Homogeneous Deformation and Instabilities

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Abstract

Homogeneous deformation is investigated systematically.

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I. STRESS, STRAIN AND ELASTIC CONSTANTS

Stress and strain have many definitions. Although how they are defined doesn't actually change the physics, there are differences in effectiveness.

Strain should be a *relative* quantity. Before defining strains, we must first declare the reference state. That's reasonable because strain depicts deformation. Strain should also be rotationally invariant, as how much an object is deformed doesn't depend on the angle we look at it. From now on we'll specify the configuration of an object using configurational variable X, Y or Z, which tells the shape of the material, i.e., its surface constraints. The deformation of an object from one configuration to the other is specified by the deformation gradiant J, usually $Y = JX$. The deformation is assumed to be macroscopically homogeneous, i.e., the surface constraints of that object change uniformly according to J. However, it doesn't have to be a microscopically homogeneous process as different types of atoms on each sublattices may have different atomic-scale relaxations.

Let X be deformed into Y: $Y = JX$. The Lagrangian strain is defined to be

$$\eta_X^Y = \frac{1}{2}(J^T J - 1) \tag{1.1}$$

Here superscript T means transpose. The X in η_X^Y is to denote the reference state and Y to denote the final state. When the final state is clear we'll omit the superscript and simply write as η_X. The polar decomposition theorem states that every matrix can be uniquely decomposed into the product of its symmetric part and its rotational part,

$$\begin{cases} J = RM = ML \\ \\ M^T = M,\ R^T R = L^T L = 1 \end{cases} \tag{1.2}$$

So

$$\eta_X = \frac{1}{2}(J^T J - 1) = \frac{1}{2}(M^2 - 1) \tag{1.3}$$

and so

$$M = \sqrt{1+2\eta_X} = 1 + \eta_X - \frac{1}{2}\eta_X^2 + ... \tag{1.4}$$

We see that there is a one to one correspondence between the Lagrangian strain and the symmetric part of the deformation gradiant J.

Let $Y = JX,\ Z = KY = KJX$. There is

$$\begin{aligned}
\eta_Y^Z &= \frac{1}{2}(K^T K - 1) \\
\eta_X^Z &= \frac{1}{2}(J^T K^T K J - 1) \\
&= \frac{1}{2}(J^T(1+2\eta_Y^Z)J - 1) \\
&= J^T \eta_Y^Z J + \eta_X^Y
\end{aligned} \tag{1.5}$$

which is the law of transformation between reference systems.

Contary to strain, stress should be defined as an *absolute* quantity, which means it shouldn't depend on any reference state. We'll use two kinds of stresses in this paper: the first kind is the outside stress τ_{ij}, which is just the conventional "force per area" tensor used in engineering:

$$dF_i = \tau_{ij} n_j dS \tag{1.6}$$

τ_{ij} is the thermodynamic field that the outside world applies onto the object. To avoid macroscopic rotation, it should satisfy $\tau_{ij} = \tau_{ji}$.

The second kind of stress is the thermodynamic stress t_{ij}, whose definition depends on the Helmholtz free energy of the system:

$$\begin{aligned}
F(N,T,X) &= E - TS \\
&= -k_B T \ln Z(N,T,X)
\end{aligned} \tag{1.7}$$

with

$$Z = \int_X \exp(-\beta \mathcal{H}(q^N, p^N)) dq^N dp^N \tag{1.8}$$

Here F is a function of particle number N, temperature T, and configurational variable (surface constraints) X. Since the Hamiltonian $\mathcal{H}(q^N, p^N)$ is usually rotationally invariant, F will be rotationally invariant. Thus,

$$\begin{aligned} F(N,T,Y) &= F(N,T,JX) \\ &= F(N,T,RMX) \\ &= F(N,T,MX) \\ &= F(N,T,\sqrt{1+2\eta_X}X) \\ &= F(N,T,\eta_X,X) \end{aligned} \tag{1.9}$$

i.e., F is a *function* of the Lagrangian strain η_X once the reference state X is specified. We can always expand a function of η_X into its Taylor series:

$$\begin{aligned} F(\eta_X,X) = F(0,X) &+ \Big(\frac{\partial F}{\partial \eta_{ij}}\Big|_{\eta_X=0}\Big)\eta_{ij} \\ &+ \frac{1}{2}\Big(\frac{\partial^2 F}{\partial \eta_{ij}\partial \eta_{kl}}\Big|_{\eta_X=0}\Big)\eta_{ij}\eta_{kl} + ... \end{aligned} \tag{1.10}$$

Because η_{ij} is symmetric, the actual expansion should have only 6 independent variables: η_{11}, η_{22}, η_{33}, η_{12}, η_{13}, η_{23}. However, it would cause confusion when summing over Cartesian indices, so what we do is to symmetrize the coefficients over η_{ij} and η_{ji} whenever possible, but treat η_{ij} and η_{ji} as seperate summation variables. Define 2nd and 4th rank symmetrization operators:

$$\hat{S}_2(G_{ij}) = \frac{1}{2}(G_{ij}+G_{ji}) \tag{1.11}$$

$$\hat{S}_4(H_{ijkl}) = \frac{1}{4}(H_{ijkl}+H_{ijlk}+H_{jikl}+H_{jilk}) \tag{1.12}$$

The thermodynamic stress at configuration X is defined to be

$$t_{ij}(X) = \frac{1}{\Omega(X)}\hat{S}_2\Big(\frac{\partial F(\eta_X,X)}{\partial \eta_{ij}}\Big|_{\eta_X=0}\Big) \tag{1.13}$$

and the elastic constant:

$$C_{ijkl}(X) = \frac{1}{\Omega(X)}\hat{S}_4\Big(\frac{\partial^2 F(\eta_X,X)}{\partial \eta_{ij}\partial \eta_{kl}}\Big|_{\eta_X=0}\Big) \tag{1.14}$$

Here $\Omega(X)$ is the volume of the object at X, so $t_{ij}(X)$ and $C_{ijkl}(X)$ are made intensive quantities. From definition we can see that:

$$F(\eta_X, X) = F_0 + \Omega(X)\{t_{ij}(X)\eta_{ij} + \frac{1}{2}C_{ijkl}(X)\eta_{ij}\eta_{kl}\}...$$
$$t_{ij} = t_{ji},\ C_{ijkl} = C_{ijlk} = C_{jikl} = C_{jilk}. \tag{1.15}$$

Note that since t_{ij} and C_{ijkl} are only expansion coefficients of $F(\eta_X, X)$ at $\eta_X = 0$, they themselves are not functions of η_X, but only of X. This is to say that the definition of thermodynamic stress and elastic constants do not require a reference state, because when evaluating these quantities the configuration always use *itself* at that instant to be the reference state. This frame-moving reference system will bring in uncommon properties, as theorized in tensor analysis and geometry. For instance

$$t_{ij}(Y) \neq t_{ij}(X) + C_{ijkl}(X)(\eta_X^Y)_{kl} + ...$$

in contrast to what would have been expected for the expansion of "first order derivatives" in terms of "second order derivatives" in a fixed frame. In fact, since

$$\begin{aligned}
F(Z) &= F(\eta_Y^Z, Y) \\
&= F(Y) + \Omega(Y)\mathrm{Tr}\Big(t(Y)\eta_Y^Z\Big) + ... \qquad (1.16) \\
&= F(\eta_X^Z, X) \\
&= F(X) + \Omega(X)\mathrm{Tr}\Big(t(X)\eta_X^Z\Big) \\
&\quad + \frac{\Omega(X)}{2}\mathrm{Tr}\Big(\eta_X^Z\mathbf{C}(X)\eta_X^Z\Big) + ... \qquad (1.17)
\end{aligned}$$

take (1.5) into (1.17) and keep the linear orders of η_Y^Z, we have

$$\begin{aligned}
F(Z) &= \mathrm{const} + \Omega(X)\mathrm{Tr}\Big(Jt(X)J^T\eta_Y^Z\Big) \\
&\quad + \Omega(X)\mathrm{Tr}\Big(J\mathbf{C}(X)\eta_X^Y J^T\eta_Y^Z\Big) + ...
\end{aligned} \tag{1.18}$$

Comparing the coefficients of η_Y^Z with (1.16) and to first order accuracy in $(J-1)$, we have

$$t(Y) = \frac{Jt(X)J^T}{\det|J|} + \mathbf{C}(X)\eta_X^Y + ... \tag{1.19}$$

It will be shown later that (1.19) can be evaluted in symmetric deformation space to give the correct expansion

$$t_{ij}(Y) = t_{ij}(X) + B_{ijkl}(X)(\eta_X^Y)_{kl} + ... \tag{1.20}$$

where $B_{ijkl}(X)$ is the elastic stiffness coefficient.

II. FLUCTUATION FORMULA AND 0°K ELASTIC CONSTANTS

Expressions in terms of particle motion for thermodynamic stress and elastic constants can be derived in a straightforward manner[3,10]. The partition function for a deformed system is

$$Z = Z(X, M) = \int_{MX} \exp(-\beta\mathcal{H}(\tilde{q}^N, \tilde{p}^N))d\tilde{q}^N d\tilde{p}^N,$$

and in general

$$\mathcal{H}(\tilde{q}^N, \tilde{p}^N) = \sum_{n=1}^{N} \frac{\tilde{\mathbf{p}}_n^T \cdot \tilde{\mathbf{p}}_n}{2m_n} + V(\tilde{\mathbf{q}}_1, \tilde{\mathbf{q}}_2, ..., \tilde{\mathbf{q}}_N) \tag{2.1}$$

then under a canonical transformation ($\tilde{\mathbf{q}}_n = M\mathbf{q}_n, \tilde{\mathbf{p}}_n = M^{-1}\mathbf{p}_n$), the Hamiltonian is transformed into:

$$\begin{aligned}\mathcal{H}(q^N, p^N) = \sum_{n=1}^{N} &\frac{\mathbf{p}_n^T M^{-2}\mathbf{p}_n}{2m_n} \\ &+V(M\mathbf{q}_1, M\mathbf{q}_2, ..., M\mathbf{q}_N).\end{aligned} \tag{2.2}$$

Using (1.4) and also

$$M^{-2} = \frac{1}{1+2\eta_X} = 1 - 2\eta_X + 4\eta_X^2 + ... \tag{2.3}$$

the partition function can be written as:

$$Z(X, \eta_X) = \int_X \exp[-\beta\{\sum_{n=1}^{N} \frac{\mathbf{p}_n^T(1-2\eta_X+4\eta_X^2)\mathbf{p}_n}{2m_n} + V((1+\eta_X-\frac{1}{2}\eta_X^2)q^N)\}]dq^N dp^N \tag{2.4}$$

Using tensor notation η_{ij} for matrix η_X:

$$
\begin{aligned}
\frac{\partial F}{\partial \eta_{ij}} &= -\frac{1}{\beta Z} \cdot \frac{\partial Z}{\partial \eta_{ij}} \\
&= \frac{1}{Z} \int_X T_{ij} \exp(-\beta \mathcal{H}) dq^N dp^N
\end{aligned}
\tag{2.5}
$$

where

$$
\begin{aligned}
\mathcal{H}(q^N, p^N) \approx \sum_{n=1}^{N} & \frac{\mathbf{p}_n^T (1 - 2\eta_X + 4\eta_X^2) \mathbf{p}_n}{2m_n} \\
& + V((1 + \eta_X - \frac{1}{2}\eta_X^2) q^N),
\end{aligned}
$$

and

$$
\begin{aligned}
T_{ij} = \frac{\partial \mathcal{H}}{\partial \eta_{ij}} = \sum_{n=1}^{N} & \frac{p_i^n (-\delta_{jk} + 4\eta_{jk}) p_k^n}{m_n} + \\
& (\delta_{ik} - \eta_{ik}) q_k^n \nabla_j^n V((1 + \eta_X) q^N).
\end{aligned}
\tag{2.6}
$$

Here n denotes particles. Variables which don't not appear on the left hand side of the equation are dummy summation variables on the right hand side, ranging from 1 to 3.

