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Geometric approach to the pressure tensor and the elastic constants

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Expressions are obtained for the pressure tensor in the canonical and the microcanonical ensemble for both isolated and periodic systems, using the same geometric approach to thermodynamic derivatives as has been used previously to define the configurational temperature. The inherent freedom of the method leads to a straightforward proof of the equivalence of atomic and molecular pressures, for short molecules and for molecules exceeding the dimensions of a periodic simulation box. The effect of holonomic constraints on the pressure is discussed. Expressions for the elastic constants are derived in the same manner.

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I. INTRODUCTION

A number of recent papers have discussed an intuitive geometric approach to the partial derivatives of thermodynamic potentials, as appearing in statistical mechanics and atomic simulations [1–6]. Any partition function, i.e., the phase space integral underlying a thermodynamic potential, can be expressed as an integral over a surface defined by the characteristic variables of that potential. The basic idea, now, is that the derivative of a surface integral, with respect to a parameter defining that surface, can itself be expressed as an integral over the very same surface. By expressing the displacements of the surface elements under an infinitesimal parameter change as a vector field, the change of the integrand during the displacement is readily calculated, to first order, as the dot product of the vector field and the gradient of the integrand. The accompanying change of the area of the surface element also follows from the vector field, again to first order. Integrating both contributions over the surface area yields the desired result, in this case the derivative of a partition function.

Although the vector field must correspond to a bijective projection, there still is ample freedom in its construction. Consider, for example, the energy derivative of the entropy in a microcanonical ensemble, i.e., the inverse temperature. The energy of a system of interacting atoms can be increased by adding to every atomic momentum a vector proportional to that momentum. With this vector field the usual relation between the temperature and the overall kinetic energy is recovered [2,5]. Alternatively, one could simultaneously move all atoms along the gradient of the potential, i.e., against the forces. With this vector field one arrives at the recently introduced configurational temperature [1–5], which distills a temperature from the configurations sampled in a molecular dynamics or Monte Carlo simulation. As a second example, in reaction rate calculations the geometric approach can be used to calculate the free energy profile along a reaction coordinate, and hence the equilibrium constant and the transition-state theory rate. The conventional thermodynamic integration method [7] and the potential of mean constraint force method [8,9] are but two appearances of the one underlying geometric approach, obtained by introducing different vector fields [6].

In Sec. II of this paper, we derive an expression for the pressure by applying the geometric approach to the volume derivative of the free energy in the canonical ensemble. The common atomic pressure expressions are then arrived at by inserting a particular choice of the vector field. In Sec. III a different field leads to the common molecular pressure expression, thus giving a direct proof of the thermodynamic equivalence of the two pressures. Alternative perspectives on the pressure expressions are discussed. Expressions for the elastic constants, in atomic, molecular, and mixed form, are derived in Sec. IV.

II. ATOMIC PRESSURE

The free energy A of a closed system is a function of the temperature T, the number of atoms N, and of the matrix of edge vectors $\underline{\mathbf{h}}=(\mathbf{h}_1,\mathbf{h}_2,\mathbf{h}_3)$ specifying the location of the enclosing walls. It proves advantageous to position the origin of the coordinate system at the center of the box. For infinitely hard walls, the restriction that the coordinates $\mathbf{x}_i$ of the ith atom must lie within the box then read $|(\underline{\mathbf{h}}^{-1}\mathbf{x}_i)_\lambda|\leqslant\frac{1}{2}$, with $\lambda\in\{1,2,3\}$. But for soft walls this condition is less strict: although atoms are mostly within the box, there is a finite chance for an atom to penetrate deeply into the wall. This is tacitly implied whenever we write that the particle is ‘‘in the box $\underline{\mathbf{h}}$.’’ The free energy of a periodic system, as commonly used in computer simulations, is also a function of N, T, and $\underline{\mathbf{h}}$, where $\underline{\mathbf{h}}$ denotes the matrix of edge vectors of the repeated cell. We shall follow the convention that the atoms are at all times within the central box $\underline{\mathbf{h}}$; the space outside the box is filled with periodic images of the atoms inside the box. The discussion of periodic systems will be limited to short-ranged potentials, with a cutoff of less than half the smallest box size. In addition, we assume that there are no external body forces working on the system.

Regarding our notation, we will use bold lower case Latin

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letters for three-dimensional vectors. The corresponding upper case is short-hand for a complete set of atomic vectors, e.g., $\mathbf{V}^{\alpha}=\{\mathbf{v}_1^{\alpha},\ldots,\mathbf{v}_N^{\alpha}\}$ with the superscript α acting as the ordinal. Bold Greek letters are reserved for six-dimensional vectors, and underscores are added to distinguish between vectors and matrices.

Under the above conditions, the potential energy of the system of interacting atoms is a function of the atomic coordinates and of the box dimensions, $\Phi(\mathbf{X},\underline{\mathbf{h}})$. This potential can always be split into a part that explicitly depends on the box dimensions and a part that does not, $\Phi=U(\mathbf{X})+W(\mathbf{X},\underline{\mathbf{h}})$. For a nonperiodic system, U describes all interatomic interactions and W captures the interactions between atoms and the walls. In a periodic system, W includes all interactions between atoms and periodic images of atoms, i.e., those atom pairs for which $\mathbf{x}_{ij}=\mathbf{x}_i-\mathbf{x}_j$ is larger than the cutoff distance but which do interact after applying the nearest image convention. This convention obviously makes these interaction energies explicitly dependent on the box dimensions. The potential U includes all direct interactions, i.e., those atom pairs for which $\mathbf{x}_{ij}$ is less than the cutoff distance.

For small perturbations of the box, $\underline{\mathbf{h}}\rightarrow\underline{\mathbf{h}}'=\underline{\mathbf{e}}\underline{\mathbf{h}}$, we define a deformation matrix $\underline{\mathbf{e}}$ and a deformation vector $\boldsymbol{\varepsilon}$ by

$$\underline{\mathbf{e}}(\boldsymbol{\varepsilon})=\underline{\mathbf{1}}+\begin{pmatrix} \varepsilon_1 & \frac{1}{2}\varepsilon_4 & \frac{1}{2}\varepsilon_5 \\ \frac{1}{2}\varepsilon_4 & \varepsilon_2 & \frac{1}{2}\varepsilon_6 \\ \frac{1}{2}\varepsilon_5 & \frac{1}{2}\varepsilon_6 & \varepsilon_3 \end{pmatrix}=\underline{\mathbf{1}}+\sum_{a=1}^{6}\varepsilon_{\alpha}\underline{\mathbf{b}}^{\alpha}, \tag{1}$$

where the $\underline{\mathbf{b}}^{\alpha}$’s represent the six independent deformations of the box. Rotations of the box are excluded here, as are translations, since they do not affect the potential energy nor the free energy of the system. The factors $\frac{1}{2}$ are introduced to adhere to conventions of the literature. The response of the system’s free energy to small perturbations is given by $dA=-S\,dT-V\boldsymbol{\pi}\cdot d\boldsymbol{\varepsilon}+\mu\,dN$, where S is the entropy, $V=|\underline{\mathbf{h}}|$ the volume, $\boldsymbol{\pi}$ the pressure vector, and μ the chemical potential. At constant N and T, the α component of the pressure then reads

$$\pi_{\alpha}=-\frac{1}{V}\frac{\partial A}{\partial\varepsilon_{\alpha}}\bigg|_{\boldsymbol{\varepsilon}=\mathbf{0}}=\frac{1}{V}\frac{k_BT}{Z(\mathbf{0})}\lim_{\varepsilon_{\alpha}\rightarrow 0}\frac{Z(\varepsilon_{\alpha}\hat{\boldsymbol{\eta}}^{\alpha})-Z(\mathbf{0})}{\varepsilon_{\alpha}}, \tag{2}$$

where $\hat{\boldsymbol{\eta}}^{\alpha}$ is a unit vector in the αth direction. In the last step we used $A=-k_BT\ln(Z)+c$, where k_B is Boltzmann’s constant and c is an irrelevant function of the temperature. The configuration integral reads

$$Z(\boldsymbol{\varepsilon})=\int_{\underline{\mathbf{e}}(\boldsymbol{\varepsilon})\underline{\mathbf{h}}}\exp\{-\beta\Phi[\mathbf{X},\underline{\mathbf{e}}(\boldsymbol{\varepsilon})\underline{\mathbf{h}}]\}d\mathbf{X}, \tag{3}$$

where the integrals run over the entire box (for soft walls this could also have been $\mathbb{R}^3$, see the comment at the start of this section), and $\beta=1/k_BT$.

