Revisiting Quantum Notions of Stress

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Abstract: An important aspect of multiscale modeling of materials is to link continuum concepts such as fields to the underlying discrete microscopic behavior in a seamless manner. With the growing importance of atomistic calculations to understand material behavior, reconciling continuum and discrete concepts is necessary to interpret molecular and quantum mechanical simulations. In this work, we provide a quantum mechanical framework to a distinctly continuum quantity: mechanical stress. While the concept of the *global* macroscopic stress tensor in quantum mechanics has been well established, there still exist open issues when it comes to a spatially varying local quantum stress tensor. We attempt to shed some light on this topic by establishing a general quantum mechanical operator based approach to continuity equations and from those, introduce a local quantum mechanical stress tensor. Further, we elucidate the analogies that exist between (classical) molecular dynamics based stress definition and the quantum stress. Our derivations seem to suggest that the local quantum mechanical stress may not be an observable in quantum mechanics and therefore traces the non-uniqueness of the atomistic stress tensor to the gauge arbitrariness of the quantum mechanical state-function. Lastly, the virial stress theorem (of empirical molecular dynamics) is re-derived in a transparent manner that elucidates the analogy between quantum mechanical global stress.

1. Introduction and Background

Several processes occur in nature wherein physical phenomena occur across multiple length and temporal scales. An oft-used example is that of protein folding: the time scale for the vibration of the covalent bonds is of the order a few femto-seconds (10^{-15}s) while the folding of the proteins takes place on the order of a few seconds. The electromechanical behavior of solids is another typical example that exhibits such a multiscale characteristic. At the fundamental level, the properties of the solid can be attributed to the electronic structure while atomic interactions and crystal structures can be described at the atomistic scale by using an atomic/molecular picture. Electrical and deformation behaviors in macroscopic samples, on the other hand, are routinely described using continuum theories wherein the notion of the underlying discrete atomic structure of matter is discounted in favor of the idea of a smeared out continuum. Continuum theories introduce kinematic measures like displacement fields and electrical measures like polarization fields as opposed to discrete atomistic quantities like atomic coordinates and induced dipole moments. This process of zooming out from an electronic to atomistic to a continuum picture is accompanied by an enormous decrease in the degrees of freedom which serves to considerably simplify analysis. For several applications of practical interest in structural and electrical engineering, the accuracy and predictive power of continuum theories is known to be more than sufficient. Any minute improvement in the accuracy gained by applying atomistic methods in such situations is rendered superfluous due to the enormous increase in the computational expenses that atomistic methods require.

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The tremendous decrease in the degrees of freedom that continuum theories offer is often a result of certain simplifying assumptions based on which such continuum theories are constructed. When the discrete nature of matter becomes apparent, say in nanoscale phenomena, there is an expectation that classical continuum theories may fail to apply in some contexts and may need to be "informed" of the insights obtained through atomistic considerations. Indeed, in recent years, novel size effects are being routinely observed in a variety of contexts like plasticity, electromechanical response of nanosized dielectric thin films, quantum dots and composites amongst others.

Certain scenarios may present themselves wherein a substantial part of the system essentially behaves like a continuum with the remaining part of the system exhibiting full-fledged atomistic behavior which cannot be captured by a fully continuum theory. Multiscale modeling techniques aim to identify the multiple natural length and time scales in a phenomenon and transfer information across them in a seamless fashion (e.g. see the following representative articles and references therein: Miller and Tadmor 2002; Curtin and Miller 2003; Park and Liu 2004; Liu et al. 2006; Gavini et al. 2007; Miller and Tadmor 2007; Kulkarni et al. 2008). This often requires reconciling the atomistic notions which represent the true mechanistic underpinnings behind a process with coarse-grained (including continuum) ideas which serve to capture the essential physics in a phenomenological manner. Even with the sustained interest in multiscale modeling techniques over the past many years, a 'seamless' integration has proven to be challenging especially when it comes to bridging temporal scales (e.g. see the following review article and references therein: Jun et al. 2009).

In this paper our focus is the concept of "mechanical stress". Numerous works have appeared that have attempted reconciliation of classical molecular dynamics stress and continuum definition of stress. The reader is referred to the following representative (non-exhaustive) list of papers and the references therein: Cormier et al. 2001; Murdoch (1994; 2003a,b; 2007), Zhou 2003; Zimmerman et al. 2004; Chen 2006; Silling and Lehoucq 2007; Webb III et al. 2008 among others. In particular, we highlight here the now-classic paper by Noll 2009 originally published in 1955 in German which was recently updated (and translated by Lehoucq and Lilienfeld-Toal). The paper provides interesting methodologies that were later used by Murdoch (2007) to perform coarse-graining of discrete quantities and derive a rigorous expression for atomistic stress. In this paper, we go a step further and attempt to establish the definition of *quantum* stress and elucidate its relation to both the classical molecular dynamics based stress and its continuum counterpart.