Set η_X to zero, and we get the formula for thermodynamic stress:

$$
t_{ij} = \langle \frac{1}{\Omega(X)} \hat{S}_2 \left(\sum_{n=1}^{N} \frac{-p_i^n p_j^n}{m_n} + q_i^n \nabla_j^n V(q^N) \right) \rangle
\tag{2.7}
$$

The $\langle\rangle$ means ensemble averaging in the original configuration X.

Readers may wonder why (2.7) doesn't give constant result 0 at 0°K, since $\nabla_j^n V(\bar{q}^N) \equiv 0$ for bulk atoms. The answer is that if we were to calculate the stress using (2.7) directly, we must count those atoms on the surface, whose equilibrium condition $F_j^n + \nabla_j^n V(q^N) = 0$ requires extra force F_j^n, exerted by the wall. Since weighted by q_i^n, this surface contribution doesn't vanish in the thermodynamic limit, unlike other quantities such as surface energy. One the other hand, it's obvious to us that stress originates from the bulk, and is accumulative. This can be shown since $V(q^N)$ generally is the sum of local interactions, for instance $V(q^N) = \sum_{\{lmn\}} W(q_l, q_m, q_n)$, where W is a 3-body potential. Since $W(q_l + \delta, q_m + \delta, q_n + \delta) = W(q_l, q_m, q_n)$, we have $\nabla_i^l W + \nabla_i^m W + \nabla_i^n W \equiv 0$ and the contribution from this local interaction to the total stress is $(q_i^l - q_i^n)\nabla_j^l W + (q_i^m - q_i^n)\nabla_j^m W$, which's accumulative. This *localization* procedure can and should be done as soon as the model potential becomes known.

To get the formula for elastic constants, we need to further differentiate (2.5):

$$\begin{aligned}\frac{\partial^2 F}{\partial\eta_{ij}\partial\eta_{kl}} &= \frac{1}{Z}\int_X \left(\frac{\partial T_{ij}}{\partial\eta_{kl}} - \beta T_{ij}T_{kl}\right)\exp(-\beta\mathcal{H})dq^N dp^N + \frac{\beta}{Z}\left(\int_X T_{kl}\exp(-\beta\mathcal{H})dq^N dp^N\right)\langle T_{ij}\rangle \\ &= \beta\{\langle T_{ij}\rangle\langle T_{kl}\rangle - \langle T_{ij}T_{kl}\rangle\} + \langle\frac{\partial T_{ij}}{\partial\eta_{kl}}\rangle \end{aligned} \tag{2.8}$$

From (2.6) we can get:

$$\begin{aligned}\left.\frac{\partial T_{ij}}{\partial\eta_{kl}}\right|_{\eta_X=0} &= \sum_{n=1}^{N}\frac{4p_i^n p_k^n}{m_n}\delta_{jl} + \\ &\sum_{m,n=1}^{N}\{q_k^m q_i^n \nabla_l^m \nabla_j^n V(q^N) - \delta_{il} q_k^n \nabla_j^n V(q^N)\}\end{aligned} \tag{2.9}$$

So we get the unsymmetrized form of elastic constants:

$$\begin{aligned} D_{ijkl} &= \beta\Omega(X)(\langle t_{ij}\rangle\langle t_{kl}\rangle - \langle t_{ij}t_{kl}\rangle) + \\ &\frac{1}{\Omega(X)}\langle\sum_{n=1}^{N}\frac{4p_i^n p_k^n}{m_n}\delta_{jl}\rangle + \\ &\frac{1}{\Omega(X)}\langle\sum_{m,n=1}^{N} q_k^m q_i^n \nabla_l^m \nabla_j^n V(q^N) - \sum_{n=1}^{N} q_k^n \nabla_j^n V(q^N)\delta_{il}\rangle \end{aligned} \tag{2.10}$$

The first term is defined as the fluctuation term, while the last term is defined as the Born term, usually written as C_{ijkl}^B. The elastic constant is therefore

$$C_{ijkl} = \hat{S}_4(D_{ijkl}) \tag{2.11}$$

and the expression is valid for finite temperature and stress.

It is interesting to look at the zero temperature limit of the first term in (2.10), because as we approach 0°K the fluctuation will become very small, and the statistical error of evaluating two contrasting limits will become high. The school starting from Born and Huang[8] study the 0°K elastic constants from a different stand point: since $F \equiv V$ at 0°K, they directly evaluate the 2nd order derivatives in total potential energy due to deformation, with the constraint that it's always at potential energy minimum. After careful calculations the formula was derived[9], by which the 0°K elastic constants can be sought from lattice sum. Here we give a new and more straightforward derivation, by seperating surface and bulk atoms. The equivalence of the (2.9) at 0°K with this static result will be shown in the Appendix, by directly taking the limit.

Seperate q^N (total) into q^S (surface) and q^B (bulk) atoms. We know from our previous discussion that they play different roles in expression (2.7): although accumulated mainly by interactions between bulk atoms q^B, it's through q^S that it is manifested. For bulk atoms at equilibrium configuration X, there are

$$\nabla^B V(q^N)\Big|_{\bar{q}^N} = 0 \tag{2.12}$$

but it isn't the case for surface atoms.

Define dynamical matrix $\mathbf{D}$ at X to be

$$D_{mi,nj} = \frac{\partial V(q^N)}{\partial q_i^m \partial q_j^n}\Bigg|_{\bar{q}^N} \tag{2.13}$$

Thus, we can do the quadratic expansion

$$\begin{aligned} V(q^N) &= V(q^N) + \nabla V(q^N) \cdot (q^N - \bar{q}^N) \\ &+ \frac{1}{2}(q^N - \bar{q}^N)^T \mathbf{D}(q^N - \bar{q}^N) + \ldots \end{aligned} \tag{2.14}$$

sometimes we use $\mathbf{D}^{bb}$ and $\mathbf{D}^{tb}$ to denote interaction between bulk-bulk or total-bulk atoms.

The free energy at 0°K is the minimized potential energy:

$$F(M, X) = \min_{\{q^N \in MX\}} \{V(q^N)\} \tag{2.15}$$

In order to study the M dependence of F, we can either put a variable potential barrier $W(q^N; MX)$ and minimize $V + W$ with respect to the entire q^N, or directly go through localization and coordinate transformation procedures. A very simple approach, however, is just to "stick" the surface atoms on transparent walls, and minimize with respect to bulk atoms. We know from experience that the actual surface state doesn't affect bulk properties in thermodynamic limit. Here although surface atoms are not allowed to relax, the method will still give the correct general expression. And we achieve good intuition.

Denote η_X by matrix $\boldsymbol{\eta}$. Since traction are given to surface atoms

$$\begin{cases} q^S = M\bar{q}^S = \bar{q}^S + \boldsymbol{\eta}\bar{q}^S - \frac{1}{2}\boldsymbol{\eta}^2\bar{q}^S \\ \\ q^B = M\bar{q}^B + r^B = \bar{q}^B + \boldsymbol{\eta}\bar{q}^B + r^B + \mathcal{O}(\boldsymbol{\eta}^2) \end{cases} \tag{2.16}$$

where in addition to uniform traction, the bulk atoms are allowed to relax by r^B. It'll be shown later that $r^B \propto \boldsymbol{\eta}$.

And so,

$$\begin{aligned} F(M,X) &= \min_{\{r^B\}} \{V(q^S;q^B)\} \\ &= \min_{\{r^B\}} \{V(\bar{q}^S + \boldsymbol{\eta}\bar{q}^S - \frac{1}{2}\boldsymbol{\eta}^2\bar{q}^S; \bar{q}^B + \boldsymbol{\eta}\bar{q}^B + r^B)\} \\ &= V(q^N) + \nabla^S V \cdot (\boldsymbol{\eta}\bar{q}^S - \frac{1}{2}\boldsymbol{\eta}^2\bar{q}^S) + \frac{1}{2}(\bar{q}^N)^T\boldsymbol{\eta}\mathbf{D}\boldsymbol{\eta}\bar{q}^N \\ &\quad + \min_{\{r^B\}} \{(\bar{q}^N)^T\boldsymbol{\eta}\mathbf{D}^{tb}r^B + \frac{1}{2}(r^B)^T\mathbf{D}^{bb}r^B\} + ... \end{aligned} \tag{2.17}$$

where we had used the fact that $\nabla^B V(\bar{q}^N) \equiv 0$, and so first-order expansion for $M\bar{q}^B$ would be enough.

The minimum obviously happens at

$$(\bar{q}^N)^T\boldsymbol{\eta}\mathbf{D}^{tb} + (r^B)^T\mathbf{D}^{bb} = 0 \tag{2.18}$$

and so

$$\begin{aligned} r^B &= -(\mathbf{D}^{bb})^{-1}\mathbf{D}^{bt}\boldsymbol{\eta}\bar{q}^N \\ &\propto \boldsymbol{\eta} \end{aligned} \tag{2.19}$$

And so to 2nd order in $\boldsymbol{\eta}$, the relaxed total energy is

$$\begin{aligned} F(\boldsymbol{\eta},X) &= V(q^N) + \nabla^S V \cdot \boldsymbol{\eta}\bar{q}^S - \frac{1}{2}\nabla^S V \cdot \boldsymbol{\eta}^2\bar{q}^S \\ &+ \frac{1}{2}(\bar{q}^N)^T\boldsymbol{\eta}\mathbf{D}\boldsymbol{\eta}\bar{q}^N - \frac{1}{2}(\bar{q}^N)^T\boldsymbol{\eta}\mathbf{D}^{tb}(\mathbf{D}^{bb})^{-1}\mathbf{D}^{bt}\boldsymbol{\eta}\bar{q}^N \end{aligned} \tag{2.20}$$

where the last term results from relaxation. Then we can evaluate the unsymmetrized $\mathbf{t}(X)$ and $\mathbf{C}(X)$ using definition (1.13), (1.14)

$$\mathbf{t}(X) = \frac{\bar{q}^S \nabla^S V(\bar{q}^N)}{\Omega(X)} = \frac{1}{\Omega(X)} \left.\mathbf{T}(q^N)\right|_{\bar{q}^N} \tag{2.21}$$

where we define the total stress functional $\mathbf{T}(q^N)$ to be

$$\mathbf{T}(q^N) = q^N \nabla V(q^N) \tag{2.22}$$

which is the same as what's defined in (2.7) at finite temperature. We can see that the relaxation process doesn't alter the stress expression because it's first-order derivative.