In the evaluation of Eq. (2) it proves advantageous to introduce a projection that couples *every* point $\mathbf{X}$ of the configuration space in the box $\underline{\mathbf{e}}(\mathbf{0})\underline{\mathbf{h}}$ with a *unique* point $\mathbf{X}'$ of the configuration space in the box $\underline{\mathbf{e}}(\varepsilon_{\alpha}\hat{\boldsymbol{\eta}}^{\alpha})\underline{\mathbf{h}}$, and vice versa. In the limit of $\varepsilon_{\alpha}\rightarrow 0$, such a projection is achieved by a configuration-dependent vector field $\mathbf{V}^{\alpha}$ [1–6],

$$\mathbf{X}'=\mathbf{X}+\varepsilon_{\alpha}\mathbf{V}^{\alpha}(\mathbf{X}). \tag{4}$$

This field allows us to express the partition function of the deformed ensemble as an integral over the reference ensemble,

$$\begin{aligned} Z(\varepsilon_{\alpha}\hat{\boldsymbol{\eta}}^{\alpha})&=\int_{\underline{\mathbf{e}}(\varepsilon_{\alpha}\hat{\boldsymbol{\eta}}^{\alpha})\underline{\mathbf{h}}}\exp\{-\beta\Phi[\mathbf{X}',\underline{\mathbf{e}}(\varepsilon_{\alpha}\hat{\boldsymbol{\eta}}^{\alpha})\underline{\mathbf{h}}]\}d\mathbf{X}' \\ &=\int_{\underline{\mathbf{e}}(\mathbf{0})\underline{\mathbf{h}}}\exp\{-\beta\Phi[\mathbf{X}+\varepsilon_{\alpha}\mathbf{V}^{\alpha}(\mathbf{X}),\underline{\mathbf{h}}+\varepsilon_{\alpha}\underline{\mathbf{b}}^{\alpha}\underline{\mathbf{h}}]\} \\ &\quad\times\left|\frac{\partial\mathbf{X}'}{\partial\mathbf{X}}\right|d\mathbf{X}. \end{aligned} \tag{5}$$

Taylor expanding the Jacobian of the coordinate transformation of Eq. (4) gives

$$\begin{aligned}\left|\left(\frac{\partial x'_{i\lambda}}{\partial x_{j\mu}}\right)\right|&=\left|\left(\delta_{ij}\delta_{\lambda\mu}+\varepsilon_{\alpha}\frac{\partial v_{i\lambda}^{\alpha}}{\partial x_{j\mu}}\right)\right|=1+\varepsilon_{\alpha}\sum_{i=1}^{N}\sum_{\lambda=1}^{3}\frac{\partial v_{i\lambda}^{\alpha}}{\partial x_{i\lambda}} \\ &\quad+O(\varepsilon_{\alpha}^{2}),\end{aligned} \tag{6}$$

where δ is the Kronecker delta. Both lowest order terms originate from the multiplication of the diagonal elements of the Jacobi matrix. Next, Taylor expanding the exponential in Eq. (5), which contains ε_{α} twice, yields

$$\begin{aligned} Z(\varepsilon_{\alpha}\hat{\boldsymbol{\eta}}^{\alpha})&=\int_{\underline{\mathbf{h}}}\exp[-\beta\Phi(\mathbf{X},\underline{\mathbf{h}})] \\ &\quad\times\left(1-\beta\varepsilon_{\alpha}\sum_{i=1}^{N}\sum_{\lambda=1}^{3}v_{i\lambda}^{\alpha}\frac{\partial\Phi(\mathbf{X},\underline{\mathbf{h}})}{\partial x_{i\lambda}}\right) \\ &\quad\times\left(1-\beta\varepsilon_{\alpha}\sum_{\lambda,\mu=1}^{3}\frac{\partial\Phi(\mathbf{X},\underline{\mathbf{h}})}{\partial h_{\lambda\mu}}\sum_{\nu=1}^{3}\frac{\partial e_{\lambda\nu}h_{\nu\mu}}{\partial\varepsilon_{\alpha}}\right) \\ &\quad\times\left(1+\varepsilon_{\alpha}\sum_{i=1}^{N}\sum_{\lambda=1}^{3}\frac{\partial v_{i\lambda}^{\alpha}}{\partial x_{i\lambda}}\right)d\mathbf{X}+O(\varepsilon_{\alpha}^{2}). \end{aligned} \tag{7}$$

Multiplying the three terms in large parentheses, one readily sees that the zeroth order term recovers $Z(\mathbf{0})$, and that the first order term produces the derivative of Z needed in Eq. (2). Note how the geometric approach allows us to convert the derivative of an integral into the integral of a derivative, under conditions in which the two operations do not commute. Combining the above steps, and reverting to a more compact notation, we arrive at our central pressure expression,

$$\pi_{\alpha}=\frac{k_BT}{V}\langle\boldsymbol{\nabla}_X\cdot\mathbf{V}^{\alpha}\rangle-\frac{1}{V}\langle\mathbf{V}^{\alpha}\cdot\boldsymbol{\nabla}_X\Phi\rangle-\frac{1}{V}\left\langle\frac{\partial\Phi}{\partial\underline{\mathbf{h}}}:(\underline{\mathbf{b}}^{\alpha}\underline{\mathbf{h}})^{T}\right\rangle. \tag{8}$$

Here angular brackets denote a canonical average over the reference box $\underline{\mathbf{h}}$, the colon indicates a double contraction, and the superscript T stands for transposed. The first term on the right-hand side measures the change of the accessible volume of configuration space during the box deformation. It is the only term that would remain for an ideal gas. The second and third term describe the change of the potential energy accompanying the deformation of the box and its contents. In Appendix A we derive the equivalent expression for the microcanonical ensemble.

At this point we want to stress that one is free to choose any convenient $\mathbf{V}^{\alpha}$, subject only to the condition that the $\underline{\mathbf{h}} \rightarrow \underline{\mathbf{h}}'$ projection must be a bijection. This one-to-one mapping is essential when writing the integral over the deformed ensemble as an integral over the reference ensemble. It ensures that by integrating over the *entire* reference ensemble we sample the *entire* deformed ensemble in a consistent manner, without omissions, without double counting, and with traceable corrections for the dilations and contractions incurred during the projection. It therefore guarantees that the derivative of the integral, in this case the pressure, becomes independent of the chosen projection method. Some care is needed in simulations, however, as the convergence rate of the averages in Eq. (8) may strongly depend on the chosen field.

An obvious choice for the vector field is to distort the conformation inside the box in the same way as the box itself. This choice is commonly made when deriving the hydrostatic pressure, $p=\frac{1}{3}\Sigma_{\alpha=1}^{3}\pi_{\alpha}$, from the free energy change under a uniform scaling of the box [10]. For the six box deformations considered here, the vector fields are then of the form

$$\mathbf{v}_i^{\alpha}=\lim_{\varepsilon_{\alpha}\rightarrow 0}\frac{\underline{\mathbf{e}}(\varepsilon_{\alpha}\hat{\boldsymbol{\eta}}^{\alpha})\mathbf{x}_i-\mathbf{x}_i}{\varepsilon_{\alpha}}=\underline{\mathbf{b}}^{\alpha}\mathbf{x}_i\,. \tag{9}$$

Inserting this field into Eq. (8), and using the aforementioned partitioning of the potential energy, gives

$$\pi_{\alpha}=\frac{Nk_BT}{V}\Delta_{\alpha}-\frac{1}{V}\left\langle\sum_i \nabla_i U\cdot\underline{\mathbf{b}}^{\alpha}\mathbf{x}_i\right\rangle-\frac{1}{V}\left\langle\sum_i \nabla_i W\cdot\underline{\mathbf{b}}^{\alpha}\mathbf{x}_i\right\rangle-\frac{1}{V}\left\langle\frac{\partial W}{\partial\underline{\mathbf{h}}}:(\underline{\mathbf{b}}^{\alpha}\underline{\mathbf{h}})^T\right\rangle, \tag{10}$$

where $\Delta_{\alpha}=\mathrm{Tr}(\underline{\mathbf{b}}^{\alpha})$ equals one for $\alpha\leqslant 3$ and zero otherwise. The first two terms on the right-hand side reproduce the six unique elements of the regular pressure matrix [11]. We show below that the sum of the last two terms is vanishingly small in the thermodynamic limit of increasing N and V to infinity at constant N/V. Although it is stated in the literature that the pressure of a periodic system can only be expressed in terms of a double summation, *vide infra*, Eq. (10) is a point to the contrary [11,12].

