \text{ where } J = j \equiv 1 \text{ at } \lambda = \lambda_0, \quad (18)$$

where $J_\nu \equiv (\partial J / \partial \nu)_{\mathbf{X}, \mu}$. Equation (18) enables the Lagrangian derivative of the Jacobian to be evaluated in terms of Eulerian quantities.

Following the arguments above involving the substantial derivative, the 2nd derivative of the Jacobian in Lagrangian coordinates may be evaluated as:

$$\begin{aligned}
J_{\mu\nu} &= \left(\frac{\partial}{\partial\mu} + \mathbf{v}^\mu \cdot \nabla \right) (j \nabla \cdot \mathbf{v}^\nu) \\
&= \frac{\partial}{\partial\mu} (j \nabla \cdot \mathbf{v}^\nu) + \mathbf{v}^\mu \cdot \nabla (j \nabla \cdot \mathbf{v}^\nu) \\
&= j_\mu \nabla \cdot \mathbf{v}^\nu + j \nabla \cdot \mathbf{v}_\mu^\nu + (\mathbf{v}^\mu \cdot \nabla j) (\nabla \cdot \mathbf{v}^\nu) + j \mathbf{v}^\mu \cdot \nabla (\nabla \cdot \mathbf{v}^\nu) \\
&= j (\nabla \cdot \mathbf{v}^\nu) (\nabla \cdot \mathbf{v}^\mu) + j \nabla \cdot \mathbf{v}_\mu^\nu + j \mathbf{v}^\mu \cdot \nabla (\nabla \cdot \mathbf{v}^\nu)
\end{aligned} \tag{19}$$

in which we have used the expression (17) to remove the appearance of j_μ . Commutability of the Lagrangian derivatives should allow us to write the second derivative alternatively as:

$$J_{\mu\nu} = J_{\nu\mu} = j (\nabla \cdot \mathbf{v}^\nu) (\nabla \cdot \mathbf{v}^\mu) + j \nabla \cdot \mathbf{v}_\nu^\mu + j \mathbf{v}^\nu \cdot \nabla (\nabla \cdot \mathbf{v}^\mu) \tag{20}$$

The proof that Eqs. (19) and (20) are in fact equal is provided in Sec. II C below.

Of particular importance is the value of the Lagrangian derivatives (18) and (20) at $\lambda = \lambda_0$, at which $j \equiv 1$, allowing us also to use Eq. (18) to introduce $J_\mu J_\nu$:

$$J_\nu = \nabla \cdot \mathbf{v}^\nu \tag{21a}$$

$$J_{\mu\nu} - J_\mu J_\nu = \nabla \cdot \mathbf{v}_\mu^\nu + \mathbf{v}^\mu \cdot \nabla (\nabla \cdot \mathbf{v}^\nu) \tag{21b}$$

These are the formulas for the J derivatives given by Eq. (10) of the main text, and they apply for $\lambda = \lambda_0$.

C. Proof of equivalence of equations (19) and (20)

The proof of the equivalence of equations (19) and (20) proceeds as follows. The Lagrangian velocity vector $\mathbf{V}^\nu(\mathbf{X}, \lambda)$ is defined as:

$$\mathbf{V}^\nu(\mathbf{X}, \lambda) = \left(\frac{\partial \mathcal{X}}{\partial \nu} \right)_{\mathbf{x}, \mu}. \tag{22}$$

Note that $\mathbf{V}^\nu(\mathbf{X}, \lambda)$ is related to its Eulerian counterpart $\mathbf{v}^\nu(\mathbf{x}, \lambda)$ by inverting (11) as $\mathbf{X} = \mathcal{X}^{-1}(\mathbf{x}, \lambda)$ and writing $\mathbf{V}^\nu(\mathbf{X}, \lambda) = \mathbf{V}^\nu(\mathcal{X}^{-1}(\mathbf{x}, \lambda), \lambda) \equiv \mathbf{v}^\nu(\mathbf{x}, \lambda)$. The following relationship is assured from the commutability of cross derivatives in Lagrangian coordinates:

$$\mathbf{V}_\mu^\nu = \left(\frac{\partial \mathbf{V}^\nu}{\partial \mu} \right)_{\mathbf{x}, \nu} = \left(\frac{\partial^2 \mathcal{X}}{\partial \mu \partial \nu} \right)_{\mathbf{x}} = \left(\frac{\partial^2 \mathcal{X}}{\partial \nu \partial \mu} \right)_{\mathbf{x}} = \left(\frac{\partial \mathbf{V}^\mu}{\partial \nu} \right)_{\mathbf{x}, \mu} = \mathbf{V}_\nu^\mu \tag{23}$$

When expressed in Eulerian form, the derivatives in (23) are substantial derivatives in accordance with standard continuum mechanics theory [1], and thus we may write:

$$\mathbf{v}_\mu^\nu + \mathbf{v}^\mu \cdot \nabla \mathbf{v}^\nu = \mathbf{v}_\nu^\mu + \mathbf{v}^\nu \cdot \nabla \mathbf{v}^\mu \quad (24)$$

Equation (24) is an Eulerian identity required for the proof.