Then

$$\begin{aligned} \mathbf{C}(X) = \frac{1}{\Omega(X)} \{ & (\bar{q}^N)^T \mathbf{D} \bar{q}^N - \mathbf{T}(X)\mathbf{I} \\ & -(\bar{q}^N)^T \mathbf{D}^{tb} (\mathbf{D}^{bb})^{-1} \mathbf{D}^{bt} \bar{q}^N \} \end{aligned} \tag{2.23}$$

the first two terms are identified to be the $T = 0$ Born term, while the last one corresponds to relaxation. To eliminate the surface entirely from our derivation, we observe that

$$\begin{aligned} \left.\frac{\partial \mathbf{T}(q^N)}{\partial q^B}\right|_{\bar{q}^N} &= \left.\frac{\partial (q^N \nabla V(q^N))}{\partial q^B}\right|_{\bar{q}^N} \\ &= \left.\nabla^B(q^N)\right|_{\bar{q}^N} + \bar{q}^N \mathbf{D}^{tb} \\ &= \mathbf{D}^{bt} \bar{q}^N \end{aligned} \tag{2.24}$$

and so if we define matrix constant

$$A_{ij,mc} = \left.\frac{\partial T_{ij}(q^N)}{\partial q_c^m}\right|_{\bar{q}^N} \tag{2.25}$$

which could be evaluated in any localized model, we will have

$$\begin{aligned} & C_{ijkl}(X) = C^B_{ijkl}(X) + C^R_{ijkl}(X) \\ & = \frac{1}{\Omega(X)} \{ \bar{q}_k^m \bar{q}_i^n D_{ml,nj} - T_{kj}\delta_{il} - A_{ij,mc} D^{-1}_{mc,nd} A_{kl,nd} \} \end{aligned} \tag{2.26}$$

which yet need to be symmetrized. This expression is exactly the same as Martin's result[9], and is valid under general stressed condition.

The mentioned relaxation process doesn't happen in regular monoatomic crystals, as well as for crystals with inversion symmetry[12]. This can be proven by (2.19), since both

$\mathbf{D}$ and $\boldsymbol{\eta}$ are even under inversion, while $\bar{q}^N$ is odd, so $r^B \equiv 0$. It would be interesting to have some group-theoretical conclusions about C^R_{ijkl} for other types of symmetries. We have a simple tested example, where elastic constants for SiC (zinc-blende structure) were calculated using the fluctuation formula, with C^R_{ijkl} identified as the fluctuation term in (2.10) (see Appendix). Long enough MD runs were taken to ensure numerical convergence, at the classical temperature of about 2°K. What happens is that $C^R_{11} = C^R_{12} = 0$, but C^R_{44} gives finite value, counting for about 20% of the total C_{44}. A drawing of the crystal structure at three different deformation modes will immediately show why. The combined Born and relaxation term agrees very well with results from direct MD stress-strain experiments.

III. DEFORMATION SPACE, $(NT\tau)$ ENSEMBLE AND THE GIBBS INTEGRAL

All homogeneous deformations can be described by the movement of a configurational variable in deformation space, in general a 9 dimensional space with origin at an arbitrarily chosen reference state X. In this space any configuration can be represented by the deformation gradient J (relative to X). Morever, if there exists particular constraints which allow us to uniquely determine J from η_X, then deformation space becomes 6 dimensional, which we call *unique* to stress the fact that any configuration can be specified in terms of η_X instead of J. As an example, in the Parrinello-Rahman method[1] for performing atomistic simulation at constant stress, J is usually constrained to be symmetric. Because J in this case can then be uniquely determined by η_X from the equation

$$J = \sqrt{1 + 2\eta_X} = 1 + \eta_X - \frac{1}{2}\eta_X^2 + \ldots$$

it is unique and we will give it a special name: symmetric deformation space.

There can be other unique deformation spaces. For instance, we can constrain J to be always upper triangular: this case corresponds to deforming a cube while constraining one edge on the x axis and one face on the xy plane. Thus J has 6 non-zero elements which can also be uniquely determined by η_X. The opposite of unique is called *general*.

The classification of deformation space is necessary: because once we have some constraints on how J can be perturbed, there might be instability paths in general deformation space, but which is forbidden in unique spaces. So when the general case is already unstable, the unique case might still be stable in the same configuration.

Since every point in deformation space is either denoted by J or η_X, we can treat it as a 9 or 6 dimensional *vector* instead of a 3×3 matrix. Define the inner product between two vectors(matrices) in deformation space to be:

$$A \cdot B = \mathrm{Tr}(A^T B) = \sum_{i,j}^{3} A_{ij} B_{ij} \tag{3.1}$$

We have

$$\begin{aligned} & A \cdot B = B \cdot A \\ & A \cdot (B + C) = A \cdot B + A \cdot C \\ & A \cdot A \geq 0 \end{aligned} \tag{3.2}$$

thus it has the properties of Euclidian space and the measure of distance beween vectors is well defined.

The purpose of this paper is to study the stability behaviour of materials under finite deformation. Obviously some kind of outside loading must be present. It turns out that the accurate description of this loading condition is crucial to our stablity analysis because we rely on 2nd-order expansions: thus the loading condition itself should be exactly determined to at least 2nd order. A certain stability criterea is only for a certain loading condition.

From now on we'll focus our attention on the so called $(NT\tau)$ ensemble, meaning constant particle number N, constant temperature T, and constant *outside stress* τ, which is defined in previous section and commonly used in engineering. Before going further, the authors want to make it clear that we choose this ensemble to be our model system not because we have impeccable justifications for it, nor do we insist on using it if a better description for a specific problem is available. Nevertheless, the approach we took here is universal and can be applied onto any system once the loading condition is known, so that the virtual work integral can be written down. The $(NT\tau)$ ensemble is considered to be the appropriate carrier for our discussion because it's the most commonly used scenario, and leads to analytical results quickly.

As a warning, we think that some researchers might be unsatisfied with the fact (as we'll show later) that $(NT\tau)$ ensemble is a dissipative system and no valid thermodynamic potential exists: we want to say that (as far as in our knowledge) we are the ones to first point out this feature clearly, not because we like it. On the other hand, this situation enable us to set up an *ad hoc* theory based on thermodynamic driving force in deformation space in the absence of a potential, and stability criterea derived from this formalism will natually lead to the symmetrization of the B matrix, which in turn can be understood as mapping a dissipative system onto an equivalent conservative system with a symmetric A. This justifies the practical applicabilty of the $(NT\tau)$ stability criterea, because in realistic situations when the 2nd order feature of a certain loading condition isn't known, we can use the $(NT\tau)$ criterea as a reasonable guess, which only requires input from the stress condition. Since constant τ does capture the main feature of many applications, we'd expect the criterea to be of some predictive value.

Let's start from the beginning: there is a direct analogy between the commonly used (NTP) ensemble and $(NT\tau)$ ensemble, in fact the former belongs to the latter. The thermodynamic potential for (NTP) ensemble is the Gibbs free energy

$$G = F(N,T,V) + PV \tag{3.3}$$

The stability criterea for this system is the requirement of convexity of V under constant thermodynamic field (NTP). The term PV in (3.3) is just the virtual work integral. (The significance of thermodynamic potentials come from the 2nd law of thermodynamics: $dS \geq 0$, and are generated by integrating the inequality under different constraint conditions.) We'll get the corresponding virtual work term for $(NT\tau)$ ensemble.

Imagine a path l in deformation space which starts from X and ends at Z. We want to know the net work done by outside stress τ when we reach Z if we deform the object along this path. To calculate this, let Y to be any point on the path: $Y = JX$, and make a small deformation: $J \to J + \delta J$. This would cause displacements on the surface area of this material by δu_i, and the work done by τ is then given by surface integral

$$\begin{aligned}\delta W &= \oint_S \tau_{ij} n_j \cdot \delta u_i dS \\ &= \int_Y \nabla \cdot (\tau \delta u) dV \\ &= \Omega(Y) \tau_{ij} \frac{\partial \delta u_i}{\partial Y_j} \\ &= \Omega(Y) \frac{\tau_{ij}}{2} \left(\frac{\partial \delta u_i}{\partial Y_j} + \frac{\partial \delta u_j}{\partial Y_i}\right) \end{aligned} \tag{3.4}$$

Here δu is the virtual displacement on the surface. Making use the fact that $\delta u = (\delta J)X = \delta J \cdot J^{-1} Y$, which leads to

$$\delta W = \Omega(Y) \frac{\tau_{ij}}{2} (\delta J \cdot J^{-1} + J^{-T} \cdot \delta J^T)_{ij} \tag{3.5}$$

and the fact that the differential of (1.1) is

$$\delta \eta_X = \frac{1}{2} [J^T \delta J + (\delta J^T) J] \tag{3.6}$$

or

$$J^{-T} \delta \eta_X J^{-1} = \frac{1}{2} [\delta J \cdot J^{-1} + J^{-T} \cdot \delta J^T]$$

we obtain for the incremental (differential) work,

$$\delta W = \Omega(Y) \mathrm{Tr}(J^{-1} \tau J^{-T} \delta \eta_X) \tag{3.7}$$

The work done over the deformation path l is therefore

$$\Delta W(l) = \int_l \Omega(Y) \mathrm{Tr}(J^{-1} \tau J^{-T} d\eta_X) \tag{3.8}$$

To examine system stability at configuration X we consider the difference between the increase in Helmholtz free energy and the work done by outside stress,

$$\begin{aligned}\Delta G(Y, l) &= \Delta F(X, \eta_X) - \Delta W(l) \\ &= \int_l \mathrm{Tr}\Big(g(Y) d\eta_X\Big) \\ &= \int_l \vec{g}(Y) \cdot d\vec{\eta}_X \end{aligned} \tag{3.9}$$

with

$$g(Y) = \frac{\partial F}{\partial \eta_X} - \Omega(Y) J^{-1} \tau J^{-T} \tag{3.10}$$

We define ΔG to be the *Gibbs integral* in analogy with the Gibbs free energy, and identify $-\vec{g}(Y)$ as the Gibbs driving force, a *vector* field spanning deformation space whose path integral has the meaning of work. However, we have to show that this "work" is path independent to establish it as a potential. If it is, then everything is fine. If it's not, and yet we want to do something about the problem, we can go to the lower level and study the properties of $-\vec{g}(Y)$ as a force field around equilibrium position, to formulate an *ad hoc* theory. In both cases the Gibbs driving force and its derivatives will play a central role.