We can split the total boundary force on the atoms of the system into six parts, one for each side of the box, $\mathbf{w}^{\beta}=\Sigma_i\nabla_i W\theta_i^{\beta}$, where θ_i^{β} equals unity if the ith atom interacts with the βth face and zero otherwise. On average, $\mathbf{w}^{\beta}$ is proportional to the area of the βth wall, directed perpendicular to that wall, and of opposite sign to its counterpart of the opposing wall. After multiplication by the coordinates $\mathbf{x}_i$, which are about half the box dimension (because $W_i\neq 0$ we only need to consider atoms near a wall) and are also of opposite sign for opposite faces of the box, we conclude that $\Sigma_{\beta}\Sigma_i\nabla_i W\cdot\mathbf{x}_i\theta_i^{\beta}=\Sigma_{i,\alpha}\nabla_i W\cdot\underline{\mathbf{b}}^{\alpha}\mathbf{x}_i\Delta_{\alpha}$ is of the order of the volume of the box. This is easily verified by considering a rectangular box with a wall potential depending on the perpendicular distance between the atom and the wall. In this particular system, the terms with $\alpha\leqslant 3$ are proportional to the volume of the box and to the strength and range of the wall potential, while the terms with $\alpha\geqslant 4$ are identically zero. The first W term in Eq. (10) therefore makes an $O(1)$ contribution to the pressure. The second W average is the product of $\partial W/\partial\underline{\mathbf{h}}$, which by the definition of W is proportional to the surface area, and a box dimension. Again, this yields an $O(1)$ contribution to the pressure, as will also be argued on different grounds at the end of this section. The energy changes by moving the atoms towards the wall (the first W average) and by moving the walls away from the atoms (the second W average) are roughly equal but of opposite sign, and therefore largely cancel each other. The remainder, after division by V, is less than $O(1)$, and may be omitted from the pressure expression. This is also borne out by the observation that W is a surface term, so its averaged total derivative $\langle\partial W/\partial\varepsilon_{\alpha}\rangle$ [the sum of the two W averages in Eq. (10)] is also proportional to the surface area, and therefore contributes a term $O(V^{-1/3})$ to the pressure. Consequently, leaving out just the last term, retaining a pressure expression of the form [13]

$$\tilde{\pi}_{\alpha}=\frac{Nk_BT}{V}\Delta_{\alpha}-\frac{1}{V}\left\langle\sum_i \nabla_i\Phi\cdot\underline{\mathbf{b}}^{\alpha}\mathbf{x}_i\right\rangle \tag{11}$$

is unfortunately not permitted. As the Nosé-Andersen barostat of Ref. [14] is derived from the energy change under a uniform scaling of the box, its equation of motion for the volume momentum should therefore also contain $\boldsymbol{\pi}$ rather than $\tilde{\boldsymbol{\pi}}$.

The interatomic interactions in simulations are more usually expressed in terms of the relative positions of all atom pairs, $\mathfrak{R}$. By rewriting U in terms of direct difference vectors, $\mathfrak{R}=\{\mathbf{x}_{ij}\}$, the potential becomes $\Phi=U'(\mathfrak{R})+W(\mathbf{X},\underline{\mathbf{h}})$. The boundary term still requires absolute coordinates. The energy change under a perturbation $\mathbf{x}_{ij}\rightarrow(\mathbf{x}_i+\varepsilon_{\alpha}\mathbf{v}_i^{\alpha})-(\mathbf{x}_j+\varepsilon_{\alpha}\mathbf{v}_j^{\alpha})$ with a field of the form of Eq. (9) is then straightforward, and Eq. (8) gives

$$\pi_{\alpha}=\frac{Nk_BT}{V}\Delta_{\alpha}-\frac{1}{V}\left\langle\sum_{i<j}\frac{\partial U'}{\partial\mathbf{x}_{ij}}\cdot\underline{\mathbf{b}}^{\alpha}\mathbf{x}_{ij}\right\rangle-\frac{1}{V}\left\langle\sum_i \nabla_i W\cdot\underline{\mathbf{b}}^{\alpha}\mathbf{x}_i\right\rangle-\frac{1}{V}\left\langle\frac{\partial W}{\partial\underline{\mathbf{h}}}:(\underline{\mathbf{b}}^{\alpha}\underline{\mathbf{h}})^T\right\rangle, \tag{12}$$

which recovers the usual pressure expression in the thermodynamic limit [11]. This result also follows directly from Eq. (10) for a pairwise additive potential,

$$\sum_i \boldsymbol{\nabla}_i U \cdot \underline{\mathbf{b}}^{\alpha}\mathbf{x}_i = \tfrac{1}{2}\left(\sum_{i\neq j}\frac{\partial U'}{\partial \mathbf{x}_{ij}}\cdot \underline{\mathbf{b}}^{\alpha}\mathbf{x}_i + \sum_{j\neq i}\frac{\partial U'}{\partial \mathbf{x}_{ji}}\cdot \underline{\mathbf{b}}^{\alpha}\mathbf{x}_j\right)$$
$$= \frac{1}{2}\sum_{i\neq j}\frac{\partial U'}{\partial \mathbf{x}_{ij}}\cdot \underline{\mathbf{b}}^{\alpha}\mathbf{x}_{ij}\,, \tag{13}$$

where Newton's third law is used in the last step [11].

Although the above expression also holds for periodic systems, it is not elegant to split the potential energy of a periodic system into an internal U and a boundary W part, as both terms are of the same origin. The entire potential energy of such a system is more conveniently expressed by a single function, $\Phi = U''(\mathfrak{R})$ and $\mathfrak{R} = \{\mathbf{r}_{ij}\}$, through the use of the nearest image convention, $\mathbf{r}_{ij} = \mathbf{x}_{ij} - \underline{\mathbf{h}}\mathbf{n}(\underline{\mathbf{h}}^{-1}\mathbf{x}_{ij})$. Here $\mathbf{n}$ returns a vector of the three nearest integers to its three arguments (thus making the condition of placing all atoms inside the central box superfluous). In line with Eq. (9), the interatomic vectors are perturbed into $\mathbf{r}_{ij} \to \mathbf{r}_{ij} + \varepsilon_{\alpha}\underline{\mathbf{b}}^{\alpha}\mathbf{r}_{ij}$, which combines with Eq. (8) to give [11]

$$\pi_{\alpha} = \frac{Nk_BT}{V}\Delta_{\alpha} - \frac{1}{V}\left\langle \sum_{i<j}\frac{\partial U''}{\partial \mathbf{r}_{ij}}\cdot \underline{\mathbf{b}}^{\alpha}\mathbf{r}_{ij}\right\rangle . \tag{14}$$

Again, this result is derivable from Eq. (10). For the U part of the pressure the derivation is as stated above, where automatically $\mathbf{r}_{ij} = \mathbf{x}_{ij}$ because of the definition of U. Applying the same steps to the third term on the right-hand side of Eq. (10) gives $-\langle \Sigma_{i<j}\partial W/\partial \mathbf{r}_{ij}\cdot \underline{\mathbf{b}}^{\alpha}\mathbf{x}_{ij}\rangle$, with all $\mathbf{x}_{ij}$ exceeding the cutoff distance by definition. Only when the last term of Eq. (10) is added, which expressed as a sum of atomic interactions gives

$$\frac{\partial W}{\partial \underline{\mathbf{h}}} : (\underline{\mathbf{b}}^{\alpha}\underline{\mathbf{h}})^T = \sum_{i<j}\frac{\partial W[\mathbf{x}_{ij} - \underline{\mathbf{h}}\mathbf{n}(\underline{\mathbf{h}}^{-1}\mathbf{x}_{ij})]}{\partial \underline{\mathbf{h}}} : (\underline{\mathbf{b}}^{\alpha}\underline{\mathbf{h}})^T$$
$$= -\sum_{i<j}\left(\frac{\partial W(\mathbf{r}_{ij})}{\partial \mathbf{r}_{ij}}\cdot \frac{\partial \underline{\mathbf{h}}\mathbf{n}(\underline{\mathbf{h}}^{-1}\mathbf{x}_{ij})}{\partial \underline{\mathbf{h}}}\right) : (\underline{\mathbf{b}}^{\alpha}\underline{\mathbf{h}})^T$$
$$= -\sum_{i<j}\frac{\partial W}{\partial \mathbf{r}_{ij}}\underline{\mathbf{b}}^{\alpha}\underline{\mathbf{h}}\mathbf{n}(\underline{\mathbf{h}}^{-1}\mathbf{x}_{ij}), \tag{15}$$