Investigations into the quantum mechanical definition of stress were well preceded by early fundamental work on the concept of quantum mechanical force (Ehrenfest 1927; Pauli 1933; Hellmann 1937; Feynman 1939; Feynman 1939) and pressure (Born et al. 1926; Finkelstein 1928; Hylleraas 1929; Fock 1930; Slater 1933; Slater 1963; Slater 1967). The Ehrenfest's theorem (Ehrenfest 1927), which states that the net force on a particle is given by the expectation value of the negative of the gradient of the potential, is such an example. We will discuss the Ehrenfest's theorem in more detail shortly. Pauli, Hellmann and Feynman (Pauli 1933; Hellmann 1937; Feynman 1939; Feynman

1939) modified the Ehrenfest's theorem to a form appropriate for application to forces between molecules. The consequences of the so-called Hellmann-Feynman theorem are significant. Previously, forces within molecules and associated problems involving the estimation of lattice constants, calculations of phase transitions, elastic properties, phonon dispersion, stiffness of valence bonds and others were addressed invoking the energy formalism in an indirect manner. These usually involve calculations of energy for several neighboring configurations of the molecule; the force is then obtained by determining the slope of the plot of energy vs. position. The Hellmann-Feynman theorem offers a direct way to estimate the force for a given configuration, given that only the particular configuration of interest is known. The quantum mechanical virial theorem, which states that the total pressure in a many-body quantum mechanical system is defined by the kinetic energy and the virial of the potential (much like its classical counterpart) also attracted attention from authors including Born, Heisenberg, and Jordan, Fock and several others (Born et al. 1926; Finkelstein 1928; Hylleraas 1929; Fock 1930; Slater 1933; Slater 1963; Slater 1967; Ross 1969). Though several early works of varying levels of sophistication have considered the quantum mechanical stress tensor (Schrödinger 1927; Pauli 1933; Feynman 1939; Feynman 1939; Martin and Schwinger 1959; Kugler 1967; McLellan 1974; McLellan 1984; Folland 1986), we mainly use the seminal work by Nielsen and Martin's (Nielsen and Martin 1983; Nielsen and Martin 1985) as a starting point.

The outline of our paper is as follows. In Section 2, we introduce the concept of a global macroscopic stress in three different settings: continuum mechanics, classical (empirical) molecular dynamics and finally quantum mechanics. An attempt will be made to relate the well-known kinetic and potential contributions to the stress in continuum mechanics to analogous quantities in discrete settings such as molecular dynamics and quantum mechanics. In Section 3, we delve into the idea of stress as a locally varying field theoretic quantity. While this idea is quite intuitive in continuum mechanics, there is still a lack of consensus about how best to represent a locally varying stress in a discrete setting. In this respect, we introduce Murdoch's (Murdoch 2007) formulation for a locally varying stress field from discrete atomistic quantities using the approach of weighting functions. In the same spirit, we also introduce a novel approach to a local spatially varying stress field in quantum mechanics by deriving the continuity equations for an arbitrary Hermitian operator. The concept of the virial pressure is closely tied with the ideas of stress which are introduced in Sections 2 and 3. In Section 4, we outline an alternate derivation of the well-known Clausius' virial theorem which brings out some interesting physical insights and makes the comparison with quantum global stress quite transparent. We conclude in Section 5 with a summary of the physical insights gained out of the previous sections along with a brief discussion of our perspective on some open issues that remain in the area of quantum mechanical description of stress.

2. The Macroscopic Stress

Macroscopic Stress in Continuum Mechanics: We first review the expression for the macroscopic stress in continuum mechanics. Consider a continuum body occupying region Ω, the equation of motion can be written as

$$\text{div } \boldsymbol{\sigma} + \rho\mathbf{b} = \rho\ddot{\mathbf{r}} \tag{1}$$

Here $\boldsymbol{\sigma}$ is the Cauchy stress, ρ is the mass density, $\mathbf{b}$ is the body force density. Here, $\mathbf{r}$ is taken to be the displacement with respect to a fixed point (assumed to be at the origin). The mean Cauchy stress, $\bar{\boldsymbol{\sigma}}$ is given by

$$V_\Omega \bar{\boldsymbol{\sigma}} = \int_\Omega \boldsymbol{\sigma} dV = \int_\Omega \boldsymbol{\sigma} \text{ grad } \mathbf{r} \, dV \tag{2}$$