Next, we equate the Lagrangian mixed derivative expressions in equations (19) and (20), cancel terms, and divide by j to obtain:

$$\nabla \cdot \mathbf{v}_\mu^\nu + \mathbf{v}^\mu \cdot \nabla (\nabla \cdot \mathbf{v}^\nu) \stackrel{?}{=} \nabla \cdot \mathbf{v}_\nu^\mu + \mathbf{v}^\nu \cdot \nabla (\nabla \cdot \mathbf{v}^\mu) \quad (25)$$

In (25), the question mark over the equal sign indicates that the equivalence of the left and right hand side of this expression is to be proven. Upon substitution of equation (24) into (25) and upon rearrangement, we obtain the following expression, which involves no derivatives with respect to μ or ν :

$$\nabla \cdot (\mathbf{v}^\nu \cdot \nabla \mathbf{v}^\mu) + \mathbf{v}^\mu \cdot \nabla (\nabla \cdot \mathbf{v}^\nu) \stackrel{?}{=} \nabla \cdot (\mathbf{v}^\mu \cdot \nabla \mathbf{v}^\nu) + \mathbf{v}^\nu \cdot \nabla (\nabla \cdot \mathbf{v}^\mu) \quad (26)$$

We can use the vector identity $\nabla \cdot ((\nabla \cdot \mathbf{a})\mathbf{b}) = \mathbf{b} \cdot \nabla (\nabla \cdot \mathbf{a}) + (\nabla \cdot \mathbf{a})(\nabla \cdot \mathbf{b})$ on each side and eliminate the common term this generates. Each side can then be written as the divergence of a single quantity:

$$\nabla \cdot [(\mathbf{v}^\nu \cdot \nabla \mathbf{v}^\mu) + (\nabla \cdot \mathbf{v}^\nu)\mathbf{v}^\mu] \stackrel{?}{=} \nabla \cdot [(\mathbf{v}^\mu \cdot \nabla \mathbf{v}^\nu) + (\nabla \cdot \mathbf{v}^\mu)\mathbf{v}^\nu] \quad (27)$$

A second vector identity $\nabla \cdot (\mathbf{a}\mathbf{b}) = \mathbf{a} \cdot \nabla \mathbf{b} + (\nabla \cdot \mathbf{a})\mathbf{b}$ can be applied, to yield:

$$\nabla \cdot \nabla \cdot (\mathbf{v}^\nu \mathbf{v}^\mu) \stackrel{?}{=} \nabla \cdot \nabla \cdot (\mathbf{v}^\mu \mathbf{v}^\nu)$$

or

$$\nabla \cdot \nabla \cdot (\mathbf{v}^\nu \mathbf{v}^\mu - \mathbf{v}^\mu \mathbf{v}^\nu) = 0 \quad (28)$$

The question mark over the equal sign has been removed, as this result may be verified by carrying out all vector operations in Rectangular Cartesian coordinates. The result (28) closes our proof, as it assures that equations (19) and (20) are equivalent, i.e., it confirms that the indices in the mixed Eulerian derivatives of the Jacobian are commutable when expressed in Eulerian form.

III. DERIVATION OF MAPPED AVERAGE FOR CRYSTAL HEAT CAPACITY

Each particle's coordinate $\Delta \mathbf{r}_i$ is expressed relative to its lattice-site position, with radial coordinate $r_i \equiv |\Delta \mathbf{r}_i|$ so $\Delta \mathbf{r}_i = r_i \hat{\mathbf{e}}_r$. We have the independent-particle approximation to p and q , with :

$$p_1(r_i, \beta) = \exp(-\beta c r_i^2), \quad (29)$$

$$q_1(\beta) = (\pi/\beta c)^{3/2}. \quad (30)$$

Writing ∇_i for $\nabla_{\Delta \mathbf{r}_i}$, the mapping function is derived from:

$$\nabla_i \cdot \left(p_1(r_i, \beta) \mathbf{v}_i^\beta \right) = -p_1 \frac{\partial \ln(p_1/q_1)}{\partial \beta} \quad (31)$$

$$\frac{1}{r_i^2} \frac{\partial}{\partial r_i} \left[r_i^2 e^{-\beta c r_i^2} \mathbf{v}_{r,i}^\beta \right] = -e^{-\beta c r_i^2} \left(\frac{3}{2\beta} - c r_i^2 \right). \quad (32)$$

where $\mathbf{v}_{r,i}^\beta$ is the radial coordinate of \mathbf{v}_i^β (in the same system as $\Delta \mathbf{r}_i$); we assert by symmetry that $\mathbf{v}_{\theta,i}^\beta = \mathbf{v}_{\phi,i}^\beta = 0$. Integration from $\mathbf{v}_{r,i}^\beta = 0$ at $r_i = 0$ yields, in terms of the full vectors:

$$\mathbf{v}_i^\beta = -\frac{\Delta \mathbf{r}_i}{2\beta}, \quad (33)$$

which is Eq. (13) of the main manuscript. Then

$$\mathbf{v}_{\beta,i}^\beta = \frac{\Delta \mathbf{r}_i}{2\beta^2}, \quad (34)$$

and

$$\begin{aligned} J_\beta &= \sum_{i=1}^N \nabla_i \cdot \mathbf{v}_i^\beta \\ &= \sum_i \frac{1}{r_i^2} \frac{\partial}{\partial r_i} \left(r_i^2 \mathbf{v}_{r,i}^\beta \right) \\ &= \sum_i \frac{1}{r_i^2} \frac{\partial}{\partial r_i} \left(r_i^2 \left(-\frac{r_i}{2\beta} \right) \right) \\ &= -\frac{3(N-1)}{2\beta} \end{aligned} \quad (35)$$

$$\begin{aligned} J_{\beta\beta} - J_\beta^2 &= \sum_{i=1}^N \nabla_i \cdot \mathbf{v}_{\beta,i}^\beta + \mathbf{v}_i^\beta \cdot \nabla_i \left(\nabla_i \cdot \mathbf{v}_i^\beta \right) \\ &= \sum_i \frac{1}{r_i^2} \frac{\partial}{\partial r_i} \left(r_i^2 \mathbf{v}_{\beta,r,i}^\beta \right) + \mathbf{v}_i^\beta \cdot \nabla_i \left(-\frac{3}{2\beta} \right) \\ &= \sum_i \frac{1}{r_i^2} \frac{\partial}{\partial r_i} \left(r_i^2 \frac{r_i}{2\beta^2} \right) + 0 \\ &= \frac{3(N-1)}{2\beta^2} \end{aligned} \quad (36)$$