are the absolute $\mathbf{x}_{ij}$ converted into the nearest image vectors $\mathbf{r}_{ij}$ needed to complete the proof. The manipulations of both W terms are based upon the assumption that the nearest integer periodicity correction $\mathbf{n}(\underline{\mathbf{h}}^{-1}\mathbf{x}_{ij})$ is unaffected by the box and coordinate changes, as is the case if the range of the potential is sufficiently small with respect to the box dimensions. In the last step of Eq. (15) we used $\partial h_{\beta\gamma}/\partial h_{\lambda\mu} = \delta_{\beta\lambda}\delta_{\gamma\mu}$. Some authors [13,14] derived Eq. (14) from Eq. (11) by employing Newton's third law and simply interpreting every occurrence of an $\mathbf{x}_{ij}$ as an $\mathbf{r}_{ij}$, thus in the process inadvertently adding $V^{-1}\Sigma_{i<j}\partial\Phi/\partial \mathbf{r}_{ij}\cdot \underline{\mathbf{b}}^{\alpha}(\mathbf{x}_{ij} - \mathbf{r}_{ij})$ to the pressure. Using the above results, it is straightforward to show that this extra term exactly retrieves the $\partial W/\partial \underline{\mathbf{h}}$ term that was left out in going from Eq. (10) to Eq. (11), as was to be expected.

Another well-known pressure expression is recovered when we consider a system with soft walls under a box deformation small compared to the width of the wall potential. The configurations in the $\underline{\mathbf{h}}$ and $\underline{\mathbf{e}}\underline{\mathbf{h}}$ boxes of Eq. (2) then sample exactly the same set of configurations ($\mathbf{X} \in \mathbb{R}^{3N}$, see the comment at the start of this section), be it with slightly different Boltzmann factors because of the shifted wall potential. Under these conditions a simple vector field $\mathbf{V}^{\alpha} = \mathbf{0}$ already suffices to calculate the pressure. Equations (8) and (10) are then reduced to just their last term, recovering the trivial result that the pressure is the force exerted on the walls per unit area. This kind of argument cannot be applied to systems with infinitely hard walls, nor to periodic systems, as there the $\underline{\mathbf{h}}$ and $\underline{\mathbf{e}}\underline{\mathbf{h}}$ boxes do not sample identical sets of configurations.

III. MOLECULAR PRESSURE

So far, we have shown how the geometric approach recovers the conventional atomic pressure expressions. The interesting feature of the approach is that we are not limited to this single field of Eq. (9). For molecular systems, for instance, it proves advantageous to introduce a field in which entire molecules are moved as rigid bodies. In a two-index notation, with the Greek index referring to a molecule and the Latin index referring to either an atom $(1 \leqslant i \leqslant N_{\lambda})$ of this molecule or to the entire molecule $(i = 0)$, the proposed field reads

$$\mathbf{v}^{\alpha}_{\lambda i} = \mathbf{v}^{\alpha}_{\lambda 0} = \underline{\mathbf{b}}^{\alpha}\mathbf{x}_{\lambda 0}\,. \tag{16}$$

The coordinate of the molecule is conveniently identified with the center of mass of the molecule, $\mathbf{x}_{\lambda 0} = m^{-1}_{\lambda 0}\Sigma^{N_{\lambda}}_{i=1} m_{\lambda i}\tilde{\mathbf{x}}_{\lambda i}$ with masses $m_{\lambda i}$. In a periodic system the coordinates ought to be "unfolded" to restore any bonds that were broken by placing the individual atoms in the central box. The unfolded atoms may lie outside the box and are therefore marked by a tilde; the resulting center of mass $\tilde{\mathbf{x}}_{\lambda 0}$ is then replaced by its periodic copy $\mathbf{x}_{\lambda 0}$ within the box. But, one could equally well opt for, say, the coordinate of the first atom of the molecule, $\mathbf{x}_{\lambda 0} = \mathbf{x}_{\lambda 1}$. As will be shown in Appendix B, expressing the vector field in the above form implies that a molecule may interact with at most one copy of every other molecule. This condition is obviously met in nonperiodic systems. In periodic systems, it requires the molecules to be small with respect to the box dimensions. Long molecules in periodic boxes are discussed in Appendix B, along with a more extensive discussion of the above issues.

In order for a vector field to be acceptable for the geometric approach, it must correspond to a bijective projection from the $\underline{\mathbf{h}}$ box to the $\underline{\mathbf{e}}\underline{\mathbf{h}}$ box. This is readily shown to be the case in a periodic system and in a box surrounded by soft walls. But, strictly speaking, this is not the case in a box with infinitely hard walls—if a cubic box with sides h is elongated in the x direction, there will be no molecules in the elongated box that touch the walls at $x = \pm(1+\varepsilon_1)h/2$ with just a single atom—though the error is negligible in the thermodynamic limit. We may now introduce the field of Eq. (16) into Eq. (8). Substitution of either of the above choices for $\mathbf{x}_{\lambda 0}$ into the divergence term gives $\Sigma^{N_{\lambda}}_{i=1}\boldsymbol{\nabla}_{\lambda i}\cdot \mathbf{v}^{\alpha}_{\lambda i} = \Delta_{\alpha}$ for each of the n molecules. With the centers of the molecules located inside the box, one trivially arrives at the well-known expression for *nonperiodic* systems [15]

$$\pi_\alpha=\frac{nk_BT}{V}\Delta_\alpha-\frac{1}{V}\left\langle\sum_{\lambda=1}^{n}\sum_{i=1}^{N_\lambda}\boldsymbol{\nabla}_{\lambda i}U\cdot\underline{\mathbf{b}}^{\alpha}\mathbf{x}_{\lambda 0}\right\rangle-\frac{1}{V}\left\langle\sum_{\lambda=1}^{n}\sum_{i=1}^{N_\lambda}\boldsymbol{\nabla}_{\lambda i}W\cdot\underline{\mathbf{b}}^{\alpha}\mathbf{x}_{\lambda 0}\right\rangle-\frac{1}{V}\left\langle\frac{\partial W}{\partial\underline{\mathbf{h}}}:(\underline{\mathbf{b}}^{\alpha}\underline{\mathbf{h}})^{T}\right\rangle, \tag{17}$$

where the W terms again vanishes in the thermodynamic limit. Expressing the potential energy in terms of the relative positions, as in Eq. (14), directly yields the familiar molecular pressure expression for the periodic system [11,12]

$$\pi_\alpha=\frac{nk_BT}{V}\Delta_\alpha-\frac{1}{V}\left(\sum_{\lambda<\mu}\sum_{i=1}^{N_\lambda}\sum_{j=1}^{N_\mu}\frac{\partial U''}{\partial\mathbf{r}_{\lambda i,\mu j}}\cdot\underline{\mathbf{b}}^{\alpha}\mathbf{r}_{\lambda 0,\mu 0}\right). \tag{18}$$

The summation over i and j yields the total force between the molecules λ and μ. All intramolecular contributions have vanished here because the rigid body translation leaves the internal coordinates and internal energy untouched (this does not hold true for long molecules in a periodic box, see Appendix B). Note how both the atomic and molecular pressure expressions, Eqs. (10) and (14) vs Eqs. (17) and (18), have been derived from the central expression of Eq. (8) by selecting two convenient vector fields, which implies that both definitions are thermodynamically equivalent. Alternative ways of proving this result have appeared in Refs. [12] and [15].