By employing the divergence theorem and defining, $\mathbf{t} = \boldsymbol{\sigma}.\mathbf{n}$, it can be proved that

$$V_\Omega \bar{\boldsymbol{\sigma}} = \int_\Omega \rho\dot{\mathbf{r}} \otimes \dot{\mathbf{r}} dV - \frac{d}{dt}\int_\Omega \rho(\dot{\mathbf{r}} \otimes \dot{\mathbf{r}})dV + \int_\Omega \rho\mathbf{b} \otimes \mathbf{r} dV + \int_{\partial\Omega} \mathbf{t} \otimes \mathbf{r} dA \tag{3}$$

The trace of the first term on the RHS can be seen to be twice the kinetic energy K_Ω for the body.

Taking an average over "a very long time"[†], and assuming that the quantity $\int_\Omega \rho(\dot{\mathbf{r}} \otimes \mathbf{r})dV$ remains bounded in time, one can conclude that the space and time averaged macroscopic stress becomes

$$V_\Omega \langle\bar{\boldsymbol{\sigma}}\rangle = \left\langle \int_\Omega \rho\dot{\mathbf{r}} \otimes \dot{\mathbf{r}} dV + \int_\Omega \rho\mathbf{b} \otimes \mathbf{r} dV + \int_{\partial\Omega} \mathbf{t} \otimes \mathbf{r} dA \right\rangle \tag{4}$$

where the symbol $\langle \, \rangle$ denotes the temporal average.

We note that the above derivation holds when the object is not in equilibrium. For the latter case, we have:

$$V_\Omega \langle\bar{\boldsymbol{\sigma}}\rangle = \left\langle \int_\Omega \rho\mathbf{b} \otimes \mathbf{r} dV + \int_{\partial\Omega} \mathbf{t} \otimes \mathbf{r} dA \right\rangle \tag{5}$$

Macroscopic Stress in Molecular Dynamics: This section is partly based on Zimmerman et. al. (2004) and Murdoch (2007). The aim here is to establish a link between the continuum global virial stress of a macroscopic body (discussed previously in this section) and its molecular content. Accordingly, let us consider a set of interacting point masses P_i (i = 1, 2, 3, …N). The motion of P_i in an inertial frame is governed by

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† Here we avoid the rigor needed to justify this statement.

$$\dot{\mathbf{p}}_i = \frac{d}{dt}(m_i \mathbf{v}_i) = \mathbf{f}_i \qquad (6)$$

f_i are the forces on the particles while m_i and v_i signify masses and velocities respectively. Now let us define a quantity **G** such that

$$\mathbf{G} := \sum_i \mathbf{p}_i \otimes \mathbf{r}_i \qquad (7)$$

r_i denotes the displacement‡ of the point particles from a fixed point. Taking the time derivative of **G**

$$\frac{d\mathbf{G}}{dt} = \sum_i m_i \mathbf{v}_i \otimes \mathbf{v}_i + \sum_i \mathbf{f}_i \otimes \mathbf{r_i} \qquad (8)$$

Taking a sufficiently long time average and assuming that the quantity **G** remains bounded in time, we have

$$\left\langle \sum_i m_i \mathbf{v}_i \otimes \mathbf{v}_i \right\rangle + \left\langle \sum_i \mathbf{f}_i \otimes \mathbf{r_i} \right\rangle = 0 \qquad (9)$$

Now, the force f_i on a particle can be written as a summation of an inter-particular force $f_{i,int}$ (which the particle experiences due to interaction with other particles in the system), a body force $f_{i,body}$, and a confinement force $f_{i,confine}$ which serves to confine a particle say enclosed within a vessel.
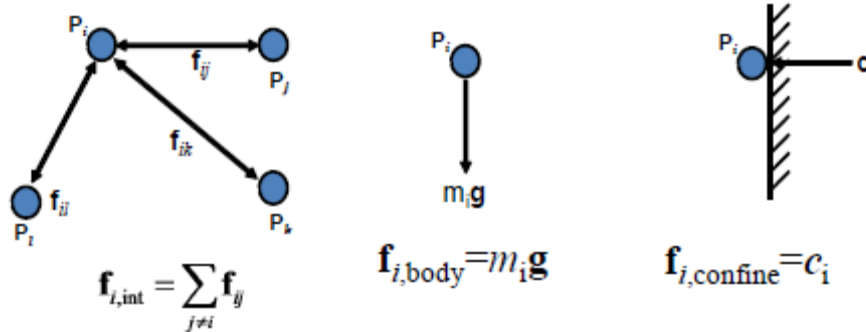

Figure 1: The different types of forces acting on a particle

Pictorially the above situation has been depicted in Figure 1.