Virtual work expression (3.8) is correct for general deformation spaces. However, when J isn't a function of η_X it is not always convienient to use the form. Sometimes we use another quantity

$$U = J - 1 \tag{3.11}$$

which fully describe the configuration and has 9 degrees of freedom, thus

$$\eta_X = \frac{1}{2}\{(1 + U^T)(1 + U) - 1\} \tag{3.12}$$

Differentiate (3.12) and take back into (3.9). Make use of the fact that g_{ij} is a symmetric matrix, we get the integral expression for general deformation space in U representation:

$$\begin{aligned}
\Delta G(Y, l) &= \Delta F(X, \eta_X) - \Delta W(l) \\
&= \int_l \mathrm{Tr}\Big(g^*(Y) dU\Big) \\
&= \int_l \vec{g}^*(Y) \cdot d\vec{U}
\end{aligned} \tag{3.13}$$

with

$$\begin{aligned}
g^*(Y) &= g(1 + U^T) \\
&= \{\frac{\partial F}{\partial \eta_X} - \Omega(Y) J^{-1} \tau J^{-T}\}(1 + U^T)
\end{aligned}$$

IV. STABILITY ANALYSIS IN SYMMETRIC DEFORMATION SPACE

In this section and next we'll study stability behaviours in symmetric deformation space, which's often used in computer simulation. Since there is a one to one correspondence between η_X and J, the space is 6 dimensional and all related second-rank tensors(strain,stress) can be treated as *vectors* in space.

$-\vec{g}(Y)$ is defined as the Gibbs driving force in view of (3.9). Under the metrics of the space in which the forces are defined, $-\vec{g}(Y)$ points to the direction of *steepest descent* of the Gibbs integral, i.e, if a virtual move is made in ths same direction as $-\vec{g}(Y)$, the system will have the most significant net loss combining the effect of decreasing its Helmholtz free energy and letting work done by the outside world. So in a quasi-static process, the direction $-\vec{g}(Y)$ is pointing at should the be the most likely direction of action for system at Y, and its trajectory would be the flow line of this vector field. As an example, suppose we put a point charge into an electric field and make such that it moves quasi-staticly, the trajectory will follow the flow line of the electric field, although in order to do this, the electric field doesn't need to have a potential: $\nabla \times \vec{E} = 0$.

The condition for equilibrium at X is simply the requirement of vanishing driving force:

$$\begin{aligned} g_{ij}(X) &= [\frac{\partial F}{\partial \eta_{ij}} - \Omega(Y)(J^{-1}\tau J^{-T})_{ij}]_{J=1} \\ &= \Omega(X)[t_{ij}(X) - \tau_{ij}] \\ &= 0 \end{aligned} \tag{4.1}$$

or

$$t_{ij}(X) = \tau_{ij} \tag{4.2}$$

which states the equality between thermodynamic stress and outside stress means equilibrium.

Suppose the system, initially at equilibrium: $\vec{g}(X) = 0$, is perturbed to configuration Y with corresponding strain η_X. In view of (3.10) the first-order expansion for $\vec{g}(Y)$ becomes

$$
\begin{aligned}
g_{ij}(Y) &= g_{ij}(\eta_X^Y, X) \\
&= \Omega(X) B_{ijkl}\eta_{kl} + ...
\end{aligned} \tag{4.3}
$$

where

$$
B_{ijkl} = C_{ijkl} - \frac{\partial(\det|J| J_{im}^{-1}\tau_{mn}J_{nj}^{-1})}{\partial\eta_{kl}}\Big|_{\eta_X=0,J=1} \tag{4.4}
$$

Since

$$
J^{-1} = \frac{1}{\sqrt{1+2\eta_X}} = 1 - \eta_X + ... \tag{4.5}
$$

$$
\det|J| = 1 + \mathrm{Tr}(\eta_X) + ... \tag{4.6}
$$

(4.4) can be evaluated to give

$$
B_{ijkl} = C_{ijkl} - \delta_{kl}\tau_{ij} + \delta_{ik}\tau_{jl} + \delta_{jl}\tau_{ik} \tag{4.7}
$$

As η_{ij} and η_{ji} (η_{kl} and η_{lk}) are not separate variables, we need to symmetrize (4.7) with respect to the interchange of indices $(i \leftrightarrow j)$ and $(k \leftrightarrow l)$. Thus,

$$
\begin{aligned}
&B_{ijkl} \\
&= C_{ijkl} + \frac{1}{2}(\delta_{ik}\tau_{jl} + \delta_{jk}\tau_{il} + \delta_{il}\tau_{jk} + \delta_{jl}\tau_{ik} - 2\delta_{kl}\tau_{ij}).
\end{aligned} \tag{4.8}
$$

(4.8) is the expression defining the elastic stiffness coefficient[2] B. We can see that B does not possess $(ij) \leftrightarrow (kl)$ symmetry, so ΔG is path dependent in general, unless the applied load is hydrostatic, i.e., $\tau_{ij} \propto \delta_{ij}$.

The physical meaning of (4.3) is that in deformation space the shape of force field around the origin is described by the "second-rank tensor" B. Consider the following inner product between two vectors

$$
\lambda = \vec{\eta}_X \cdot B\vec{\eta}_X \tag{4.9}
$$

$\vec{\eta}_X$ is the displacement from the origin, $-B\vec{\eta}_X$ is the direction of driving force, thus the most likely direction for system evolution, at point Y. If we can show that $\lambda > 0$ for any $\vec{\eta}_X$, then in a quasi-static process the perturbed system will always be decreasing its distance with the origin. And thus the system is stable. On the other hand if there exists an $\vec{\eta}_X$ for which $\lambda < 0$, then a kinetic path could lead the system to instability.

Given that B is asymmetric in general, the stability of the system is governed by its symmetrized counterpart,

$$A = \frac{1}{2}(B^T + B) \tag{4.10}$$

because

$$\begin{aligned} \lambda &= \vec{\eta}_X \cdot B\vec{\eta}_X \\ &= \frac{1}{2}\vec{\eta}_X \cdot (B^T + B)\vec{\eta}_X \end{aligned} \tag{4.11}$$

for any vector $\vec{\eta}_X$. The stability criterion is then the requirement that all the eigenvalues of A be positive. Stated another way, the system becomes unstable when

$$\det |A| = 0 \tag{4.12}$$

for the first time. We can also think of it as mapping a dissipative system unto its equivalent conservative system with a symmetric effective A, after some coarse-graining.

V. IMPLEMENTATION IN SYMMETRIC DEFORMATION SPACE

In the actual implementation of the criterea, we use Voigt's notation:

Original ij (or kl):	11	22	33	23	13	12
Contracted notation:	1	2	3	4	5	6

As said before, symmetric deformation space has only 6 independent variables, but since it's easier to sum over Cartesian indices, we had always treated it as if we had 9. Time has come to change back to explicitly 6 variables, because η_{ij} and η_{ji} are bound together and an instability eigenmode which has $\eta_{ij} \neq \eta_{ji}$ is not possible. Please be reminded that when we use Voigt's notation the times of η_4 (or η_5, η_6) appearing should be doubled because it represent both η_{12} and η_{21}.

In general a 9×9 matrix (not necessarily $(ij)\leftrightarrow(kl)$ symmetric, but has $(i\leftrightarrow j)$ and $(k\leftrightarrow j)$ symmetry), with row and column index arraying as {11, 22, 33, 12, 13, 23, 21, 31, 32}, contracts into a 6×6 matrix in Voigt's notation in the following manner:

$$\begin{vmatrix} A & B & B \\ C & D & D \\ C & D & D \end{vmatrix} \Rightarrow \begin{vmatrix} A & 2B \\ 2C & 4D \end{vmatrix} \tag{5.1}$$

Following this contraction rule, we can write down:

$$B_{6\times 6} = C_{6\times 6} + W_{6\times 6} \tag{5.2}$$

In view of (4.8), we get the general form of W:

$$W_{6\times 6} = \begin{bmatrix} \tau_{11} & -\tau_{11} & -\tau_{11} & 2\tau_{12} & 2\tau_{13} & 0 \\ -\tau_{22} & \tau_{22} & -\tau_{22} & 2\tau_{12} & 0 & 2\tau_{23} \\ -\tau_{33} & -\tau_{33} & \tau_{33} & 0 & 2\tau_{13} & 2\tau_{23} \\ 0 & 0 & -2\tau_{12} & 2\tau_{11}+2\tau_{22} & 2\tau_{23} & 2\tau_{13} \\ 0 & -2\tau_{13} & 0 & 2\tau_{23} & 2\tau_{11}+2\tau_{33} & 2\tau_{12} \\ -2\tau_{23} & 0 & 0 & 2\tau_{13} & 2\tau_{12} & 2\tau_{22}+2\tau_{33} \end{bmatrix} \tag{5.3}$$

Because $W_{6\times 6}$ is asymmetric,

$$A = \frac{1}{2}(B+B^T) = C + \frac{1}{2}(W+W^T) \tag{5.4}$$

so

$$A_{6\times 6} = C_{6\times 6} + \begin{bmatrix} \tau_{11} & -\frac{1}{2}(\tau_{11}+\tau_{22}) & -\frac{1}{2}(\tau_{11}+\tau_{33}) & \tau_{12} & \tau_{13} & -\tau_{23} \\ -\frac{1}{2}(\tau_{11}+\tau_{22}) & \tau_{22} & -\frac{1}{2}(\tau_{22}+\tau_{33}) & \tau_{12} & -\tau_{13} & \tau_{23} \\ -\frac{1}{2}(\tau_{11}+\tau_{33}) & -\frac{1}{2}(\tau_{22}+\tau_{33}) & \tau_{33} & -\tau_{12} & \tau_{13} & \tau_{23} \\ \tau_{12} & \tau_{12} & -\tau_{12} & 2\tau_{11}+2\tau_{22} & 2\tau_{23} & 2\tau_{13} \\ \tau_{13} & -\tau_{13} & \tau_{13} & 2\tau_{23} & 2\tau_{11}+2\tau_{33} & 2\tau_{12} \\ -\tau_{23} & \tau_{23} & \tau_{23} & 2\tau_{13} & 2\tau_{12} & 2\tau_{22}+2\tau_{33} \end{bmatrix} \tag{5.5}$$