An advantage of the molecular pressure over the atomic pressure is that it is far less noisy, because the strong and high frequency intramolecular contributions are omitted [12]. A second advantage is that the intramolecular constraints, which are often introduced in simulations to increase the time step [7,11,15], do not contribute either. In the atomic pressure calculation, it is common practice to include the constraint forces in Eq. (14) in the same way as the potential forces. In the geometric approach, however, the way to treat constraints is to construct a vector field that corresponds to a box deformation whilst simultaneously maintaining all constraints [6]. Consider, for example, a system of rigid dumb bells. If $\mathbf{v}^{\alpha}_{\lambda i}=\underline{\mathbf{b}}^{\alpha}\mathbf{r}_{\lambda i}$ is the unconstrained atomic vector field and $\hat{\mathbf{r}}_\lambda$ is the unit vector parallel to the λth molecule, then a valid constrained field reads

$$\begin{aligned}\overline{\mathbf{v}}^{\alpha}_{\lambda 1}&=\mathbf{v}^{\alpha}_{\lambda 1}+\tfrac{1}{2}\hat{\mathbf{r}}_\lambda[(\mathbf{v}^{\alpha}_{\lambda 2}-\mathbf{v}^{\alpha}_{\lambda 1})\cdot\hat{\mathbf{r}}_\lambda],\\ \overline{\mathbf{v}}^{\alpha}_{\lambda 2}&=\mathbf{v}^{\alpha}_{\lambda 2}-\tfrac{1}{2}\hat{\mathbf{r}}_\lambda[(\mathbf{v}^{\alpha}_{\lambda 2}-\mathbf{v}^{\alpha}_{\lambda 1})\cdot\hat{\mathbf{r}}_\lambda].\end{aligned} \tag{19}$$

The added terms ensure that this vector field is perpendicular to the gradient of the constrained bond length. The dumb bell is thus translated as a rigid body, and at the same time rotated to align with the applied box deformation. Substitution of this field in Eq. (8) leads to a pressure expression devoid of the constraint forces (even if we were to explicitly introduce them in the normal fashion, they would be orthogonal to $\overline{\mathbf{V}}^{\alpha}$ and drop out).

These ideas are now generalized to systems with multiple internal constrained coordinates, $\sigma_{\lambda r}(\mathbf{X})=0$ with $r\in\{1,\dots,R_\lambda\}$, per molecule. In a molecular dynamics simulation these constraints are imposed by adding constraint forces of the form $\mathbf{f}^{c}_{\lambda i}=\Sigma_{r=1}^{R_\lambda}\lambda_{\lambda r}\boldsymbol{\nabla}_{\lambda i}\sigma_{\lambda r}$ to the existing potential forces. The Lagrange multipliers $\lambda_{\lambda r}$ are conveniently obtained numerically by demanding that the constraints are obeyed after every time step, as in the SHAKE algorithm [16]. Analytically, solving the Cartesian equations of motion and equating the first and second time derivatives of the constrained coordinates to zero, yields the multipliers [7]

$$\lambda_{\lambda r}=\sum_{s=1}^{R_\lambda}(\underline{\mathbf{Z}}_\lambda^{-1})_{rs}\left(\sum_{i=1}^{N_\lambda}m_{\lambda i}^{-1}\boldsymbol{\nabla}_{\lambda i}\sigma_{\lambda s}\cdot\boldsymbol{\nabla}_{\lambda i}\Phi-\sum_{i,j=1}^{N_\lambda}\dot{\mathbf{x}}_{\lambda i}\cdot\boldsymbol{\nabla}_{\lambda i}\boldsymbol{\nabla}_{\lambda j}\sigma_{\lambda s}\dot{\mathbf{x}}_{\lambda j}\right), \tag{20}$$

with overhead dots indicating a time derivative, and with the $R_\lambda\times R_\lambda$ matrices

$$(\underline{\mathbf{Z}}_\lambda)_{rs}=\sum_{i=1}^{N_\lambda}m_{\lambda i}^{-1}\boldsymbol{\nabla}_{\lambda i}\sigma_{\lambda r}\cdot\boldsymbol{\nabla}_{\lambda i}\sigma_{\lambda s}. \tag{21}$$

Because of the constraints, the Cartesian velocities are correlated by [6,15]

$$\langle\dot{\mathbf{x}}_{\lambda i}\dot{\mathbf{x}}^{T}_{\mu j}\rangle_c=\delta_{\lambda\mu}k_BT\left[\frac{\delta_{ij}}{m_{\lambda i}}\underline{\mathbf{1}}-\sum_{r,s=1}^{R_\lambda}(\underline{\mathbf{Z}}_\lambda^{-1})_{rs}\frac{\boldsymbol{\nabla}_{\lambda i}\sigma_{\lambda r}\boldsymbol{\nabla}^{T}_{\lambda j}\sigma_{\lambda s}}{m_{\lambda i}m_{\lambda j}}\right], \tag{22}$$

where $\langle\cdots\rangle_c$ denotes the average over the constrained ensemble. The sampled configuration integral reads

$$Z_c(\boldsymbol{\varepsilon})=\int_{\underline{\mathbf{e}}(\varepsilon)\underline{\mathbf{h}}}\exp\{-\beta\Phi(\mathbf{X},\underline{\mathbf{e}}(\boldsymbol{\varepsilon})\underline{\mathbf{h}})\}z^{1/2}\times\prod_{\lambda=1}^{n}\left(\prod_{r=1}^{R_\lambda}\delta(\sigma_{\lambda r}(\mathbf{X}))\right)d\mathbf{X}, \tag{23}$$

with δ the Dirac δ function and $z=\Pi_{\lambda=1}^{n}|\underline{\mathbf{Z}}_\lambda|$. The factor $z^{1/2}$ arises because the integral of the Boltzmann factor over the unconstrained momenta is no longer independent of the configuration, as it was in the unconstrained system. Note that the objective of the constraints is to enhance the sampling of the phase space of an unconstrained system, so normally one would include Fixman's metric tensor correction $z^{-1/2}$ to the constrained run to correct for this artifact introduced with the constraints [7,9,17].

If we omit the wall terms for the time being, the pressure expression obtained by differentiation of the constrained configuration integral reads

$$\pi_\alpha^c = \frac{k_B T}{V}\,\frac{1}{Z_c(\mathbf{0})}\,\frac{\partial Z_c}{\partial \varepsilon_\alpha}\bigg|_{\boldsymbol{\varepsilon}=\mathbf{0}} = \frac{k_B T}{V}\langle \boldsymbol{\nabla}_X \cdot \overline{\mathbf{V}}^\alpha\rangle_c - \frac{1}{V}\langle \overline{\mathbf{V}}^\alpha \cdot \boldsymbol{\nabla}_X U\rangle_c + \frac{k_B T}{V}\sum_{\lambda=1}^{n}\left\langle |\underline{\mathbf{Z}}_\lambda|^{-1/2}\sum_{i=1}^{N_\lambda}\overline{\mathbf{v}}_{\lambda i}^\alpha \cdot \boldsymbol{\nabla}_{\lambda i}|\underline{\mathbf{Z}}_\lambda|^{1/2}\right\rangle_c, \tag{24}$$

where the last term arises from differentiating z. The vector field $\overline{\mathbf{V}}^\alpha$ must conserve all constraints, $\sigma_{\lambda r}(\mathbf{X}+\varepsilon_\alpha \overline{\mathbf{V}}^\alpha) = \sigma_{\lambda r}(\mathbf{X}) = 0$. Given a field $\mathbf{V}^\alpha$, we can construct $\overline{\mathbf{V}}^\alpha$ by using these conditions in combination with the assumption that both fields displace the molecular centers of mass by an equal amount, $\Sigma_{i=1}^{N_\lambda} m_{\lambda i}\mathbf{v}_{\lambda i}^\alpha = \Sigma_{i=1}^{N_\lambda} m_{\lambda i}\overline{\mathbf{v}}_{\lambda i}^\alpha$, since the constraint forces are internal forces. We thus obtain

$$\overline{\mathbf{v}}_{\lambda i}^\alpha = \mathbf{v}_{\lambda i}^\alpha - \sum_{r,s=1}^{R_\lambda} m_{\lambda i}^{-1}(\boldsymbol{\nabla}_{\lambda i}\sigma_{\lambda r})(\underline{\mathbf{Z}}_\lambda^{-1})_{rs}\sum_{j=1}^{N_\lambda}\mathbf{v}_{\lambda j}^\alpha \cdot \boldsymbol{\nabla}_{\lambda j}\sigma_{\lambda s}. \tag{25}$$

Combining Eqs. (24) and (25) with the atomic vector field yields a voluminous expression. The configurational averages can be rewritten as phase space averages of the constrained system, using the relations provided in Eqs. (20) through (22), to arrive at [11,15]

$$\pi_\alpha^c = \frac{1}{V}\left\langle \sum_{\lambda=1}^{n}\sum_{i=1}^{N_\lambda} m_{\lambda i}\dot{\mathbf{x}}_{\lambda i}\cdot \underline{\mathbf{b}}^\alpha \dot{\mathbf{x}}_{\lambda i}\right\rangle_c - \frac{1}{V}\left\langle \sum_{\lambda=1}^{n}\sum_{i=1}^{N_\lambda}\mathbf{x}_{\lambda i}\cdot \underline{\mathbf{b}}^\alpha(\boldsymbol{\nabla}_{\lambda i}U - \mathbf{f}_{\lambda i}^c)\right\rangle_c. \tag{26}$$

Note how the first term has lost its previous simplicity, and how the constraint force has appeared in the second term. For a molecular field obviously $\overline{\mathbf{V}}^\alpha = \mathbf{V}^\alpha$ and the last term of Eq. (24) equals zero; the geometric approach ensures that the resulting pressure is identical to that of Eq. (26).