Further, identification can be made between the effect of discrete confinement forces c_i with that of an applied traction field $\mathbf{t(r)}$ and between the discrete body forces on a

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‡ We use different symbols in the discrete context; compare with Equation (3)

particle $\mathbf{b}_i$ on particles with that of a continuum body force density $\mathbf{b}(\mathbf{r})$ as shown in Figure 2.
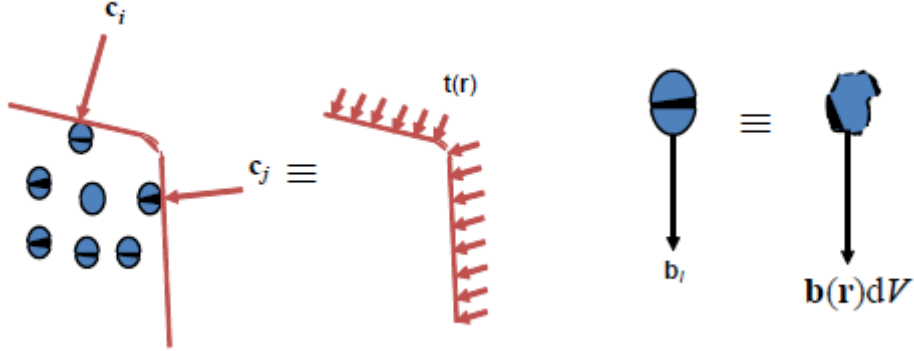

Figure 2: Identifying the discrete confinement forces with the continuum traction field and discrete body forces with continuum body force density

Therefore we can write

$$\sum_i \mathbf{c}_i \otimes \mathbf{r}_i \equiv \int_{\partial R} \mathbf{t} \otimes \mathbf{r} ds \qquad (10)$$

$$\sum_i \mathbf{b}_i \otimes \mathbf{r}_i \equiv \int_R \rho \mathbf{b} \otimes \mathbf{r} dV \qquad (11)$$

So from Equations (10-11) and (8),

$$\frac{d\mathbf{G}}{dt} + \frac{1}{2} \sum_i \mathbf{f}_{ij} \otimes (\mathbf{r}_j - \mathbf{r}_i) - \sum_i m_i \mathbf{v}_i \otimes \mathbf{v}_i = \int_R \left((\mathrm{div}\mathbf{T} + \rho\mathbf{b}) \otimes \mathbf{r} + \mathbf{T} \right) dV \qquad (12)$$

For suggestions of macroscopic equilibrium in which $\mathbf{G}$ remains bounded in time, an average over sufficiently long times yields the following expression for the macroscopic stress (Murdoch, 2007):

$$\langle \overline{\mathbf{T}} \rangle = \frac{1}{\Omega} \left(\left\langle \frac{1}{2} \sum_i \mathbf{f}_{ij} \otimes (\mathbf{r}_j - \mathbf{r}_i) \right\rangle - \left\langle \sum_i m_i \mathbf{v}_i \otimes \mathbf{v}_i \right\rangle \right) \qquad (13)$$

Macroscopic Stress in Quantum Mechanics: The total stress of a stationary system can be obtained by applying a variational principle together with a scaling of the wavefunction. The derivation follows the same methodology as that given for the virial theorem by Fock. See also (Nielsen and Martin 1985) and our review article (Maranganti et al. 2007). Firstly, we consider a many-body Hamiltonian of the form

$$H = \sum_i \frac{\mathbf{p}_i^2}{2m_i} + V_{\mathrm{int}} + V_{\mathrm{ext}} \qquad (14)$$

where V:= V_{int} + V_{ext} denotes the potential energy of the whole system: it is a function of the positions of all the particles. Note that both nuclei and electrons are regarded as particles. V_{int} is the intrinsic contribution consisting of inter-atomic potentials, while V_{ext} incorporates the potentials associated with external influences such as body forces. We will only consider potentials which are not velocity dependent (i.e. potentials are only dependent upon coordinates of the particles). One can solve the Schrodinger equation, Equation (15), to obtain the many body eigenstates ψ.

$$H\psi = E\psi \tag{15}$$

The quantum mechanical variational principle requires that the ground state is the minimum of the energy E with respect to the allowed variations in ψ

$$E = \langle \psi | H | \psi \rangle \tag{16}$$

It should be noted that in the context of quantum mechanics, the symbol $\langle \ \rangle$ denotes expectation value. To derive the stress, a homogeneous scaling is applied to the ground state $\psi(\mathbf{r})$, where $\mathbf{r}$ denotes a list of all particle coordinates. Consider a transformation on this coordinates of the form:

$$r_{i\alpha} \rightarrow r_{i\alpha} + \sum_{\beta} \varepsilon_{\alpha\beta} r_{i\beta} \tag{17}$$

Here, $\varepsilon_{\alpha\beta}$ is a symmetric strain tensor. The change in the wave function is given by:

$$\psi_\varepsilon(\mathbf{r}) \rightarrow \det(1+\varepsilon)^{-1/2} \psi\left((1+\varepsilon)^{-1} \mathbf{r}\right) \tag{18}$$

The above scaling of the wave function can be explained diagrammatically as shown in Figure 3.