A. Example 1: Hydrostatic Tension

Hydrostatic tension[5,6] is the only case which retains the original symmetry of the crystal, and with true Gibbs free energy. For crystals with cubic symmetry:

$$C_{6\times 6} = \begin{bmatrix} C_{11} & C_{12} & C_{12} & & & \\ C_{12} & C_{11} & C_{12} & & & \\ C_{12} & C_{12} & C_{11} & & & \\ & & & 4C_{44} & & \\ & & & & 4C_{44} & \\ & & & & & 4C_{44} \end{bmatrix} \tag{5.6}$$

Let $\tau_{11} = \tau_{22} = \tau_{33} = T$ and refer to (5.3), we get

$$W_{6\times 6} = \begin{bmatrix} T & -T & -T & & & \\ -T & T & -T & & & \\ -T & -T & T & & & \\ & & & 4T & & \\ & & & & 4T & \\ & & & & & 4T \end{bmatrix} \tag{5.7}$$

so

$$B_{6\times 6} = \begin{bmatrix} C_{11}+T & C_{12}-T & C_{12}-T & & & \\ C_{12}-T & C_{11}+T & C_{12}-T & & & \\ C_{12}-T & C_{12}-T & C_{11}+T & & & \\ & & & 4(C_{44}+T) & & \\ & & & & 4(C_{44}+T) & \\ & & & & & 4(C_{44}+T) \end{bmatrix} \tag{5.8}$$

Just by inspection we can see that

$$C_{44} + T = 0 \tag{5.9}$$

$$C_{11} - C_{12} + 2T = 0 \tag{5.10}$$

$$C_{11} + 2C_{12} - T = 0 \tag{5.11}$$

are the three instability modes. The first one is 3-fold degenerate, and is called shear instability because the crystal tends to change shape without changing volume. The second one is 2-fold degenerate, and is defined as the Born instability: it shows that the material will automatically break the symmetry by elongating in one direction and shrinking in the other. The third one is defined as spinodal instability in the sense of weak bulk modulus, this is the case where the material is collapsing as a whole, which happens in solid state amorphization[4].

B. Example 2: Uniaxial Tension

Impose uniaxial tension $\tau_{11} = T$ on an originally cubic crystal. It will break the symmetry, with

$$C_{6\times 6} = \begin{bmatrix} C_{11} & C_{12} & C_{12} & & & \\ C_{12} & C_{22} & C_{23} & & & \\ C_{12} & C_{23} & C_{22} & & & \\ & & & 4C_{44} & & \\ & & & & 4C_{44} & \\ & & & & & 4C_{66} \end{bmatrix} \tag{5.12}$$

and

$$W_{6\times 6} = \begin{bmatrix} T & -T & -T & & & \\ 0 & 0 & 0 & & & \\ 0 & 0 & 0 & & & \\ & & & 2T & & \\ & & & & 2T & \\ & & & & & 0 \end{bmatrix} \tag{5.13}$$

so

$$A_{6\times 6} = \begin{bmatrix} C_{11}+T & C_{12}-\frac{T}{2} & C_{12}-\frac{T}{2} & & & \\ C_{12}-\frac{T}{2} & C_{22} & C_{23} & & & \\ C_{12}-\frac{T}{2} & C_{23} & C_{22} & & & \\ & & & 4C_{44}+2T & & \\ & & & & 4C_{44}+2T & \\ & & & & & 4C_{66} \end{bmatrix} \tag{5.14}$$

From lower half of matrix we get two modes,

$$C_{66} = 0 \tag{5.15}$$

$$C_{44} + \frac{1}{2}T = 0 \tag{5.16}$$

corresponding to the shear instability.

From the upper half we get one obvious mode

$$C_{22} - C_{23} = 0 \tag{5.17}$$

corresponding to the Born instability.

The last two modes are not obvious, but has to rely on this quadratic equation:

$$2(C_{12} - \frac{T}{2})^2 - (C_{22} + C_{23})(C_{11} + T) = 0 \tag{5.18}$$

VI. STABILITY ANALYSIS IN GENERAL DEFORMATION SPACE

All arguments used in constructing the "A criterea" for symmetric deformation space still hold for general deformation space, the only difference is that we have 9 degrees of freedom, so we should use the representation of (3.13),

$$\Delta G(Y, l) = \int_l \mathrm{Tr}\Big(g^*(Y)dU\Big)$$

with

$$
\begin{aligned}
g^*(Y) &= g(1+U^T) \\
&= \{\frac{\partial F}{\partial \eta_X} - \Omega(Y)J^{-1}\tau J^{-T}\}(1+U^T)
\end{aligned}
$$

It's easy to show that

$$J^{-1} = \frac{1}{1+U} = 1 - U + ... \tag{6.1}$$

$$J^{-T} = 1 - U^T + ... \tag{6.2}$$

$$\det|J| = 1 + \mathrm{Tr}(U) + ... \tag{6.3}$$

and

$$
\begin{aligned}
\eta_X &= \frac{1}{2}(J^TJ - 1) \\
&= \frac{1}{2}(U^T + U) + ...
\end{aligned} \tag{6.4}
$$

The condition for equilibrium at X remains to be:

$$
\begin{aligned}
g^*_{ij}(X) &= g(1+U^T)\Big|_{J=1,U=0} \\
&= \Omega(X)(t_{ij}(X) - \tau_{ij}) \\
&= 0
\end{aligned} \tag{6.5}
$$

Suppose $g^*(X) = 0$ and we want to do first order expansion for $g^*(Y)$ near X. Since g is first order itself, we can ignore the $(1+U^T)$ term behind it. Thus

$$g^* \simeq g \tag{6.6}$$

and

$$
\begin{aligned}
g_{ij} \ &= \partial F/\partial \eta_X - \Omega(Y)J^{-1}\tau J^{-T} \\
&\simeq \Omega(X)\{C_{ijkl}\eta_{kl} - U_{kk}\tau_{ij} + U_{ik}\tau_{kj} + \tau_{ik}U_{jk}\} \\
&\simeq \Omega(X)\{\frac{1}{2}C_{ijkl}(U_{kl} + U_{lk}) - U_{kk}\tau_{ij} + U_{ik}\tau_{kj} + \tau_{ik}U_{jk}\} \\
&= \Omega(X)\{C_{ijkl}U_{kl} - U_{kk}\tau_{ij} + U_{ik}\tau_{kj} + \tau_{ik}U_{jk}\}
\end{aligned} \tag{6.7}
$$

So

$$g_{ij}^* = \Omega(X) B_{ijkl}^* U_{kl} + ... \tag{6.8}$$

with

$$B_{ijkl}^* = C_{ijkl} - \tau_{ij}\delta_{kl} + \tau_{jl}\delta_{ik} + \tau_{il}\delta_{jk} \tag{6.9}$$

Similiar to the arguments in symmetric deformation space, stability behaviour in general deformation space is governed by

$$A^* = (B^* + (B^*)^T)/2 \tag{6.10}$$

When

$$\det |A^*| = 0 \tag{6.11}$$

for the first time, the system become unstable. Note that A^* is a 9×9 matrix.

As an observation, when a configuration is stable in general deformation space, i.e., none of the eigenvalues of A^* are negative, the configuration would be stable in all deformation spaces.

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APPENDIX: ZERO TEMPERATURE LIMIT OF THE CANONICAL FLUCTUATION FORMULA

We want to show that in the limit of $T \to 0$ the fluctuation formula (2.10) reduce to the same result as (2.26). This conclusion was first arrived at by Lutsko[11], here we put down more detailed derivation.

In the limit of $T \to 0$, the second term in (2.10) will vanish because $\langle (p_i^n)^2 \rangle$ scales as T. The third term just gives C_{ijkl}^B, the unrelaxed elastic constant. The limit of the first line, the fluctuation term, is not yet obvious: but if one inspects (2.7), it could be seen that the momentum part, $-p_i^n p_j^n / m_n$, gives zero contribution to the fluctuation limit because its magnitude scales as T, and it is also not correlated with the second term, $q_i^n \nabla_j^n V$, which is defined as $\mathbf{T}(q^N)$ in (2.22). So there must be

$$C_{ijkl}(X, T=0) = C_{ijkl}^F + C_{ijkl}^B, \tag{A1}$$

where

$$C_{ijkl}^F = \lim_{\beta \to +\infty} \beta \Big(\langle T_{ij} \rangle \langle T_{kl} \rangle - \langle T_{ij} T_{kl} \rangle \Big) / \Omega(X). \tag{A2}$$

When T is small, the atomic displacements

$$\Delta q_i^n = q_i^n - \bar{q}_i^n \tag{A3}$$

from equilibrium positions are also small, and so one is eligible to expand

$$\Delta T_{ij} = \sum_{m=1}^{N} \sum_{c=1}^{3} A_{ij,mc} \Delta q_c^m + \mathcal{O}(q^2), \tag{A4}$$

following A's definition in (2.25). Thus,

$$\begin{aligned} & \langle T_{ij} T_{kl} \rangle - \langle T_{ij} \rangle \langle T_{kl} \rangle \\ = & \langle \Delta T_{ij} \Delta T_{kl} \rangle \\ = & \sum_{m,n=1}^{N} \sum_{c,d=1}^{3} A_{ij,mc} A_{kl,nd} \langle \Delta q_c^m \Delta q_d^n \rangle + \mathcal{O}(\langle q^4 \rangle). \end{aligned} \tag{A5}$$

One can also expand the potential energy as (2.14) when Δq_i^n's are small. Except for atoms near the wall, the probability distribution of atomic displacements approaches that of Gaussian, with

$$dP = dq^N \exp(-\beta V(q^N))/Z \tag{A6}$$
$$= dq^N \exp(-\beta D_{mc,nd}\Delta q_c^m \Delta q_d^n/2 + \mathcal{O}(\Delta q^3))/Z.$$

What we have in mind, essentially, is a saddle point expansion of the partition function in order to get the leading order fluctuation amplitudes. The wall atoms, though having the same problem of $\nabla_j^n V(q^N) \neq 0$ as which leads to the stress localization procedure in section II, is not a big problem here because unlike q, $\langle \Delta q^2 \rangle$ is always finite. For the bulk atoms, one can show that

$$\langle \Delta q_c^m \Delta q_d^n \rangle = (\beta D)^{-1}_{mc,nd} + \mathcal{O}(\beta^{-2}), \tag{A7}$$

which follows from the well-known identities

$$\int_{-\infty}^{+\infty} \prod_i d\alpha_i \exp(-\frac{1}{2}\alpha^T K \alpha) = \sqrt{\frac{(2\pi)^N}{\det|K|}} \tag{A8}$$

and

$$\frac{\partial \ln(\det|K|)}{\partial K_{ij}} = \frac{K_{ij}^*}{\det|K|} = (K^{-1})_{ij}, \tag{A9}$$

where α is a vector and K is a Hermitian matrix.