Note, however, that the pressure π_α^c is not necessarily equal to the pressure π_α of the unconstrained system, because the two pressures are based on different phase space distributions. One may derive the unconstrained pressure from a constrained simulation, assuming the actual potential of the constrained coordinates is sufficiently hard so they are righteously assumed constant, by invoking Fixman's correction [7,9]. In Eq. (24) one would have to remove the last term on the right-hand side, and replace both remaining averages $\langle f\rangle_c$ by $\langle f z^{-1/2}\rangle_c / \langle z^{-1/2}\rangle_c$. The last term of Eq. (24) should also be subtracted from Eq. (26) and the three averages need to be replaced in the same manner. An easier way of achieving these corrections is to simply run the constrained simulation with the modified potential $\Phi + \frac{1}{2}k_B T \ln z$, or by introducing artificial momenta to the same effect [18], in combination with Eq. (26).

Lue and Evans [19] recently applied a field with the structure $\mathbf{v}_{\lambda i} = \mathbf{v}_{\lambda 0}$ in their definition of the configurational temperature for a system with constraints. Considering the above discussion, it would perhaps be more appropriate to call this the molecular configurational temperature, as none of the internal degrees of freedom contributes to this temperature calculation. An extension of their model to include the orientational degrees of freedom in the temperature calculation is readily constructed. The construction of an appropriate constrained vector field, along the above lines, is under investigation.

IV. ELASTIC CONSTANTS

In the preceding two sections we have seen how the pressure in a box $\underline{\mathbf{h}}$ is expressed as a canonical average over a microscopic pressure function $\sigma_\alpha(\mathbf{X},\underline{\mathbf{h}})$, for which there are several alternatives. This result can be applied to any box. For one that is only slightly different from the reference box, we may write in the above notation

$$\pi_\alpha(\boldsymbol{\varepsilon}) = \frac{1}{Z(\boldsymbol{\varepsilon})}\int_{\underline{\mathbf{e}}(\boldsymbol{\varepsilon})\underline{\mathbf{h}}}\sigma_\alpha(\mathbf{X},\underline{\mathbf{e}}(\boldsymbol{\varepsilon})\underline{\mathbf{h}})\exp\{-\beta\Phi(\mathbf{X},\underline{\mathbf{e}}(\boldsymbol{\varepsilon})\underline{\mathbf{h}})\}d\mathbf{X}. \tag{27}$$

The matrix of elastic constants $\underline{\Gamma}$ of a system measures the response of the pressure to the deformation (or strain) of the box,

$$\Gamma_{\alpha\beta} = -\frac{\partial \pi_\alpha}{\partial \varepsilon_\beta}\bigg|_{\boldsymbol{\varepsilon}=\mathbf{0}} = -\frac{\dfrac{\partial}{\partial \varepsilon_\beta}\int_{\underline{\mathbf{e}}(\boldsymbol{\varepsilon})\underline{\mathbf{h}}}\sigma_\alpha \exp(-\beta\Phi)d\mathbf{X}\bigg|_{\boldsymbol{\varepsilon}=\mathbf{0}}}{Z(\mathbf{0})} + \frac{\int_{\underline{\mathbf{h}}}\sigma_\alpha \exp(-\beta\Phi)d\mathbf{X}}{Z(\mathbf{0})}\,\frac{\partial Z/\partial \varepsilon_\beta|_{\boldsymbol{\varepsilon}=\mathbf{0}}}{Z(\mathbf{0})}. \tag{28}$$

In the last term, the first fraction obviously equals the pressure π_α, while the second fraction relates to the pressure π_β through Eq. (2). The numerator of the first term, being itself the derivative of an integral, can be further rewritten using the geometric approach. A derivation analogous to the steps leading from Eq. (2) to Eq. (8) then yields

$$\Gamma_{\alpha\beta} = -\left\langle \sigma_\alpha\left(\boldsymbol{\nabla}_X \cdot \mathbf{V}^\beta - \beta\mathbf{V}^\beta \cdot \boldsymbol{\nabla}_X\Phi - \beta\frac{\partial\Phi}{\partial \underline{\mathbf{h}}}:(\underline{\mathbf{b}}^\beta\underline{\mathbf{h}})^T\right)\right\rangle_{\underline{\mathbf{h}}} - \left\langle \mathbf{V}^\beta \cdot \boldsymbol{\nabla}_X\sigma_\alpha + \frac{\partial \sigma_\alpha}{\partial \underline{\mathbf{h}}}:(\underline{\mathbf{b}}^\beta\underline{\mathbf{h}})^T\right\rangle_{\underline{\mathbf{h}}} + \frac{V}{k_B T}\pi_\alpha\pi_\beta. \tag{29}$$

The terms in the first average originate from the first order of the Taylor expansions of the Jacobian and the potential, while the terms in the second average result from the Taylor expansion of the microscopic pressure function. In the first average, the term between round brackets is proportional to the microscopic pressure σ_β, whose average already appears in the last term of Eq. (29). Hence, they combine to form a cross correlation of the microscopic pressure fluctuations, $\delta\sigma_\beta = \sigma_\beta - \pi_\beta$. For a large system, where the boundary contribution W to the pressure may conveniently be ignored, introducing the microscopic pressure of Eq. (8) gives

$$\Gamma_{\alpha\beta}=-\frac{V}{k_BT}\langle\delta\sigma_a\delta\sigma_\beta\rangle -\frac{1}{V}\langle\mathbf{V}^\beta\cdot\boldsymbol{\nabla}_X(k_BT\boldsymbol{\nabla}_X\cdot\mathbf{V}^\alpha-\mathbf{V}^\alpha\cdot\boldsymbol{\nabla}_XU)\rangle +\frac{\pi_\alpha}{V}\frac{\partial V}{\partial\underline{\mathbf{h}}}:(\underline{\mathbf{b}}^\beta\underline{\mathbf{h}})^T. \tag{30}$$

The last term, arising from the differentiation of the explicit volume factor in σ_α, is readily shown to simplify to $\pi_\alpha\Delta_\beta$. In a periodic system with nearest image convention, see Eq. (14), the divergence of the vector field is constant, and

$$\Gamma_{\alpha\beta}=-\frac{V}{k_BT}\langle\delta\sigma_\alpha\delta\sigma_\beta\rangle +\frac{1}{V}\left\langle\sum_{k<l}\frac{\partial}{\partial\mathbf{r}_{kl}}\left(\sum_{i<j}\frac{\partial U''}{\partial\mathbf{r}_{ij}}\cdot\underline{\mathbf{b}}^\alpha\mathbf{r}_{ij}\right)\cdot\underline{\mathbf{b}}^\beta\mathbf{r}_{kl}\right\rangle+\pi_\alpha\Delta_\beta, \tag{31}$$

in agreement with the conventional elasticity expression [11,20].

Instead of analytically evaluating all second derivatives in the hypervirial [11] or Born term [20] of Eq. (31), it is often easier to perform these differentiations numerically. This can be achieved by tackling the Born term directly. But if the first derivatives of the potential are known, i.e., if the pressure is readily available, it is advantageous to write the first line of Eq. (28) in a finite difference or perturbation form,

$$\Gamma_{\alpha\beta}=-\lim_{\varepsilon_\beta\to0}\frac{\pi_\alpha(\varepsilon_\beta\hat{\boldsymbol{\eta}}^\beta)-\pi_\alpha(\mathbf{0})}{\varepsilon_\beta} =-\lim_{\varepsilon_\beta\to0}\frac{1}{\varepsilon_\beta}\left[\frac{\langle\sigma_a'(\varepsilon_\beta\hat{\boldsymbol{\eta}}^\beta)\exp[-\beta\Delta\Phi(\varepsilon_\beta\hat{\boldsymbol{\eta}}^\beta)]J\rangle_{\underline{\mathbf{h}}}}{\langle\exp[-\beta\Delta\Phi(\varepsilon_\beta\hat{\boldsymbol{\eta}}^\beta)]J\rangle_{\underline{\mathbf{h}}}} -\pi_\alpha(\mathbf{0})\right]. \tag{32}$$

The fraction between square brackets exactly equals Eq. (27), rewritten as the ratio of two canonical averages over configurations $\mathbf{X}$ within the $\underline{\mathbf{h}}$ box. In the denominator we have used Eq. (5), J is the Jacobian, and the quantity $\Delta\Phi(\varepsilon_\beta\hat{\boldsymbol{\eta}}^\beta)=\Phi(\mathbf{X}',\underline{\mathbf{h}}')-\Phi(\mathbf{X},\underline{\mathbf{h}})$ measures by how much the energy of a configuration changes during the deformation. The numerator is derived in a similar fashion, with $\sigma_\alpha'(\varepsilon_\beta\hat{\boldsymbol{\eta}}^\beta)=\sigma_\alpha(\mathbf{X}',\underline{\mathbf{h}}')$. For linear vector fields, like that of Eq. (9), the Jacobian is the same constant in both averages and therefore cancels out. Evidently, Eqs. (30) and (31) are obtained by Taylor expanding Eq. (32).