Figure 3: Rescaling of the wavefunction under a homogeneous "stretch"

The additional factor of $\det(1+\varepsilon)^{-1/2}$ is included so that the normalization of the wave function is preserved. The expectation value of H with respect to ψ involves an integral over all the coordinates, $\mathbf{r}$.

$$\langle\psi_\varepsilon|H|\psi_\varepsilon\rangle = \int \psi_\varepsilon^*(\mathbf{r})\left[\sum_i \frac{\mathbf{p}_i^2}{2m_i} + V_{int} + V_{ext}\right]\psi_\varepsilon(\mathbf{r})d\mathbf{r} \tag{19}$$

By substituting $\mathbf{r}\rightarrow(1+\varepsilon)\mathbf{r}$, we can re-write the integral in Equation (19) to be

$$\langle\psi_\varepsilon|H|\psi_\varepsilon\rangle = \int \psi^*(\mathbf{r})\left[\begin{array}{c}\sum_i \dfrac{-1}{2m_i}\dfrac{d^2}{d\left((1+\varepsilon)\mathbf{r}_i\right)^2} + V_{int}\left((1+\varepsilon)\mathbf{r}\right)\\ + V_{ext}\left((1+\varepsilon)\mathbf{r}\right)\end{array}\right]\psi(\mathbf{r})d\mathbf{r} \tag{20}$$

On further simplification, the above integral can be re-written as

$$\langle\psi_\varepsilon|H|\psi_\varepsilon\rangle = \int \psi^*(\mathbf{r})\left[\begin{array}{c}\sum_i\left(\dfrac{\mathbf{p}_i^2 - 2\varepsilon_{\alpha\beta}p_{i\alpha}p_{i\beta} + 3\varepsilon_{\alpha\beta}\varepsilon_{\alpha\gamma}p_{i\beta}p_{i\gamma} + ...}{2m_i}\right)\\ + V_{int}\left((1+\varepsilon)\mathbf{r}\right) + V_{ext}\left((1+\varepsilon)\mathbf{r}\right)\end{array}\right]\psi(\mathbf{r})d\mathbf{r} \tag{21}$$

The variational principle requires that $\langle\psi_\varepsilon|H|\psi_\varepsilon\rangle$ vary from $\langle\psi|H|\psi\rangle$ only to second order in the strain, therefore

$$\frac{\partial\langle\psi_\varepsilon|H|\psi_\varepsilon\rangle}{\partial\varepsilon_{\alpha\beta}} = 0 = \int \psi^*(\mathbf{r})\left[\sum_i\left(\frac{p_{i\alpha}p_{i\beta}}{m_i} - r_{i\beta}\nabla_{i\alpha}\left(V_{int} + V_{ext}\right)\right)\right]\psi(\mathbf{r})d\mathbf{r} \tag{22}$$

The term involving V_{ext} in Equation (22) represents the stress exerted by the external environment upon the solid. This stress is symmetric for a system in equilibrium in the absence of external torques.

$$T_{\alpha\beta} = -\left\langle\psi\left|\sum_i r_{i\beta}\nabla_{i\alpha}V_{ext}\right|\psi\right\rangle \tag{23}$$

The net torque due to external forces is given by

$$\tau_\alpha = \in_{\alpha\beta\gamma}\left\langle\psi\left|\sum_i r_{i\beta}f_{i\gamma}\right|\psi\right\rangle = -\in_{\alpha\beta\gamma}\left\langle\psi\left|\sum_i r_{i\gamma}f_{i\beta}\right|\psi\right\rangle \tag{24}$$

Here, $\in_{\alpha\beta\gamma}$ is the Levi-Cevita symbol defined by

$$\in_{ijk} = \begin{cases}+1, \text{if (i,j,k) is an even permutation of (1,2,3)}\\ -1, \text{if (i,j,k) is an odd permutation of (1,2,3)}\\ 0, \text{ if any index is repeated}\end{cases} \tag{25}$$