These sum to $N - 1$ terms rather than N because we keep the center of mass fixed. The heat capacity is given via Eq. (3b) of the main text, and because J_β is a constant, the covariances involving it are zero. This leaves:

$$\begin{aligned}
C_V/k_B &= -\beta^2 \mathcal{A}_{\beta\beta} \\
&= \beta^2 \langle J_{\beta\beta} - J_\beta J_\beta \rangle - \beta^2 \langle \mathcal{U}_{\beta\beta} \rangle + \beta^2 \text{Cov} [\mathcal{U}_\beta, \mathcal{U}_\beta] \\
&= \frac{3(N-1)}{2} - \beta^2 \langle \mathcal{U}_{\beta\beta} \rangle + \text{Var} [\beta \mathcal{U}_\beta].
\end{aligned} \tag{37}$$

The energy derivatives are (remembering that $u \equiv \beta \times \text{configuration-energy}$, and likewise for \mathbf{f}):

$$\begin{aligned}
\mathcal{U}_\beta &= u_\beta - \mathbf{v}^\beta \cdot \mathbf{f} \\
&= \frac{1}{\beta} \left(u + \frac{1}{2} \Delta \mathbf{r} \cdot \mathbf{f} \right)
\end{aligned} \tag{38}$$

$$\begin{aligned}
\mathcal{U}_{\beta\beta} &= u_{\beta\beta} - \left(\mathbf{v}_\beta^\beta + \mathbf{v}^\beta \cdot \nabla \mathbf{v}^\beta \right) \cdot \mathbf{f} + \mathbf{v}^\beta \cdot \boldsymbol{\phi} \cdot \mathbf{v}^\beta - 2\mathbf{v}^\beta \cdot \mathbf{f}_\beta, \\
&= 0 - \left(\frac{\Delta \mathbf{r}}{2\beta^2} + \left(-\frac{\Delta \mathbf{r}}{2\beta} \right) \cdot \nabla \left(-\frac{\Delta \mathbf{r}}{2\beta} \right) \right) \cdot \mathbf{f} + \left(-\frac{\Delta \mathbf{r}}{2\beta} \right) \cdot \boldsymbol{\phi} \cdot \left(-\frac{\Delta \mathbf{r}}{2\beta} \right) - 2 \left(-\frac{\Delta \mathbf{r}}{2\beta} \right) \cdot \mathbf{f}_\beta, \\
&= - \left(\frac{\Delta \mathbf{r}}{2\beta^2} + \frac{\Delta \mathbf{r}}{4\beta^2} \right) \cdot \mathbf{f} + \left(-\frac{\Delta \mathbf{r}}{2\beta} \right) \cdot \boldsymbol{\phi} \cdot \left(-\frac{\Delta \mathbf{r}}{2\beta} \right) - 2 \left(-\frac{\Delta \mathbf{r}}{2\beta} \right) \cdot \frac{\mathbf{f}}{\beta}, \\
&= - \frac{3\Delta \mathbf{r}}{4\beta^2} \cdot \mathbf{f} + \frac{1}{4\beta^2} \Delta \mathbf{r} \cdot \boldsymbol{\phi} \cdot \Delta \mathbf{r} + \frac{\Delta \mathbf{r}}{\beta^2} \cdot \mathbf{f}, \\
&= \frac{1}{4\beta^2} (\Delta \mathbf{r} \cdot \mathbf{f} + \Delta \mathbf{r} \cdot \boldsymbol{\phi} \cdot \Delta \mathbf{r}).
\end{aligned} \tag{39}$$

Assembly of Eqs. (37), (38), (39) yields Eq. (15) in the main text.

A. Comment on the mapping for crystalline systems

Of the three examples presented in the main text, the application of mapped averaging to the crystalline heat capacity is unique in that the Eulerian probability density $p(\mathbf{x}, \lambda)$ corresponds to a Lagrangian form, P , that is independent of the parameter λ :

$$P(\mathbf{X}, \lambda) = P(\mathbf{X}); \tag{40}$$

in other words, the mapping is such that \mathbf{x} changes with λ such that $p(\mathbf{x}, \lambda)$ is invariant. We will comment here on some features that are connected to this form, as this case is relevant to formulation of harmonically mapped averages for volume derivatives of the free energy for crystalline systems [2], and probably to other systems as well.

We first motivate that indeed such a form may arise by extracting the Lagrangian probability associated with the harmonic mapping (33). Based on the relationship between Lagrangian and Eulerian “velocities,” we may write (returning for now to the notation used above for variables describing the crystalline system):

$$\frac{dr_i}{d\beta} = \mathbf{v}_{r,i}^\beta = -\frac{r_i}{2\beta} \quad \text{with } r_i = R_i \text{ at } \beta = \beta_0. \quad (41)$$

The solution of (41) yields the mapping:

$$r_i = R_i \left(\frac{\beta_0}{\beta} \right)^{1/2}; \quad (42)$$

this is the $\beta^{-1/2}$ scaling of r_i that was described following Eq. (13) in the main text. Substitution of equation (42) into equation (29) leads to its equivalent Lagrangian function $P_1(R_i, \beta)$:

$$P_1 = \exp(-\beta_0 c R_i^2). \quad (43)$$

This is however independent of β , so for this case indeed $P_1 = P_1(R_i)$.