The interesting point is that there are several different ways of calculating the elasticities, besides the usual atomic approach. One could, for instance, take a molecular approach by twice inserting the field of Eq. (16) into Eq. (31), which is equivalent to calculating the effect of a rigid-body center of mass rescaling on the molecular pressure in Eq. (32). A combination of one atomic and one molecular deformation is also possible. The main argument for using the molecular field is that it drastically reduces the statistical noise in the pressure [12], though it does not necessarily guarantee a more rapidly converging calculation.

V. CONCLUSIONS

A geometric approach towards calculating derivatives of partition functions has been used here to derive a general expression for the pressure tensor. The appealing feature of the method is that it has an inherent element of freedom, allowing one to generate, within certain limits, a variety of explicit equations from the general expression. We have shown how a number of conventional pressure expressions, for periodic and nonperiodic simulation boxes, all stem from the same equation. The ability to recover both the atomic and molecular pressure proves the equivalence of the two in a straightforward, but unconventional, manner. Applying the geometric approach to the derivative of the pressure yields a general expression for the elastic constants, with the same inherent freedom.

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APPENDIX A: MICROCANONICAL PRESSURE

The calculation of the pressure in a microcanonical ensemble has the added complication of the total energy of the system being conserved during the box deformation. The response of the relevant thermodynamic potential, i.e., the entropy, to small perturbations reads $T\,dS=dE+V\boldsymbol{\pi}\cdot d\boldsymbol{\varepsilon}-\mu\,dN$, with E the total energy. The entropy is related to a partition function by $S=k_B\ln\Omega$, with

$$\Omega(\boldsymbol{\varepsilon},E)=\int_{\underline{\mathbf{e}}(\boldsymbol{\varepsilon})\underline{\mathbf{h}}}\int\delta\{\Phi(\mathbf{X}',\underline{\mathbf{e}}(\boldsymbol{\varepsilon})\underline{\mathbf{h}})+K(\mathbf{P}')-E\}d\mathbf{X}'d\mathbf{P}'. \tag{A1}$$

Here the $\mathbf{P}'$ are the momenta conjugate to the Cartesian coordinates, and K is the kinetic energy. Analogous to Eq. (2), the pressure reads

$$\pi_\alpha=\frac{T}{V}\left(\frac{\partial S}{\partial\varepsilon_\alpha}\right)_E\bigg|_{\boldsymbol{\varepsilon}=\mathbf{0}}=\frac{k_BT}{V}\lim_{\varepsilon_\alpha\to0}\frac{\Omega(\varepsilon_\alpha\hat{\boldsymbol{\eta}}^\alpha,E)-\Omega(\mathbf{0},E)}{\varepsilon_\alpha}. \tag{A2}$$

Since the box deformation and coordinate displacements $\mathbf{X}\to\mathbf{X}'=\mathbf{X}+\varepsilon_\alpha\mathbf{V}^{x\alpha}(\mathbf{X})$ inevitably will change the potential energy of the system, the momenta have to change to keep the total energy of the system constant: $\mathbf{P}\to\mathbf{P}'=\mathbf{P}+\varepsilon_\alpha\mathbf{V}^{p\alpha}(\mathbf{X},\mathbf{P})$ (The particular case of K being too low to compensate for a rise in Φ is too improbable to be of any effect [2]). Introducing the combined vector field into Eq. (A1) gives

$$\Omega(\boldsymbol{\varepsilon},E)=\int_{\underline{\mathbf{h}}}\int \delta\{\Phi(\mathbf{X}+\varepsilon_\alpha \mathbf{V}^{x\alpha},\underline{\mathbf{h}}+\varepsilon_\alpha \underline{\mathbf{b}}^\alpha\underline{\mathbf{h}})+K(\mathbf{P}+\varepsilon_\alpha \mathbf{V}^{p\alpha})-E\}\left|\frac{\partial \mathbf{X}'}{\partial \mathbf{X}}\right|\left|\frac{\partial \mathbf{P}'}{\partial \mathbf{P}}\right| d\mathbf{X}\, d\mathbf{P}. \tag{A3}$$

Here the momentum vector field must be chosen such that the argument of the δ function is, to first order in ε_α, identical before and after the deformation, hence

$$\sum_{i=1}^{N} \mathbf{v}_i^{x\alpha}\cdot\boldsymbol{\nabla}_i\Phi+\frac{\partial\Phi}{\partial\underline{\mathbf{h}}}:(\underline{\mathbf{b}}^\alpha\underline{\mathbf{h}})^T+\sum_{i=1}^{N}\mathbf{v}_i^{p\alpha}\cdot\frac{\mathbf{p}_i}{m_i}=0. \tag{A4}$$

Because the argument of the δ function is constant, this function needs not be Taylor expanded. It is then straightforward to show, see Eq. (6), that

$$\pi_\alpha=\frac{k_BT}{V}\langle\boldsymbol{\nabla}_X\cdot\mathbf{V}^{x\alpha}+\boldsymbol{\nabla}_P\cdot\mathbf{V}^{p\alpha}\rangle_E, \tag{A5}$$

where the average is over states of equal energy.

An obvious, but in no way unique, choice for the momentum vector field is a uniform scaling, $\mathbf{V}^{p\alpha}=\gamma\mathbf{P}$. From Eq. (A4) follows

$$\gamma=-\frac{1}{2K}\left[\mathbf{V}^{x\alpha}\cdot\boldsymbol{\nabla}_X\Phi+\frac{\partial\Phi}{\partial\underline{\mathbf{h}}}:(\underline{\mathbf{b}}^\alpha\underline{\mathbf{h}})^T\right], \tag{A6}$$

and substitution of this field in Eq. (A5) gives

$$\pi_\alpha=\frac{k_BT}{V}\langle\boldsymbol{\nabla}_X\cdot\mathbf{V}^{x\alpha}\rangle_E-\frac{k_BT}{V}(3N-2)\left\langle\frac{1}{2K}\left[\mathbf{V}^{x\alpha}\cdot\boldsymbol{\nabla}_X\Phi+\frac{\partial\Phi}{\partial\underline{\mathbf{h}}}:(\underline{\mathbf{b}}^\alpha\underline{\mathbf{h}})^T\right]\right\rangle_E, \tag{A7}$$

where we have used $\boldsymbol{\nabla}_P\cdot\mathbf{P}=3N$ and where the -2 arises from the kinetic energy term contained in γ. Note that the temperature in the microcanonical ensemble is not defined in the usual way, but by [2]

$$\frac{1}{T}=k_B\frac{3N-2}{2}\left\langle\frac{1}{K}\right\rangle_E. \tag{A8}$$

This pressure expression, in combination with the vector field of Eq. (9), is in agreement with the literature [21].

APPENDIX B: LONG MOLECULES

The derivation of Sec. III is slightly more involved for long molecules, e.g., polymer chains, which are longer than half the periodic box dimensions. Recall that the last two terms in Eq. (8) describe the energy change of the system under a simultaneous change of the box, $\underline{\mathbf{h}}\rightarrow\underline{\mathbf{e}}\underline{\mathbf{h}}$, and the coordinates. The vector field was introduced merely to facilitate the calculation of the latter contribution, whenever the two terms can be treated independently. For long molecules this is no longer the case.