However, if the stress is symmetric, then

$$\left\langle\psi\left|\sum_i r_{i\gamma}f_{i\beta}\right|\psi\right\rangle = \left\langle\psi\left|\sum_i r_{i\beta}f_{i\gamma}\right|\psi\right\rangle \tag{26}$$

Now from the properties of the Levi Cevita operator, we arrive at the following

$$\tau_\alpha = -\tau_\alpha \qquad (27)$$

Thus, from Equation (27), we can infer that the net external torque vanishes if the stress is symmetric. The stress intrinsic to the system is then given by

$$T_{\alpha\beta} = -\left\langle \psi \left| \sum_i \left(\frac{p_{i\alpha}p_{i\beta}}{m_i} - r_{i\beta}\nabla_{i\alpha}\left(V_{\mathrm{int}}\right) \right) \right| \psi \right\rangle \qquad (28)$$

Equation (28) is one form of the stress theorem which expresses the total macroscopic stress in terms of the expectation values of internal operators intrinsic to the system. It can be seen that the expression for the macroscopic stress in molecular dynamics (Equation 13) and the expression for the global virial stress in quantum mechanics, Equation (28), closely parallel each other.

We note that Equation (28) provides the macroscopic stress even for systems subjected to *inhomogeneous external stresses*. Is this statement justified? The answer is in the affirmative since the macroscopic stress is arrived at by applying a uniform strain to the ground state of the system and extracting its response. There is no restriction on the strain state of the ground state of the system. It may be, for example, subject to inhomogeneous residual stresses.

The stress theorem is applicable to general quantum mechanical systems with interactions which are differentiable functions of the particle coordinates. The potentials can be nonlocal in nature, i.e., functions of the coordinate of a given particle at more than one point in space. The nonlocal nature of potentials is especially relevant for the case of pseudopotentials which are extensively used in numerical quantum mechanical based computational schemes. In order to define the stress of Equation (28) in an unambiguous manner; we have to express the stress in terms of relative coordinates of the interacting particles. In case of particles acting through two-body potentials

$$V_{\mathrm{int}} = \frac{1}{2}\sum_{\substack{i,j \\ (j\neq i)}} V_{ij}\left(\left|\mathbf{r}_i - \mathbf{r}_j\right|\right) \qquad (29)$$

Then the stress theorem of Equation (28) becomes

$$T_{\alpha\beta} = -\sum_i \left\langle \frac{p_{i\alpha}p_{i\beta}}{m_i} \right\rangle - \frac{1}{2}\sum_{\substack{i,j \\ (j\neq i)}} \left\langle \frac{\left(\mathbf{r}_i - \mathbf{r}_j\right)_\alpha \left(\mathbf{r}_i - \mathbf{r}_j\right)_\beta}{\left|\mathbf{r}_i - \mathbf{r}_j\right|} V_{ij}'\left(\left|\mathbf{r}_i - \mathbf{r}_j\right|\right) \right\rangle \qquad (30)$$

This form of the stress is symmetric (torque-free) and dependent only upon the relative distances between the particles. In macroscopic systems where the volume is well defined, the average stress density can be defined as

$$\sigma_{\alpha\beta} = T_{\alpha\beta} / \Omega \qquad (31)$$

For a periodic structure, the volume can be chosen to be a unit cell and a stress density per unit cell volume may be defined. The quantum mechanical form of the virial theorem can be obtained by taking the negative of the trace of in Equation (30)

$$3P\Omega = 2\sum_i \left\langle \frac{\mathbf{p}_i^2}{2m_i} \right\rangle - \frac{1}{2}\sum_{\substack{i,j \\ (j \neq i)}} \left\langle \left| \mathbf{r}_i - \mathbf{r}_j \right| V_{ij}'\left(\left| \mathbf{r}_i - \mathbf{r}_j \right| \right) \right\rangle \tag{32}$$

Here, P denotes the pressure. Further, if the interactions are of the form $V(r) = 1/r^n$, the virial theorem can be written in terms of the potential and kinetic energy. For the case of the Coulomb potential, the virial theorem takes the form

$$3P\Omega = 2E_{kin} + E_{pot} \tag{33}$$

In most cases, it is advantageous to carry out calculations without introducing an explicit V_{ext}. Instead, often calculations are done using, $H = T_{kin} + V_{int}$ with the system being subject to constraints corresponding to V_{ext}. In this case, the wave function satisfies a restricted variational principle.