We now return to generalized notation to be consistent with previous derivations. A Lagrangian P independent of λ implies that it has zero for its derivatives with respect to the parameter(s) forming λ , which we can write as follows:

$$\frac{\partial P}{\partial \nu} = \frac{\partial p}{\partial \nu} + \mathbf{v}^\nu \cdot \nabla p = 0 \quad (44)$$

Equation (44) may be used as an alternative to equation (9) of the main text to determine the mapping \mathbf{v}^ν .

An expression for the Jacobian is easily obtained by using equation (7) of the text and noting that the functional dependence $P = P(\mathbf{X})$ yields the following:

$$J = \frac{q(\lambda)}{q(\lambda_0)} = j. \quad (45)$$

Equation (45) indicates that the Lagrangian form of the Jacobian, J , is identical to its Eulerian equivalent, j , owing to the lack of \mathbf{X} in the parameterization. By direct differentiation of (45), we obtain:

$$\frac{J_\nu}{J} = \frac{\partial \ln q}{\partial \nu}; \quad (46)$$

thus, we see that the P being independent of λ has the consequence that the Jacobian (and hence its λ derivatives) is independent of the coordinate \mathbf{X} (this is not always true for the

statement made in reverse, i.e. Eq. (40) implies (46), but (46) does not necessarily imply (40)). From equation (18) of the supplemental material and equation (46) we obtain:

$$\nabla \cdot \mathbf{v}^\nu = \frac{\partial \ln q}{\partial \nu}. \quad (47)$$

The result (47) provides yet another relationship that may be used to determine the Eulerian mapping \mathbf{v}^ν , and it shows that in cases where (40) holds, then the mapping can be determined from a free-energy model alone. This has allowed us to form mappings for volume derivatives for crystalline systems, using a quasi-harmonic treatment for the free energy [2].

Higher derivatives of the Jacobian may be obtained by direct differentiation of (46), and simplifying through use of equation (46) itself. We can write:

$$J_{\nu\mu} = J_\nu J_\mu / J + J \frac{\partial^2 \ln q}{\partial \nu \partial \mu}. \quad (48)$$

At $\lambda = \lambda_0$, $J = 1$, and we thus have,

$$J_\nu = \frac{\partial \ln q}{\partial \nu}, \quad (49a)$$

$$J_{\nu\mu} - J_\nu J_\mu = \frac{\partial^2 \ln q}{\partial \nu \partial \mu}. \quad (49b)$$

Equations (44), (47), and (49) are the key results needed for analysis.

IV. DERIVATION OF MAPPED AVERAGE FOR DIELECTRIC CONSTANT

To develop a mapped average for the FE second derivative $\mathcal{A}_{E_z E_z}$, we use an approximation to $p(\mathbf{x}, \lambda)$ that is based on independent dipoles interacting with the external field \mathbf{E} , of magnitude E_z and acting in the z direction. The energy for such a system is

$$\begin{aligned} U^{\text{approx}}(\mathbf{x}, E_z) &= - \sum_i \mathbf{E} \cdot \boldsymbol{\mu}_i \\ &= - \sum_i \mu_D E_z \cos \theta_{z,i} \\ &= - \sum_i \mu_D E_z z_i, \end{aligned} \quad (50)$$

where $\theta_{z,i}$ is the angle between the z axis and the dipole moment vector of molecule i , and $z_i = \cos \theta_{z,i}$. As the approximation is based on non-interacting molecules, we can use the formulation suggested by Eq. (11) of the main text, for which we have:

$$p_1(z_i, E_z) = \exp(\beta \mu_D E_z z_i). \quad (51)$$

Then

$$\begin{aligned} q_1(E_z) &= \int_{-1}^1 \exp(\beta\mu_D E_z z) dz \\ &= \frac{2 \sinh(\beta\mu_D E_z)}{\beta\mu_D E_z}. \end{aligned} \quad (52)$$

From Eq. (12) of the main text,

$$\begin{aligned} v_i^{E_z} &= e^{-\beta\mu_D E_z z_i} \int_1^{z_i} \left(\frac{1}{E_z} - \beta\mu_D \coth(\beta\mu_D E_z) + \beta\mu_D \tilde{z} \right) d\tilde{z} \\ &= -\frac{1}{E_z} \left(e^{-\beta\mu_D E_z z_i} \operatorname{csch}(\beta\mu_D E_z) - \coth(\beta\mu_D E_z) + z_i \right) \\ &\underset{E_z \rightarrow 0}{=} \frac{1}{2} \beta\mu_D (1 - z_i^2) \end{aligned} \quad (53)$$

Also,

$$v_{E_z, i}^{E_z} \underset{E_z \rightarrow 0}{=} -\frac{1}{6} \beta^2 \mu_D^2 z_i (1 - z_i^2), \quad (54)$$

We will require the gradient of \mathbf{v}^{E_z} , and this should in principle be taken before evaluating the limit (although here the result is the same either way), thus:

$$\begin{aligned} \frac{\partial v_i^{E_z}}{\partial z_i} &= \beta\mu_D e^{-\beta\mu_D E_z z_i} \operatorname{csch}(\beta\mu_D E_z) - \frac{1}{E_z} \\ &\underset{E_z \rightarrow 0}{=} -\beta\mu_D z_i \end{aligned} \quad (55)$$