So following (A2), (A5) and (A7), there is

$$C_{ijkl}^F = -\sum_{m,n=1}^{N}\sum_{c,d=1}^{3} A_{ij,mc} D^{-1}_{mc,nd} A_{kl,nd}/\Omega(X), \tag{A10}$$

same as what we derived in (2.26).

APPENDIX: FLUCTUATION FORMULAS IN MICRO-CANONICAL ENSEMBLE

Let us consider systems of N identical particles with mass m, contained in a volume described by geometrical configuration variable Y. Each system evolves according to the Hamiltonian

$$\mathcal{H}(\tilde{q}^N, p^N) = \sum_{n=1}^{N} \sum_{i=1}^{3} \frac{(p_n^i)^2}{2m} + V(\tilde{q}^N). \tag{B1}$$

If we consider all such systems with total energy E, we have a micro-canonical ensemble. From now on let us regard N as fixed. The appropriate thermodynamical potential for micro-canonical ensemble is system entropy[14]

$$S(E, Y) = k_{\rm B} \ln \int_Y d\tilde{q}^N dp^N \delta(E - \mathcal{H}(\tilde{q}^N, p^N)), \tag{B2}$$

with fundamental relations

$$\frac{1}{T} = \frac{\partial S}{\partial E}\Big|_Y, \tag{B3}$$

and

$$F(T, Y) = E - TS(E, Y). \tag{B4}$$

One can integrate out the momentum degrees of freedom from (B2) as follows: consider $\{p_n^i\}, n = 1..N, i = 1..3$ as a large vector $\mathbf{p}$ with $3N$ components, then the total kinetic energy K is simply $p^2/2m$ with $p = |\mathbf{p}|$. Also, for a $3N$-dimensional $\mathbf{p}$ hypersphere,

$$dp^N = \prod_{n=1}^{N} \prod_{i=1}^{3} dp_n^i = S_{3N} p^{3N-1} dp \tag{B5}$$

if all angles are integrated over, with S_{3N} being a constant. Then,

$$\begin{aligned} &\int_Y d\tilde{q}^N dp^N \delta(E - \mathcal{H}(\tilde{q}^N, p^N)) \\ &= \int_Y d\tilde{q}^N S_{3N} p^{3N-1} dp \delta(E - p^2/2m - V(\tilde{q}^N)) \\ &= \int_Y d\tilde{q}^N m p^{3N-2} d(p^2/2m) \delta(E - p^2/2m - V(\tilde{q}^N)) \\ &= \text{const} \times \int_Y d\tilde{q}^N K^{3N/2-1}, \end{aligned} \tag{B6}$$

where

$$K = E - V(\tilde{q}^N), \tag{B7}$$

and it is implicitly understood that the $\int_Y d\tilde{q}^N$ integration is carried out in $\{K(\tilde{q}^N) > 0, \tilde{\mathbf{q}}_n \in Y\}$ regions.

Thus, it follows that for any symmetric homogeneous deformation $Y = MX$ (see (1.1) to (1.9)) from a certain reference configuration X,

$$\begin{aligned} & S(E, Y = MX) \\ & = \text{const} + Nk_{\text{B}} \ln \det |M| + k_{\text{B}} \ln \Pi, \end{aligned} \tag{B8}$$

where

$$\Pi = \int dq^N (E - V(Mq^N))^{3N/2-1}, \tag{B9}$$

and q^N are particle coordinates in "undeformed frame" whose bounds are independent of M.

To get some flavor, let us derive the heat capacity at constant volume, C_V (really should be C_Y), using microcanonical ensemble samples. If we vary E (and T) in (B3),

$$-\frac{\delta T}{T^2} = \left.\frac{\partial^2 S}{\partial E^2}\right|_Y \delta E \tag{B10}$$

and so

$$\begin{aligned} C_V &= \delta E / \delta T \\ &= -T^{-2} / \left(\left.\frac{\partial^2 S}{\partial E^2}\right|_Y \right) \\ &= -k_{\text{B}} \left(\left.\frac{\partial \ln \Pi}{\partial E}\right|_Y \right)^2 / \left(\left.\frac{\partial^2 \ln \Pi}{\partial E^2}\right|_Y \right). \end{aligned} \tag{B11}$$

In order to get microscopic expressions, let us vary E in (B9),

$$\begin{aligned} & \left.\frac{\partial \Pi}{\partial E}\right|_Y \\ & = (3N/2 - 1) \int dq^N (E - V(Mq^N))^{3N/2-2} \end{aligned} \tag{B12}$$

for $3N/2 - 1 > 0$, because modifications of $\int dq^N$ integration bounds with E does not give contributions as long as the integrand vanishes there. Since N is usually much larger than unity, we will not mention this boundary term from now on. Then,

$$\frac{1}{k_{\text{B}} T} = \left.\frac{\partial \ln \Pi}{\partial E}\right|_Y = (3N/2 - 1)\langle K^{-1} \rangle, \tag{B13}$$

where the $\langle\rangle$ average is taken over microcanonical ensemble samples (or a single evolution trajectory if the ergotic hypothesis holds). One can further differentiate (B13), and it is straightforward to show that

$$\left.\frac{\partial^2 \ln \Pi}{\partial E^2}\right|_Y = (3N/2-1)(3N/2-2)\langle K^{-2}\rangle \\ -(3N/2-1)^2\langle K^{-1}\rangle^2. \tag{B14}$$

And so combining (B13), (B14) and (B11), we arrive at a fluctuation formula for C_V that can be directly evaluated in a MD or MC simulation[15].

Now let me derive fluctuation formulas for the thermodynamic stress tensor $t_{ij}(X)$ and the *isothermal* elastic constants $C_{ijkl}(X)$, defined in (1.15), using micro-canonical ensemble samples. The reason is because $t_{ij}(X)$ and $C_{ijkl}(X)$ are the more useful quantities in various applications, although micro-canonical ensembles are easier to realize in MD. Except for the $S(E,Y) \to F(T,Y)$ translation, the procedure is similar to what we did in section II using canonical ensemble samples.

Imagine a homogeneous and symmetric deformation of the system $Y = MX$, which is also uniquely determined by the small Lagrangian strain $\eta = \eta_X^Y = (M^2-1)/2$. We are thus eligible to write $S(E,Y)$ as $S(E,\eta,X)$ and $F(T,Y)$ as $F(T,\eta,X)$, and the dependence on X is usually not explicitly stated. For finite η, there is a correspondent change of energy ΔE if the temperature is to stay constant, as in (1.15). To get ΔE, we can expand (B3) around X,

$$0 = \left.\frac{\partial^2 S}{\partial E^2}\right|_X \Delta E + \frac{\partial^2 S}{\partial E \partial \eta_{ij}}\eta_{ij} + \mathcal{O}(E^2, \eta^2, E\eta), \tag{B15}$$

and thus

$$\Delta E = -\left(\frac{\partial^2 S}{\partial E \partial \eta_{ij}}\right) \Big/ \left(\left.\frac{\partial^2 S}{\partial E^2}\right|_X\right)\eta_{ij} + \mathcal{O}(\eta^2), \tag{B16}$$

where we keep track of orders because we have to do a second order expansion later. And so, if we expand (B4), holding T fixed,

$$\Delta F = \Delta E - T\frac{\partial S}{\partial E}\Big|_X \Delta E - T\frac{\partial S}{\partial \eta_{ij}}\Big|_E \eta_{ij} - \frac{T}{2}\left[\frac{\partial^2 S}{\partial \eta_{ij}\partial \eta_{kl}}\Big|_E \eta_{ij}\eta_{kl} + 2\frac{\partial^2 S}{\partial E \partial \eta_{ij}}(\Delta E)\eta_{ij} + \frac{\partial^2 S}{\partial E^2}\Big|_X (\Delta E)^2\right] + \mathcal{O}\left((\Delta E)^3, \eta^3, \text{etc.}\right)$$
$$= -T\frac{\partial S}{\partial \eta_{ij}}\Big|_E \eta_{ij} - \frac{T}{2}\left[\frac{\partial^2 S}{\partial \eta_{ij}\partial \eta_{kl}}\Big|_E \eta_{ij}\eta_{kl} + 2\frac{\partial^2 S}{\partial E \partial \eta_{ij}}(\Delta E)\eta_{ij} + \frac{\partial^2 S}{\partial E^2}\Big|_X (\Delta E)^2\right] + \mathcal{O}\left((\Delta E)^3, \eta^3, \text{etc.}\right), \quad \text{(B17)}$$

and plugging in (B16), we obtain

$$\Delta F = -T\frac{\partial S}{\partial \eta_{ij}}\Big|_E \eta_{ij} - \frac{T}{2}\left[\frac{\partial^2 S}{\partial \eta_{ij}\partial \eta_{kl}}\Big|_E - \left(\frac{\partial^2 S}{\partial E\partial \eta_{ij}} \cdot \frac{\partial^2 S}{\partial E\partial \eta_{kl}}\right) / \left(\frac{\partial^2 S}{\partial E^2}\Big|_X\right)\right] \eta_{ij}\eta_{kl} + \mathcal{O}\left(\eta^3\right). \quad \text{(B18)}$$

which, when compared with (1.15), suggests that

$$t_{ij}(X) = -\frac{T}{\Omega(X)}\hat{S}_2\left(\frac{\partial S}{\partial \eta_{ij}}\Big|_E\right), \quad \text{(B19)}$$

and

$$C_{ijkl}(X) = \frac{T}{\Omega(X)}\hat{S}_4\Big[-\frac{\partial^2 S}{\partial \eta_{ij}\partial \eta_{kl}}\Big|_E + \left(\frac{\partial^2 S}{\partial E\partial \eta_{ij}} \cdot \frac{\partial^2 S}{\partial E\partial \eta_{kl}}\right) / \left(\frac{\partial^2 S}{\partial E^2}\Big|_X\right)\Big]. \quad \text{(B20)}$$

In order to get microscopic expressions, we need to work with (B8) and (B9). First, because

$$\ln\det|M| = \mathrm{Tr}\ln M = \mathrm{Tr}\ln\sqrt{1+2\eta}$$
$$= \mathrm{Tr}\eta - \mathrm{Tr}\eta^2 + \mathcal{O}(\eta^3), \quad \text{(B21)}$$

it is easy to show that

$$\hat{S}_2\left(\frac{\partial \ln\det|M|}{\partial \eta_{ij}}\Big|_{\eta=0}\right) = \delta_{ij}, \quad \text{(B22)}$$

and

$$\hat{S}_4\left(\frac{\partial^2 \ln\det|M|}{\partial \eta_{ij}\partial \eta_{kl}}\Big|_{\eta=0}\right) = -\delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}. \quad \text{(B23)}$$