3. Stress as a microscopic field

Thus far we have considered the average macroscopic or the *global* virial stress of a system of particles both in the molecular dynamical as well as in the quantum mechanical context. However, these treatments do not bring about the field nature of stress and force. In other words, the point - to- point spatial variation of the stress and force fields is (obviously) lost in the process of averaging over a macroscopic volume. If one however knows the spatially varying stress field, the ramifications can be important. Spatial variations in the planar stress can provide an insight into the forces operating in systems which are not in equilibrium (Nielsen and Martin 1985). Filippetti and Fiorentini (Filippetti and Fiorentini 1999; Filippetti and Fiorentini 2000) envision using the microscopic stress as what they refer to as a stress microscope to examine the microscopic stress's role in explaining the physics of certain surface and interface phenomena. Ramer et al. 1998 applied the microscopic stress .field to study piezoelectric effects in perovskites. While the local force field is uniquely specified in terms of kinetic and potential operators (Pauli 1933), the stress field, on the other hand, can only be specified to an arbitrary gauge term (explained shortly) (Feynman 1939; Feynman 1939). Traditionally, the stress field is defined as any 2-tensor field whose divergence yields the force field of the system.

$$\mathbf{f}(\mathbf{r}) = div\boldsymbol{\sigma}(\mathbf{r}) \tag{34}$$

To this stress field one can add a term of the form

$$\frac{\partial A_{ijk}(\mathbf{r})}{\partial r_k} \tag{35}$$

where A_{ijk} (**r**) is an arbitrary tensor field antisymmetric in j and k and recover the same force field of Equation (34). Thus, the stress field is undetermined to an arbitrary gauge term if one chooses to define it via Equation (34). This is the gauge-arbitrariness associated with the microscopic stress field. We now examine a route to arrive at a microscopic stress field in discrete molecular dynamics by local spatial averaging.

Stress as a local spatial average: How to link continuum field values with microscopic behavior at any length scale?
In an empirical molecular dynamics setting, Murdoch 2007 has outlined the following approach to arrive at a spatially varying stress field by means of local spatial averaging. Once again, consider a set of interacting point masses P_i (i = 1, 2, 3, ..., N). The mass and momentum density fields are defined as

$$\rho_w(\mathbf{r},t) := \sum_i m_i w(\mathbf{r}_i(t) - \mathbf{r})$$

$$\mathbf{p}_w(\mathbf{r},t) := \sum_i m_i \mathbf{v}_i(t) w(\mathbf{r}_i(t) - \mathbf{r})$$

(36)

Here the sums are taken over all particles and $\mathbf{r}_i$ (t)-**r** denotes the displacement of P_i from geometrical point **r** at time t. In accordance with the continuum notion of mass density, the weighting function w should be chose such as to assign greater contributions to point masses near to r than far there from, have physical dimension L^3, and be continuously differentiable on the space of displacements in Euclidean space. To ensure that the integral of ρ_w over all space yield the total mass of the body it is necessary and sufficient that

$$\int_V w(\mathbf{u}) d\mathbf{u} = 1$$

(37)

Now holding **r** fixed

$$\partial \rho_w / \partial t = \sum_i m_i \nabla w . \mathbf{v}_i = -\sum_i m_i \nabla_{\mathbf{r}} w . \mathbf{v}_i$$

$$= -\sum_i m_i div(\mathbf{v}_i w) = -div \mathbf{p}_w$$

(38)

Whenever and wherever $\rho_w \neq 0$; the corresponding velocity field can be written as

$$\mathbf{v}_w = \mathbf{p}_w / \rho_w$$

(39)

From Expression (39), the mass balance equation can be written as
$$\partial \rho_w / \partial t + div \mathbf{p}_w = 0$$

(40)

Similarly a momentum balance equation can be arrived at as
$$div \mathbf{T}_w + \mathbf{b}_w = \rho_w \mathbf{a}_w$$

(41)

Here the following definitions hold (--the reader is referred to Murdoch's work for details, 2007):

$$\mathbf{T}_w = \mathbf{T}^-_w - \mathbf{D}_w \tag{42}$$

$$\mathbf{b}_w(\mathbf{r},t) := \sum_i b_i(t) w(\mathbf{r}_i(t) - \mathbf{r}) \tag{43}$$

$$\mathbf{a}_w := \partial \mathbf{v}_w / \partial t + (\nabla \mathbf{v}_w) \mathbf{v}_w \tag{44}$$

$$div\mathbf{T}^-_w = \mathbf{f}_w \tag{45}$$

$$\mathbf{f}_w(\mathbf{r},t) := \sum_i \sum_{j \neq i} \mathbf{f}_{ij}(t) w(\mathbf{r}_i(t) - \mathbf{r}) \tag{46}$$

$$\mathbf{D}_w(\mathbf{r},t) := \sum_i m_i \mathbf{v}_i \otimes \mathbf{v}_i w(\mathbf{r}_i(t) - \mathbf{r}) \tag{47}$$