The Jacobian derivatives are:

$$\begin{aligned} J_{E_z} &= \nabla \cdot \mathbf{v}^{E_z} \\ &= \sum_{i=1}^N \frac{\partial v_i^{E_z}}{\partial z_i} \\ &\underset{E_z \rightarrow 0}{=} -\beta\mu_D \sum_{i=1}^N z_i, \end{aligned} \quad (56)$$

and from Eq. (10b) of the main text:

$$\begin{aligned} J_{E_z E_z} - J_{E_z}^2 &= \nabla \cdot \mathbf{v}^{E_z} + \mathbf{v}^{E_z} \cdot \nabla (\nabla \cdot \mathbf{v}^{E_z}) \\ &= \sum_{i=1}^N \left(\frac{\partial v_{E_z, i}^{E_z}}{\partial z_i} + v_i^{E_z} \frac{\partial^2 v_i^{E_z}}{\partial z_i^2} \right) \\ &\underset{E_z \rightarrow 0}{=} \beta^2 \mu_D^2 \sum_{i=1}^N \left(-\frac{1}{6} (1 - 3z_i^2) + \left(\frac{1}{2} (1 - z_i^2) \right) (-1) \right) \\ &\underset{E_z \rightarrow 0}{=} \beta^2 \mu_D^2 \sum_{i=1}^N \left(z_i^2 - \frac{2}{3} \right) \end{aligned} \quad (57)$$

The energy derivatives are:

$$\begin{aligned}
\mathcal{U}_{E_z} &= u_{E_z} - \mathbf{v}^{E_z} \cdot \mathbf{f}_z \\
&= \beta\mu_D \sum_{i=1}^N \left(-z_i - \frac{1}{2}(1 - z_i^2)f_{z,i} \right)
\end{aligned} \tag{58}$$

$$\begin{aligned}
\mathcal{U}_{E_z E_z} &= u_{E_z E_z} - (\mathbf{v}_{E_z}^{E_z} + \mathbf{v}^{E_z} \cdot \nabla \mathbf{v}^{E_z}) \cdot \mathbf{f}_z + \mathbf{v}^{E_z} \cdot \boldsymbol{\phi}_z \cdot \mathbf{v}^{E_z} - 2\mathbf{v}^{E_z} \cdot \mathbf{f}_{z,E_z}, \\
&= 0 - \beta^2 \mu_D^2 \sum_{i=1}^N \left(-\frac{1}{6}z_i(1 - z_i^2) + \frac{1}{2}(1 - z_i^2)(-z_i) \right) f_{z,i} \\
&\quad + \mathbf{v}^{E_z} \cdot \boldsymbol{\phi}_z \cdot \mathbf{v}^{E_z} - 2 \sum_{i=1}^N \left(\frac{1}{2}\beta\mu_D(1 - z_i^2) \right) \times (\beta\mu_D), \\
&= \frac{2}{3}\beta^2 \mu_D^2 \sum_{i=1}^N z_i(1 - z_i^2)f_{z,i} + \mathbf{v}^{E_z} \cdot \boldsymbol{\phi}_z \cdot \mathbf{v}^{E_z} \\
&\quad - \beta^2 \mu_D^2 \sum_{i=1}^N (1 - z_i^2),
\end{aligned} \tag{59}$$

The u derivatives are based on the contribution of the field to u being $-\sum_i \beta\mu_D E_z z_i$, from which we also have $f_{z,E_z,i} = \beta\mu_D$.

The derivative of interest is:

$$\mathcal{A}_{E_z E_z} = - \langle J_{E_z E_z} - J_{E_z} J_{E_z} \rangle + \langle \mathcal{U}_{E_z E_z} \rangle - \text{Var} [J_{E_z} - \mathcal{U}_{E_z}]. \tag{60}$$

The first term is given by Eq. (57), and noting that $\langle z^2 \rangle = 1/3$ for the isotropic system, this yields:

$$\langle J_{E_z E_z} - J_{E_z} J_{E_z} \rangle = -\frac{1}{3}N\beta^2 \mu_D^2. \tag{61}$$

We still require expressions for these parts:

$$\begin{aligned}
\text{Var} [J_{E_z} - \mathcal{U}_{E_z}] &= \text{Var} \left[\frac{1}{2}\beta\mu_D \sum_i (1 - z_i^2)f_{z,i} \right] \\
&= \frac{1}{4}\beta^2 \mu_D^2 \left[\left\langle \left(\sum_i (1 - z_i^2)f_{z,i} \right)^2 \right\rangle - \left\langle \sum_i (1 - z_i^2)f_{z,i} \right\rangle^2 \right]
\end{aligned} \tag{62}$$

$$\begin{aligned}
\langle \mathcal{U}_{E_z E_z} \rangle &= \frac{2}{3} \beta^2 \mu_D^2 \left\langle \sum_{i=1}^N z_i (1 - z_i^2) f_{z,i} \right\rangle \\
&\quad + \langle \mathbf{v}^{E_z} \cdot \boldsymbol{\phi}_z \cdot \mathbf{v}^{E_z} \rangle - \beta^2 \mu_D^2 \left\langle \sum_{i=1}^N (1 - z_i^2) \right\rangle, \\
&= \frac{2}{3} \beta^2 \mu_D^2 \left\langle \sum_{i=1}^N z_i (1 - z_i^2) f_{z,i} \right\rangle \\
&\quad + \frac{1}{4} \beta^2 \mu_D^2 \left\langle \sum_i \sum_j (1 - z_i^2) \phi_{z,ij} (1 - z_j^2) \right\rangle - \frac{2}{3} N \beta^2 \mu_D^2, \tag{63}
\end{aligned}$$