Secondly, because

$$K = E - V(\tilde{q}^N) = E - V(Mq^N)$$

in (B9), where q^N are particle coordinates "before deformation", and referring to (1.4), we have

$$\tilde{q}_i^n = q_i^n + \eta_{ij} q_j^n - \eta_{ij}\eta_{jk} q_k^n/2 + \mathcal{O}\left(\eta^3\right). \tag{B24}$$

It follows that

$$\frac{\partial K}{\partial \eta_{ij}} = -\frac{\partial V}{\partial \tilde{q}_i^n} q_j^n + \frac{\partial V}{\partial \tilde{q}_i^n} \eta_{jk} q_k^n + \mathcal{O}\left(\eta^2\right), \tag{B25}$$

and so

$$\left.\frac{\partial K}{\partial \eta_{ij}}\right|_{\eta=0} = -\left.\frac{\partial V}{\partial q_i^n}\right|_X q_j^n \tag{B26}$$

and

$$\left.\frac{\partial^2 K}{\partial \eta_{ij}\partial \eta_{kl}}\right|_{\eta=0} = -\left.\frac{\partial^2 V}{\partial q_i^n \partial q_k^m}\right|_X q_j^n q_l^m + \left.\frac{\partial V}{\partial q_i^n}\right|_X \delta_{jl} q_k^n, \tag{B27}$$

where $|_X$ means taking derivatives in undeformed state X, and as before I treated η *as if* it has 9 independent components but will symmetrize the expressions in the end. Thus, following (B8), (B9) and (B26),

$$\begin{aligned} \left.\frac{\partial S}{\partial \eta_{ij}}\right|_E &= N k_{\mathrm{B}} \delta_{ij} + \\ &\quad (3N/2-1) k_{\mathrm{B}} \langle \left(-\left.\frac{\partial V}{\partial q_i^n}\right|_X q_j^n \right) /K \rangle, \end{aligned} \tag{B28}$$

and so

$$\begin{aligned} & t_{ij}(X) \\ = & -\frac{k_{\mathrm{B}} T}{\Omega(X)} \hat{S}_2 \left(N\delta_{ij} + (3N/2-1)\langle \sum_{n=1}^{N} F_i^n q_j^n / K \rangle \right), \end{aligned} \tag{B29}$$

where the first term is clearly the "ideal gas" contribution and second term the Virial contribution. (B29) is not very different from (2.7) formula for the canonical ensemble samples, beside that the Virial contribution is scaled by the total kinetic energy K, which is a persistent feature in micro-canonical ensemble expressions, reflecting the effect of constant total energy constraint on fluctuations. Because in the limit of large N the relative fluctuation of K is $\mathcal{O}(N^{-1/2})$, one only makes vanishingly small error in $t_{ij}(X)$ calculation even if (2.7) expression is used for microcanonical ensemble samples. However, as we will show next, it is not so for $C_{ijkl}(X)$ calculation, because (2.10) is a fluctuation formula, and the constant total energy constraint severely distort fluctuations.

Following (B28), it is straightforward to show that

$$\begin{aligned}
&\frac{\partial^2 S}{\partial E \partial \eta_{ij}}\Big|_{\eta=0} \\
&= (3N/2-1)(3N/2-2)k_{\mathrm{B}}\langle\left(-\frac{\partial V}{\partial q_i^n}\Big|_X q_j^n\right)/K^2\rangle \\
&\quad -(3N/2-1)^2 k_{\mathrm{B}}\langle\left(-\frac{\partial V}{\partial q_i^n}\Big|_X q_j^n\right)/K\rangle\langle K^{-1}\rangle \\
&= (3N/2-1)k_{\mathrm{B}}\hat{S}_2\Big[(3N/2-2)\langle\sum_{n=1}^{N} F_i^n q_j^n/K^2\rangle - \\
&\qquad (3N/2-1)\langle\sum_{n=1}^{N} F_i^n q_j^n/K\rangle\langle K^{-1}\rangle\Big].
\end{aligned} \tag{B30}$$

Lastly, combining (B9), (B26) and (B27), it is not difficult to show that

$$\begin{aligned}
&\frac{\partial^2 \ln \Pi}{\partial \eta_{ij}\partial \eta_{kl}}\Big|_{\eta=0} \\
&= (3N/2-1)\Big[(3N/2-2)\langle F_i^n q_j^n F_k^m q_l^m/K^2\rangle \\
&\quad -(3N/2-1)\langle F_i^n q_j^n/K\rangle\langle F_k^m q_l^m/K\rangle \\
&\quad -\langle\left(\frac{\partial^2 V}{\partial q_i^n \partial q_k^m}\Big|_X q_j^n q_l^m + F_i^n q_k^n \delta_{jl}\right)/K\rangle\Big],
\end{aligned} \tag{B31}$$

and so, with (B8), (B13) and (B20), we arrive at

$$\begin{aligned}
C_{ijkl}(X) &= \frac{N\langle K^{-1}\rangle^{-1}}{(3N/2-1)\Omega}(\delta_{ik}\delta_{jl}+\delta_{il}\delta_{jk}) + \langle K^{-1}\rangle^{-1}\cdot\hat{S}_4 \\
&\Big[\langle\Big(\sum_{n,m=1}^{N}\frac{\partial^2 V}{\partial q_i^n \partial q_k^m}\Big|_X q_j^n q_l^m + \sum_{n=1}^{N} F_i^n q_k^n \delta_{jl}\Big)/K\Omega\rangle \\
&+(3N/2-1)\langle\sum_{n=1}^{N} F_i^n q_j^n/K\sqrt{\Omega}\rangle\langle\sum_{m=1}^{N} F_k^m q_l^m/K\sqrt{\Omega}\rangle \\
&-(3N/2-2)\langle\sum_{n,m=1}^{N} F_i^n q_j^n F_k^m q_l^m/K^2\Omega\rangle\Big] + \\
&\frac{\langle K^{-1}\rangle^{-1}\left(\frac{\partial^2 S}{\partial E\partial\eta_{ij}}\big|_{\eta=0}/k_{\mathrm{B}}\sqrt{\Omega}\right)\left(\frac{\partial^2 S}{\partial E\partial\eta_{kl}}\big|_{\eta=0}/k_{\mathrm{B}}\sqrt{\Omega}\right)}{(3N/2-1)^2[(3N/2-2)\langle K^{-2}\rangle-(3N/2-1)\langle K^{-1}\rangle^2]}.
\end{aligned} \tag{B32}$$

1. Application to Hydrostatic Response

Consider mainly a liquid or gaseous system which cannot sustain static shear loading,

$$t_{ij}(X) = -P\delta_{ij}, \tag{B33}$$

and the pressure P is only a function of system volume

$$P = P(T, \Omega). \tag{B34}$$

The discussions will also apply to any solid system that has cubic symmetry and is under hydrostatic loading. With that, one can define the isothermal bulk modulus

$$B_T = -\frac{\partial P}{\partial \ln \Omega}\bigg|_T, \tag{B35}$$

and the volumetric thermal expansion coefficient

$$\alpha = \frac{\partial \ln \Omega}{\partial T}\bigg|_P. \tag{B36}$$

We want to seek relations between B_T and $C_{ijkl}(X)$, such that we could use our fluctuation formulas (B20) or (2.10). But before that, let us consider a seemingly irrelevant question: does ideal gas has finite C_{44}?

The intuitive answer is no, because ideal gas cannot provide shear stress no matter how it is deformed. However, if one refers to (B32),

$$C_{44} = C_{2323} = \frac{N\langle K^{-1}\rangle^{-1}}{(3N/2-1)\Omega} = \frac{Nk_{\mathrm{B}}T}{\Omega}, \tag{B37}$$

or work out the (2.10) expression for canonical ensembles using Gaussian variable contraction rules:

$$\langle p_i^n p_j^m / m\rangle = k_{\mathrm{B}}T\delta_{nm}\delta_{ij}, \tag{B38}$$

and thus

$$
\begin{aligned}
&\langle t_{ij}t_{kl}\rangle - \langle t_{ij}\rangle\langle t_{kl}\rangle \\
&= \frac{1}{\Omega^2}\sum_{n,m=1}^{N}\langle (p_i^n p_j^n/m)(p_k^m p_l^m/m)\rangle - \langle p_i^n p_j^n/m\rangle\langle p_k^m p_l^m/m\rangle \\
&= \frac{1}{\Omega^2}\sum_{n,m=1}^{N}\langle p_i^n p_j^n p_k^m p_l^m/m^2\rangle_{\text{linked}} \\
&= \frac{1}{\Omega^2}\sum_{n,m=1}^{N} k_{\mathrm{B}}^2 T^2(\delta_{nm}\delta_{ik}\cdot\delta_{nm}\delta_{jl} + \delta_{nm}\delta_{il}\cdot\delta_{nm}\delta_{jk}) \\
&= \frac{Nk_{\mathrm{B}}^2T^2}{\Omega^2}(\delta_{ik}\delta_{jl}+\delta_{il}\delta_{jk}), \qquad \text{(B39)}
\end{aligned}
$$

and

$$
\hat{S}_4\left(\langle\sum_{n=1}^{N}\frac{4p_i^n p_k^n}{m_n}\delta_{jl}\rangle\right) = 2Nk_{\mathrm{B}}T(\delta_{ik}\delta_{jl}+\delta_{il}\delta_{jk}), \qquad \text{(B40)}
$$

so (2.10) turns out to be

$$
C_{ijkl} = \frac{Nk_{\mathrm{B}}T}{\Omega}(\delta_{ik}\delta_{jl}+\delta_{il}\delta_{jk}) \qquad \text{(B41)}
$$

for ideal gas, which can also be derived if one simply expands

$$
F_{\text{i.g.}}(T,\Omega) = -k_{\mathrm{B}}T\ln\left(\frac{\Omega}{(h/\sqrt{2\pi m k_{\mathrm{B}}T})^3}\right)^N. \qquad \text{(B42)}
$$

So, all analytical evidence indicate that ideal gas has non-zero C_{44}, in fact on the same order of magnitude as B_T and P. How can one compromise this with the intuition that ideal gas can never have shear stress? The answer lies in the fact that C_{ijkl} is not the "derivative" of t_{ij} with strain, so $t_{23}\equiv 0$ is *not* contradictory to $C_{44}\neq 0$. One should use the elastic stiffness coefficients, $B_{ijkl}(X)$, to relate stress with strain (see (1.20)).