Consider the nearest image vector between two atoms in the box,

$$\mathbf{r}_{\lambda i,\mu j}=\mathbf{x}_{\lambda i}-\mathbf{x}_{\mu j}-\underline{\mathbf{h}}\mathbf{n}[\underline{\mathbf{h}}^{-1}(\mathbf{x}_{\lambda i}-\mathbf{x}_{\mu j})]. \tag{B1}$$

The atom with coordinates $\mathbf{x}_{\lambda i}$ (by definition in the central box) belongs to one particular unfolded copy of the λth molecule, denoted by $\lambda(i)$, whose center $\tilde{\mathbf{x}}_{\lambda(i)0}$ need not necessarily lie within the box. The combined box and coordinate deformations, treating the molecules as rigid bodies, change this nearest image vector into

$$\mathbf{r}'_{\lambda i,\mu j}=\mathbf{x}_{\lambda i}-\mathbf{x}_{\mu j}+(\underline{\mathbf{e}}-\underline{\mathbf{1}})(\tilde{\mathbf{x}}_{\lambda(i)0}-\tilde{\mathbf{x}}_{\mu(j)0})-(\underline{\mathbf{e}}\underline{\mathbf{h}})\times\mathbf{n}[(\underline{\mathbf{e}}\underline{\mathbf{h}})^{-1}\{\mathbf{x}_{\lambda i}-\mathbf{x}_{\mu j}+(\underline{\mathbf{e}}-\underline{\mathbf{1}})(\tilde{\mathbf{x}}_{\lambda(i)0}-\tilde{\mathbf{x}}_{\mu(j)0})\}]. \tag{B2}$$

If the range of the potential is short relative to the box dimensions, then $\mathbf{n}$ has the same value in both the above expressions. A further reshuffle of terms gives

$$\begin{aligned}\mathbf{r}'_{\lambda i,\mu j}&=\mathbf{r}_{\lambda i,\mu j}+(\underline{\mathbf{e}}-\underline{\mathbf{1}})(\tilde{\mathbf{x}}_{\lambda(i)0}-\tilde{\mathbf{x}}_{\mu(j)0}-\underline{\mathbf{h}}\mathbf{n}[\underline{\mathbf{h}}^{-1}(\mathbf{x}_{\lambda i}-\mathbf{x}_{\mu j})])\\&=\mathbf{r}_{\lambda i,\mu j}+(\underline{\mathbf{e}}-\underline{\mathbf{1}})\underbrace{(\tilde{\mathbf{x}}_{\lambda(i)0}-\mathbf{x}_{\lambda i}+\mathbf{r}_{\lambda i,\mu j}+\mathbf{x}_{\mu j}-\tilde{\mathbf{x}}_{\mu(j)0})}_{\mathbf{z}_{\lambda i,\mu j}}.\end{aligned} \tag{B3}$$

The vector $\mathbf{z}_{\lambda i,\mu j}$ connects the centers of the unfolded molecules λ and μ whereby, for a given copy of λ, the matching copy of μ is selected by the condition that it minimizes the distance between their respective ith and jth atom. Put differently, it describes the itinerary of going from the center of the unfolded molecule μ to its jth atom, leaping from there to the nearest copy of the λi atom, and continuing from there to the center of this unfolded copy of the λ molecule. With the displacements of Eq. (B3) one easily constructs a pressure expression of the form of Eq. (14), yielding

$$\pi_\alpha=\frac{nk_BT}{V}\Delta_\alpha-\frac{1}{V}\left\langle\sum_{\lambda<\mu}^{n}\sum_{i=1}^{N_\lambda}\sum_{j=1}^{N_\mu}\frac{\partial U''}{\partial\mathbf{r}_{\lambda i,\mu j}}\cdot\underline{\mathbf{b}}^\alpha\mathbf{z}_{\lambda i,\mu j}\right\rangle-\frac{1}{V}\left\langle\sum_{\lambda=1}^{n}\sum_{i<j}^{N_\lambda}\frac{\partial U''}{\partial\mathbf{r}_{\lambda i,\lambda j}}\cdot\underline{\mathbf{b}}^\alpha\mathbf{z}_{\lambda i,\lambda j}\right\rangle. \tag{B4}$$

This is the correct expression for the pressure in a periodic system of long molecules, as first derived by Theodorou *et al.* [12]. The intramolecular term arises, despite the rigid body translation and despite the intramolecular forces summing up to zero, because the changing periodic boundary conditions effectively alter the distances, and hence the interaction energies, between atoms of the λth molecule and the atoms of the periodic images of the λth molecule. For small molecules, where the nearest image vector can be expressed as

$$\mathbf{r}_{\lambda i,\mu j}=(\mathbf{x}_{\lambda i}-\tilde{\mathbf{x}}_{\lambda(i)0})-(\mathbf{x}_{\mu j}-\tilde{\mathbf{x}}_{\mu(j)0})+(\tilde{\mathbf{x}}_{\lambda(i)0}-\tilde{\mathbf{x}}_{\mu(j)0})-\underline{\mathbf{h}}\mathbf{n}[\underline{\mathbf{h}}^{-1}(\tilde{\mathbf{x}}_{\lambda(i)0}-\tilde{\mathbf{x}}_{\mu(j)0})] \tag{B5}$$

for all i and j, we find that $\mathbf{z}_{\lambda i,\mu j}=\mathbf{r}_{\lambda 0,\mu 0}$ and the pressure of Eq. (18) is recovered. Note that if the interaction between two atoms contributes to the U potential, i.e., $\mathbf{r}_{\lambda i,\mu j}=\mathbf{x}_{\lambda i}-\mathbf{x}_{\mu j}$, the vector field $\mathbf{z}_{\lambda i,\mu j}=(\underline{\mathbf{e}}-\underline{\mathbf{1}})(\tilde{\mathbf{x}}_{\lambda(i)0}-\tilde{\mathbf{x}}_{\mu(j)0})$ need not be identical to $(\underline{\mathbf{e}}-\underline{\mathbf{1}})(\mathbf{x}_{\lambda(i)0}-\mathbf{x}_{\mu(j)0})$, hence Eq. (17) with its current atom-based definition of U and W holds for nonperiodic systems only.

[1] H. H. Rugh, Phys. Rev. Lett. **78**, 772 (1997).
[2] H. H. Rugh, J. Phys. A **31**, 7761 (1998).
[3] B. D. Butler, G. Ayton, O. G. Jepps, and D. J. Evans, J. Chem. Phys. **109**, 6519 (1998).
[4] O. G. Jepps, G. Ayton, and D. J. Evans, Phys. Rev. E **62**, 4757 (2000).
[5] G. Rickayzen and J. G. Powles, J. Chem. Phys. **114**, 4333 (2001).
[6] W. K. den Otter, J. Chem. Phys. **112**, 7283 (2000).
[7] D. Frenkel and B. Smit, *Understanding Molecular Simulation* (Academic Press, San Diego, 1996), Chaps. 10 and 11.
[8] T. Mülders, P. Krüger, W. Swegat, and J. Schlitter, J. Chem. Phys. **104**, 4869 (1996).
[9] W. K. den Otter and W. J. Briels, J. Chem. Phys. **109**, 4139 (1998).
[10] J. Ray, Am. J. Phys. **50**, 1035 (1982).
[11] M. P. Allen and D. J. Tildesley, *Computer Simulations of Liquids* (Clarendon, Oxford, U.K., 1993), pp. 46–49, 52, 60, and 98.
[12] D. N. Theodorou, T. D. Boone, L. R. Dodd, and K. F. Mansfield, Makromol. Chem. Theory Simul. **2**, 191 (1993).
[13] M. Ferrario, in *Computer Simulation in Chemical Physics*, Vol. 397 of *NATO Advanced Study Institute, Series C: Mathematical and Physical Sciences*, edited by M. P. Allen and D. J. Tildesley (Kluwer Academic Publishers, Dordrecht, The Netherlands, 1993), p. 153.
[14] T. Mülders, S. Toxvaerd, and G. R. Kneller, Phys. Rev. E **58**, 6766 (1998), **63**, 028702 (2001).
[15] G. Ciccotti and J. P. Ryckaert, Comput. Phys. Rep. **4**, 345 (1986).
[16] J. P. Ryckaert, G. Ciccotti, and H. J. C. Berendsen, J. Comput. Phys. **23**, 327 (1977).
[17] M. Fixman, Proc. Natl. Acad. Sci. U.S.A. **71**, 3050 (1974).
[18] T. Mülders and W. Swegat, Mol. Phys. **94**, 395 (1998).
[19] L. Lue and D. J. Evans, Phys. Rev. E **62**, 4764 (2000).
[20] J. R. Ray, Comput. Phys. Rep. **8**, 109 (1988).
[21] E. M. Pearson, T. Halicioglu, and W. Tiller, Phys. Rev. A **32**, 3030 (1985).