We will cast these expressions in terms of the total torque $\boldsymbol{\tau}_i$ exerted on each molecule i . Just as a component of the force can be expressed as the change in the energy with translation in an appropriate direction, a component of torque can be related to the change in energy with rotation about an appropriate axis. Specifically, the component of the torque on a molecule in the direction $\hat{\mathbf{e}}$ is the derivative:

$$\boldsymbol{\tau}_{\hat{\mathbf{e}}} = -\frac{\partial U}{\partial \theta}, \tag{64}$$

where θ is the angle of rotation (in radians) of the molecule about the $\hat{\mathbf{e}}$ axis. Now, the generalized force $f_{z,i}$ appearing in the formulas above is the derivative:

$$f_{z,i} \equiv -\frac{\partial u}{\partial z_i} = -\frac{\partial u}{\partial \cos \theta_{z,i}} = \frac{1}{\sin \theta_{z,i}} \frac{\partial u}{\partial \theta_{z,i}}, \tag{65}$$

where here $\theta_{z,i}$ is the angle that the dipole on molecule i (with direction $\hat{\mathbf{e}}_i$) makes with $\hat{\mathbf{z}}$, the z axis. The unit vector for the axis of rotation of $\theta_{z,i}$ is

$$\hat{\mathbf{e}}_{\theta_{z,i}} = (\hat{\mathbf{e}}_i \times \hat{\mathbf{z}}) / \sin \theta_{z,i}, \tag{66}$$

and the component of $\boldsymbol{\tau}_i$ in this direction is $\boldsymbol{\tau}_i \cdot \hat{\mathbf{e}}_{\theta_{z,i}}$. Putting this together, we have

$$(1 - z_i^2) f_{z,i} = (\sin \theta_{z,i})^2 f_{z,i} = -\beta \boldsymbol{\tau}_i \cdot (\hat{\mathbf{e}}_i \times \hat{\mathbf{z}}). \tag{67}$$

The vector identity $\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c}) = \mathbf{c} \cdot (\mathbf{a} \times \mathbf{b})$ allows us to write this alternatively as:

$$\begin{aligned}
(1 - z_i^2) f_{z,i} &= -\beta \hat{\mathbf{z}} \cdot (\boldsymbol{\tau}_i \times \hat{\mathbf{e}}_i) \\
&= -\beta (\boldsymbol{\tau}_i \times \hat{\mathbf{e}}_i)_z \tag{68}
\end{aligned}$$

The vector sum-over- i of z -components is the z -component of the sum-over- i of the vectors, so we can write

$$\sum_{i=1}^N (1 - z_i^2) f_{z,i} = -\beta \left(\sum_{i=1}^N (\boldsymbol{\tau}_i \times \hat{\mathbf{e}}_i) \right)_z \tag{69}$$

Due to the isotropy of the system, positive and negative torques will cancel on average, so the ensemble average of this quantity — which is what we have for the latter term in Eq. (62) — will vanish. However, the average square of the term is nonzero, which is needed for the first term of Eq. (62). Anticipating a step to follow below, upon summing this square over coordinate directions we have

$$\sum_{\alpha=x,y,z} \sum_{i=1}^N (1 - \alpha_i^2) f_{\alpha,i} = \beta^2 \left| \sum_{i=1}^N (\boldsymbol{\tau}_i \times \hat{\mathbf{e}}_i) \right|^2. \quad (70)$$

Another term that appears in $\mathcal{A}_{E_z E_z}$ is $z_i(1 - z_i^2)f_{z,i}$, which relates to the torque as:

$$z_i(1 - z_i^2)f_{z,i} = -\beta \hat{\mathbf{e}}_{i,z} (\boldsymbol{\tau}_i \times \hat{\mathbf{e}}_i)_z. \quad (71)$$

We note that this term vanishes when summed over all coordinate directions:

$$\begin{aligned} \sum_{\alpha=x,y,z} \alpha_i (1 - \alpha_i^2) f_{\alpha,i} &= -\beta \sum_{\alpha=x,y,z} \hat{\mathbf{e}}_{i,\alpha} (\boldsymbol{\tau}_i \times \hat{\mathbf{e}}_i)_\alpha \\ &= -\beta \hat{\mathbf{e}}_i \cdot (\boldsymbol{\tau}_i \times \hat{\mathbf{e}}_i) \\ &= 0, \end{aligned} \quad (72)$$

where the last equality is based on the vector identity $\mathbf{a} \cdot (\mathbf{b} \times \mathbf{a}) = 0$.