Referring to (4.8), (B33), (B41) and ideal gas law

$$
P(T,\Omega) = \frac{Nk_{\mathrm{B}}T}{\Omega}, \qquad \text{(B43)}
$$

one has

$$
\begin{aligned}
&B_{ijkl}(X) \\
&= C_{ijkl} + \frac{1}{2}(\delta_{ik}t_{jl}+\delta_{jk}t_{il}+\delta_{il}t_{jk}+\delta_{jl}t_{ik}-2\delta_{kl}t_{ij})
\end{aligned}
$$

$$
\begin{aligned}
&= \frac{Nk_{\mathrm{B}}T}{\Omega}[\delta_{ik}\delta_{jl} + \delta_{il}\delta_{jk} + \delta_{kl}\delta_{ij} - \\
&\qquad (\delta_{ik}\delta_{jl} + \delta_{jk}\delta_{il} + \delta_{il}\delta_{jk} + \delta_{jl}\delta_{ik})/2] \\
&= \frac{Nk_{\mathrm{B}}T}{\Omega}\delta_{ij}\delta_{kl},
\end{aligned}
\tag{B44}
$$

in perfect agreement with our intuition and what would happen if one just plugs (B43) into (B33) and differentiate with respect to η_{ij}.

Since it is well established now that B_{ijkl} is the connection between stress and strain, let us study the pressure response of the system to volumetric expansion when (B33) always holds. Then

$$
t_{11} = -P = t_{22} = t_{33} \tag{B45}
$$

and

$$
\eta_{11} = \eta_{22} = \eta_{33} \approx \frac{1}{3}\Delta \ln \Omega, \tag{B46}
$$

so

$$
\begin{aligned}
B_T &= -\left.\frac{\partial P}{\partial \ln \Omega}\right|_T = \left.\frac{\partial t_{11}}{\partial \ln \Omega}\right|_T \\
&= (B_{1111} + B_{1122} + B_{1133})/3,
\end{aligned}
\tag{B47}
$$

and since

$$
B_{ijkl} = C_{ijkl} + P(\delta_{ij}\delta_{kl} - \delta_{ik}\delta_{jl} - \delta_{il}\delta_{jk}), \tag{B48}
$$

there is

$$
B_T = (C_{11} + 2C_{12} + P)/3, \tag{B49}
$$

which can be directly evaluated using fluctuations formulas (B32) or (2.10).

Let us study the thermal behavior of such systems. The geometrical condition is now only specified by one variable, Ω,

$$
S(E, Y) = S(E, \Omega), \quad F(T, Y) = F(T, \Omega), \tag{B50}
$$

whether it is genuinely so as in liquids, or only appears to be for a solid with high symmetry under hydrostatic loading. In this case, one can recover from (B19) the fundamental thermodynamical relation[14]

$$P = T\frac{\partial S}{\partial \Omega}\Big|_E, \tag{B51}$$

and so

$$\begin{aligned} &\frac{\partial P}{\partial T}\Big|_\Omega \\ &= \frac{\partial S}{\partial \Omega}\Big|_E + T\frac{\partial\left(\frac{\partial S}{\partial \Omega}\big|_E\right)}{\partial T}\Big|_\Omega \\ &= \frac{P}{T} + T\frac{\partial^2 S}{\partial\Omega\partial E}\cdot\frac{\partial E}{\partial T}\Big|_\Omega \\ &= \frac{P}{T} + C_V T\frac{\partial^2 S}{\partial E\partial\Omega}. \end{aligned} \tag{B52}$$

Following (B30), there is

$$\frac{\partial^2 S}{\partial E\partial\Omega} = \frac{(3N/2-1)k_\mathrm{B}}{3\Omega}\cdot\hat{S}_2\Big[(3N/2-2)\langle\sum_{n=1}^{N}\mathbf{F}_n\cdot\mathbf{q}_n/K^2\rangle - (3N/2-1)\langle\sum_{n=1}^{N}\mathbf{F}_n\cdot\mathbf{q}_n/K\rangle\langle K^{-1}\rangle\Big]. \tag{B53}$$

and the fluctuation formula for C_V is already given in (B11).

Because of the functional identity

$$\frac{\partial\Omega}{\partial T}\Big|_P\cdot\frac{\partial T}{\partial P}\Big|_\Omega\cdot\frac{\partial P}{\partial\Omega}\Big|_T = -1, \tag{B54}$$

the volumetric thermal expansion coefficient is simply

$$\begin{aligned} \alpha &= \frac{1}{\Omega}\frac{\partial\Omega}{\partial T}\Big|_P \\ &= -\frac{1}{\Omega}\frac{\partial P}{\partial T}\Big|_\Omega\frac{\partial\Omega}{\partial P}\Big|_T \\ &= \frac{\partial P}{\partial T}\Big|_\Omega/B_T, \end{aligned} \tag{B55}$$

and so α can be calculated by (B35) and (B52).

Lastly, let us find the representation for C_P, the constant pressure heat capacity, defined by

$$C_P = T\frac{\partial S}{\partial T}\Big|_P, \tag{B56}$$

and so

$$\begin{aligned} C_P &= T\frac{\partial S}{\partial T}\Big|_\Omega + T\frac{\partial S}{\partial \Omega}\Big|_T\frac{\partial \Omega}{\partial T}\Big|_P \\ &= C_V + \Omega T\frac{\partial P}{\partial T}\Big|_\Omega \alpha \\ &= C_V + \Omega T\alpha^2 B_T, \end{aligned} \tag{B57}$$

where we used the Maxwell's identity

$$\frac{\partial S}{\partial \Omega}\Big|_T = \frac{\partial P}{\partial T}\Big|_\Omega, \tag{B58}$$

and (B55). At this point we see that all thermodynamical derivatives are expressible in terms of microscopic fluctuation formulas that can be directly evaluated in a single MD simulation run.

APPENDIX: LOCALIZATION AND APPLICATION TO PAIR POTENTIAL

Expressions such as

$$\begin{aligned} \lambda_{ijkl} &= \Gamma_{ijkl} - \Pi_{ijkl} \\ &= \sum_{m,n=1}^{N} q_k^m q_i^n \nabla_l^m \nabla_j^n V(q^N) - \sum_{n=1}^{N} q_k^n \nabla_j^n V(q^N)\delta_{il} \end{aligned} \tag{C1}$$

appearing in (2.10) and (B32) can be localized (see discussion in section II) through the following procedure: we first note that λ_{ijkl} is linear in V. That is, if $V = V_1 + V_2$, then λ_{ijkl} is the sum of contribution only due to V_1 and contribution only due to V_2. So we only need to calculate each pair or triplet or n-let interaction, and in the end simply add their contributions together.

Secondly, we need to show that the quantity to evaluate is in fact translationally invariant, which means that if we make a rigid translation:

$$\hat{\mathbf{q}}_n = \mathbf{q}_n + \mathbf{a}, \tag{C2}$$

where **a** is the same for all particles, there is

$$
\begin{aligned}
&\hat{\Pi}_{ijkl} \\
&= \sum_{n=1}^{N} \hat{q}_k^n \hat{\nabla}_j^n V_1(\hat{q}^N)\delta_{il} \\
&= \sum_{n=1}^{N} (q_k^n + a_k) \nabla_j^n V_1(q^N)\delta_{il} \\
&= \sum_{n=1}^{N} q_k^n \nabla_j^n V_1(q^N)\delta_{il} + a_k \sum_{n=1}^{N} \nabla_j^n V_1(q^N) \\
&= \sum_{n=1}^{N} q_k^n \nabla_j^n V_1(q^N)\delta_{il} \\
&= \Pi_{ijkl},
\end{aligned} \tag{C3}
$$

since

$$\sum_{n=1}^{N} \nabla_j^n V_1(q^N) \equiv 0 \tag{C4}$$

for any translationally invariant potential $V_1(q^N)$. We can prove the same thing for

$$\Gamma_{ijkl} = \sum_{m,n=1}^{N} q_k^m q_i^n \nabla_l^m \nabla_j^n V_1(q^N)$$

by plugging in (C2) and grouping free indices. And so, it does not matter in which coordinate frame λ_{ijkl} is evaluated, and we can choose any frame that makes the evaluation simple, such as by letting the origin sit on one particle.

For instance, if the particles interact via pair potential

$$V(q^N) = \sum_{\alpha<\beta} W(\mathbf{q}_\alpha, \mathbf{q}_\beta) = \sum_{\alpha<\beta} W(|\mathbf{q}_\alpha - \mathbf{q}_\beta|), \tag{C5}$$

then we can single out any interacting pair $W(|\mathbf{q}_\alpha - \mathbf{q}_\beta|)$, and choose our frame such that $\mathbf{q}_\beta = 0$. Then, all terms in

$$\Delta\lambda_{ijkl} = \sum_{m,n=\alpha,\beta} q_k^m q_i^n \nabla_l^m \nabla_j^n W - \sum_{n=\alpha,\beta} q_k^n \nabla_j^n W \delta_{il}$$

cease to contribute except for $m = n = \alpha$, and it is simply

$$\Delta\lambda_{ijkl} = q_k q_i \nabla_l \nabla_j W(q) - q_k \nabla_j W(q)\delta_{il} \tag{C6}$$

where $q = |\mathbf{q}_\alpha|$, and we have simplified the two-body expression to a one-body expression. Since

$$\nabla_j W(q) = W' \frac{q_j}{q}, \tag{C7}$$

and

$$\nabla_l \nabla_j W = W'' \frac{q_j q_l}{q^2} - W' \frac{q_j q_l}{q^3} + W' \frac{\delta_{jl}}{q}, \tag{C8}$$

there is

$$\begin{aligned} &\Delta\lambda_{ijkl} \\ &= q_k q_i \left(W'' \frac{q_j q_l}{q^2} - W' \frac{q_j q_l}{q^3} + W' \frac{\delta_{jl}}{q} \right) - q_k W' \frac{q_j}{q} \delta_{il}, \end{aligned} \tag{C9}$$

and so

$$\hat{S}_4(\Delta\lambda_{ijkl}) = q_i q_j q_k q_l \left(\frac{W''}{q^2} - \frac{W'}{q^3} \right), \tag{C10}$$

which is just the contribution to Born elastic constant (see (2.10) from this single pair of interaction. One should remember that in this special coordinate frame $\mathbf{q}^\beta = 0$, so $\mathbf{q}$ should be replaced by $\mathbf{q}_\alpha - \mathbf{q}_\beta$ in a general frame.

For instance, in the Lennard Jones pair potential[15] for rare gas solids,

$$W(q) = 4\epsilon \left[\left(\frac{\sigma}{q} \right)^{12} - \left(\frac{\sigma}{q} \right)^{6} \right], \tag{C11}$$

one can show from (C10) that

$$\begin{aligned} &\hat{S}_4(\Delta\lambda_{ijkl}) \\ &= \epsilon \cdot \frac{q_i q_j q_k q_l}{\sigma^4} \left[672 \left(\frac{\sigma}{q} \right)^{16} - 192 \left(\frac{\sigma}{q} \right)^{10} \right]. \end{aligned} \tag{C12}$$

In general, one can always simplify a n body expression into a $n-1$ body expression using the above coordinate frame invariant observation.