Finally, we consider the contribution from $\left\langle \sum_i \sum_j (1 - z_i^2) \phi_{z,ij} (1 - z_j^2) \right\rangle$. Here, $\phi_{z,ij}$ is the second derivative:

$$\phi_{z,ij} = \frac{\partial^2 u}{\partial z_i \partial z_j}. \quad (73)$$

Paralleling the development outlined above for terms involving $f_{z,i}$, we first rewrite this in terms of the angle derivatives:

$$\phi_{z,ij} = \frac{1}{\sin \theta_{z,i} \sin \theta_{z,j}} \frac{\partial^2 u}{\partial \theta_{z,i} \partial \theta_{z,j}} - \delta_{ij} \frac{\cos \theta_{z,i}}{(\sin \theta_{z,i})^2} f_{z,i}, \quad (74)$$

where δ_{ij} is the Kronecker delta function. Then

$$(1 - z_i^2)(1 - z_j^2) \phi_{z,ij} = \sin \theta_{z,i} \sin \theta_{z,j} \frac{\partial^2 u}{\partial \theta_{z,i} \partial \theta_{z,j}} - \delta_{ij} \cos \theta_{z,i} (\sin \theta_{z,i})^2 f_{z,i}. \quad (75)$$

The latter term on the right-hand side of this expression is the same as that examined in Eq. (71), which was shown to be zero when summed over all coordinate directions; we will therefore not include this term in the subsequent development. With consideration of the direction of the θ_z rotations as given in Eq. (66), we can write the remaining term as a

component of the gradient of the torque on j with respect to rotation of i , written using the rotational-gradient operator ∇_{Ω_i} :

$$\sin \theta_{z,i} \sin \theta_{z,j} \frac{\partial^2 u}{\partial \theta_{z,i} \partial \theta_{z,j}} = -\beta (\hat{\mathbf{e}}_i \times \hat{\mathbf{z}}) \cdot \nabla_{\Omega_i} \boldsymbol{\tau}_j \cdot (\hat{\mathbf{e}}_j \times \hat{\mathbf{z}}) \quad (76)$$

(note that $\beta \boldsymbol{\tau}_j = -\nabla_{\Omega_i} u$). One can examine this form in a Cartesian rotation basis, and show that when summed over all coordinate directions, this term can be expressed as:

$$\sum_{\alpha=x,y,z} \sin \theta_{\alpha,i} \sin \theta_{\alpha,j} \frac{\partial^2 u}{\partial \theta_{\alpha,i} \partial \theta_{\alpha,j}} = -\beta ((\nabla_{\Omega_i} \cdot \boldsymbol{\tau}_j)(\hat{\mathbf{e}}_i \cdot \hat{\mathbf{e}}_j) - \hat{\mathbf{e}}_j \cdot \nabla_{\Omega_i} \boldsymbol{\tau}_j \cdot \hat{\mathbf{e}}_i). \quad (77)$$

Assembling all of the components developed from Eq. (60) onward, we sum over all three coordinate directions to arrive at the final expression:

$$\begin{aligned} \mathcal{A}_{EE} &= \sum_{\alpha=x,y,z} \mathcal{A}_{E_\alpha E_\alpha} \\ &= -N\beta^2 \mu_D^2 + \frac{\beta^4}{4} \left\langle \left| \sum_{i=1}^N \boldsymbol{\tau}_i \times \boldsymbol{\mu}_i \right|^2 \right\rangle \\ &\quad - \frac{\beta^3}{4} \left\langle \sum_{i=1}^N \sum_{j=1}^N (\nabla_{\Omega_i} \cdot \boldsymbol{\tau}_j)(\boldsymbol{\mu}_i \cdot \boldsymbol{\mu}_j) - \boldsymbol{\mu}_j \cdot \nabla_{\Omega_i} \boldsymbol{\tau}_j \cdot \boldsymbol{\mu}_i \right\rangle, \end{aligned} \quad (78)$$

which is Eq. (19) of the main text.

V. SOME DETAILS REGARDING MAPPED-AVERAGE PRESSURE

A. Intermediate Quantities in Derivation

The p/q conservation equation with p and q is as given by Eqs. (23) and (24), when evaluated at $s = 1$, is

$$\frac{1}{r^2} \frac{d}{dr} (r^2 p(r) v^s(r)) = -p(r) \frac{3\hat{q}}{V + \hat{q}} - r p'(r), \quad (79)$$

where p' is the derivative of p with respect to its argument. Using the boundary condition that $v^s = 0$ for $r = 0$, solution of this equation yields the following for the mapping derivative for r :

$$v^s(r) = -r + 3 \frac{V}{V + \hat{q}} \int_0^r d\hat{r} \left(\frac{\hat{r}}{r} \right)^2 \frac{p(\hat{r})}{p(r)} \quad (80)$$

Equation (25) in the main text results for $V \rightarrow \infty$. Via Eq. (10a), the Jacobian derivative is:

$$J_s(r) = -\frac{3\hat{q}}{V + \hat{q}} + (v^s(r) + r)\beta v_2'(r). \quad (81)$$

The energy derivative:

$$\beta U_s = \beta r u_2'(r) + \frac{1}{2}\beta v^s(r) (\mathbf{F}_1 - \mathbf{F}_2) \cdot \hat{\mathbf{r}}_{12}. \quad (82)$$

B. Correction for Long-range Contributions

Contributions are made to the mapped-average pressure of a bulk system by interactions at distances greater than those encountered in the simulation of a finite system. Even if working with a potential that is truncated by definition, such that correction for direct long-range interactions is not required in principle, consideration of long-range behavior is required for full treatment of the mapped average. In this section we develop formulas to account for these contributions.

We begin with the mapped-average expression for the pressure in terms of the radial distribution function, given by Eq. (27) of the paper:

$$P = \rho k_B T - \frac{1}{2}\hat{q}\rho^2 k_B T + \frac{\rho^2}{6} \int_0^\infty dr 4\pi r^2 g(r) [r(v'(r) - u'(r)) + r_s(r)(v'(r) - w'(r))]. \quad (83)$$

In the usual manner, we define r_c as the maximum separation distance for pair interactions, the point beyond which we no longer include contribution from terms involving $u(r)$. Similarly, we define r_0 such that we may consider $v(r) = 0$ for $r > r_0$ ($v(r)$ may be zero for some $r < r_0$; the only condition is that it be zero beyond this separation distance). We now decompose the pressure into contributions from the standard virial and the mapped virial, both within and beyond their respective cutoffs:

$$P = \rho k_B T - \frac{1}{2}\hat{q}\rho^2 k_B T + \langle P_{\text{vir}} \rangle_{r_c} + \langle P_{\text{map}} \rangle_{r_0} + P_{\text{LRC}}(r_c) + P_0(r_0), \quad (84a)$$

where

$$\langle P_{\text{vir}} \rangle_{r_c} = \frac{1}{3V} \left\langle \sum_{r_{ij} < r_c} r_{ij} [v'(r_{ij}) - u'(r_{ij})] \right\rangle, \quad (84b)$$

$$\langle P_{\text{map}} \rangle_{r_0} = \frac{1}{3V} \left\langle \sum_{r_{ij} < r_0} r_s(r_{ij}) \left[v'(r_{ij}) + \frac{1}{2} (\mathbf{F}_i - \mathbf{F}_j) \cdot \hat{\mathbf{r}}_{ij} \right] \right\rangle, \quad (84c)$$

$$P_{\text{LRC}} = \frac{\rho^2}{6} \int_{r_c}^{\infty} dr 4\pi r^2 g(r) r (v'(r) - u'(r)), \quad (84d)$$

$$P_0 = -\frac{\rho^2}{6} \int_{r_0}^{\infty} dr 4\pi r^2 g(r) r_s(r) w'(r). \quad (84e)$$

The angle brackets appearing in Eq. (84) indicate an ensemble average evaluated via molecular simulation, considering for each configuration all pairs separated by a distance less than r_c or r_0 , as indicated. Equation (84e) uses $v(r) = 0$ for $r > r_0$, while Eq (84d) does not, because r_c is not necessarily greater than r_0 . The term P_{LRC} can be handled in the usual manner [3], say by assuming $g(r) = 1$ over the range of integration. Our interest now is in the P_0 term.

The behavior of $r_s(r)$ for $r \geq r_0$ is given as follows:

$$\begin{aligned} r_s(r) &= -r + 3 \int_0^r d\hat{r} \left(\frac{\hat{r}}{r} \right)^2 e^{-\beta v(\hat{r})} & r \geq r_0 \\ &= -r + \frac{3}{r^2} \int_0^{r_0} d\hat{r} \hat{r}^2 e^{-\beta v(\hat{r})} + \frac{3}{r^2} \int_{r_0}^r \hat{r}^2 \\ &= \frac{3}{r^2} \int_0^{r_0} d\hat{r} \hat{r}^2 (e^{-\beta v(\hat{r})} - 1) \\ &= \frac{3\hat{q}}{4\pi r^2} \end{aligned} \quad (85)$$

This result can be substituted into Eq. (84e) for P_0 , with the result:

$$\begin{aligned} P_0 &= -\frac{\rho^2}{6} \int_{r_0}^{\infty} dr 4\pi r^2 g(r) \frac{3\hat{q}}{4\pi r^2} w'(r) \\ &= -\frac{\rho^2}{2} \hat{q} \int_{r_0}^{\infty} dr e^{-\beta w(r)} w'(r) \\ &= -\frac{1}{2} \rho^2 \hat{q} k_B T (g(r_0) - 1) \end{aligned} \quad (86)$$

Putting it all back together, we get the full expression for the mapped-average pressure:

$$P = \rho k_B T - \frac{1}{2} \hat{q} \rho^2 g(r_0) k_B T + \langle P_{\text{vir}} \rangle_{r_c} + \langle P_{\text{map}} \rangle_{r_0} + P_{\text{LRC}}(r_c). \quad (87)$$

C. Details regarding application

In the calculations reported here, P_{LRC} was neglected, while $g(r_0)$ was computed as follows. We collected histograms of $g(r)$ during the simulation with a bin size of 0.01 (all quantities in LJ units). Samples were taken every 1000 steps. In order to remove finite-size bias in $g(r)$, we multiplied $g(r)$ by $(1 + q_g/V)$ where

$$q_g = 4\pi \int_0^{r_c} r^2(g(r) - 1)dr$$

If we assume that $g(r)$ is flat beyond r_c , then $(1 + q_g/V)$ will make its value equal to 1.

We estimated the uncertainty in $g(r)$ for each bin using the multinomial distribution: $e(r) = [n(r)(1 - n(r)/N)]^{1/2}$.

To get $g(r = r_0 \equiv 3.8)$, we took the last 40 points ($3.6 \leq r \leq 4.0$) and fit it to polynomials of increasing order, starting with linear. We increased the order of the fit until either $\chi^2 < 1.6$, or χ^2 decreased by less than 10% from the previous order of fit.

We took the $g(r_0)$ and the uncertainty in $g(r_0)$ from the fit. The polynomial order needed to describe g varied from 1 at low density to 4 at high density.

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- [1] S. Whitaker, *Introduction to Fluid Mechanics* (Krieger Publishing, Florida, 1992).
 - [2] S. G. Moustafa, A. J. Schultz, and D. A. Kofke, Phys. Rev. E **92**, 043303 (2015).
 - [3] M. P. Allen and D. J. Tildesley, *Computer simulation of liquids*, Oxford science publications (Clarendon Press, 1987).