$\mathbf{D}_w$ represents the kinetic contribution to the stress while $\mathbf{T}^-_w$ represents the contribution due to inter-particular interaction and can be uniquely specified only up to a divergence free tensor. Therefore, this non-uniqueness can be exploited to arrive at many forms of the interaction stress tensor. Two forms, the Hardy's stress and the Noll's stress, are popular in the literature (Murdoch, 2007).

$$\mathbf{T}^-_w = \frac{1}{2} \sum_{i \neq j} \sum \mathbf{f}_{ij} \otimes \mathbf{b}_{ij} \tag{48}$$

Hardy's choice

$$\mathbf{b}_{ij} := \int_0^1 w\left(\lambda(\mathbf{r}_j - \mathbf{r}_i) + (\mathbf{r}_i - \mathbf{r})\right)(\mathbf{r}_j - \mathbf{r}_i) d\lambda \tag{49}$$

Noll's Choice

$$\mathbf{b}_{ij} := -\frac{1}{2} \int_V \int_0^1 \mathbf{u} w(\mathbf{r}_i - \mathbf{r} - \alpha \mathbf{u}) w(\mathbf{r}_j - \mathbf{r} + (1-\alpha)\mathbf{u}) d\alpha d\mathbf{u} \tag{50}$$

A Local Stress Field in Quantum Mechanics: General Formalism
In this section, we develop a general quantum mechanical operator based approach to continuity equations for densities of Hermitian operators. Consider a Hermitian operator B corresponding to some physical observable. Then, one can define a corresponding spatially varying Hermitian density operator A($\mathbf{r}$) as an anti-commutator of the form

$$A(\mathbf{r}) = \frac{1}{2}\left\{B, \delta(\hat{\mathbf{R}} - \mathbf{r})\right\} = \frac{B\delta(\hat{\mathbf{R}} - \mathbf{r}) + \delta(\hat{\mathbf{R}} - \mathbf{r})B}{2} \tag{51}$$

Note that $\hat{\mathbf{R}}$ is the position operator while $\mathbf{r}$ is the spatial location of interest. As an example the single particle mass density operator $\rho(\mathbf{r})$ is then:

$$\rho(\mathbf{r}) = \frac{1}{2}\left\{m_i, \delta(\hat{\mathbf{R}}_i - \mathbf{r})\right\} = m_i \delta(\hat{\mathbf{R}}_i - \mathbf{r}) \tag{52}$$

Consider a cluster of a finite number of nuclei and electrons. The nuclei being massive, we will consider them as classical particles. Thus, the mass density due to the nuclei becomes

$$\rho_n(\mathbf{r}) = \sum_i m_{n,i} \delta(\mathbf{R}_{n,i} - \mathbf{r}) \tag{53}$$

$m_{n,i}$ is the mass of the ith nucleus and $\mathbf{R}_{n,i}$ corresponds to its physical position. However, the mass density operator corresponding to the electrons is

$$\rho_e(\mathbf{r}) = \sum_i m_{e,i} \delta(\hat{\mathbf{R}}_{e,i} - \mathbf{r}) \tag{54}$$

Here, $m_{e,i}$ is the mass of the electron. For an electronic wavefunction of the form $\Phi(\mathbf{r}; \mathbf{r}_2 ...; \mathbf{r}_N)$, the expectation value of the electron mass density is

$$\langle \rho_e(\mathbf{r}) \rangle = N m_e \int d\mathbf{r}_2 ... d\mathbf{r}_N \Phi^*(\mathbf{r}; \mathbf{r}_2 ...; \mathbf{r}_N) \Phi(\mathbf{r}; \mathbf{r}_2 ...; \mathbf{r}_N) \tag{55}$$

For a single particle, the expectation value becomes

$$\rho(\mathbf{r}) = m_e |\Phi(\mathbf{r})|^2 \tag{56}$$

From elementary quantum mechanics, we note the interpretation of the modulus of the wavefunction squared as the probability density distribution for the particle.

What kind of continuity equation will such density operators follow? We consider again a general Hermitian density operator of the form

$$A(\mathbf{r}) = \frac{1}{2}\{A, \delta(\hat{\mathbf{R}} - \mathbf{r})\} \tag{57}$$

In order to find its time evolution we write the Heisenberg's equation of motion for this density operator resulting in:

$$\frac{\partial A(\mathbf{r})}{\partial t} = \frac{1}{i\hbar}[A(\mathbf{r}), H] \tag{58}$$

Here H is the Hamiltonian operator. Expanding the commutator and anti-commutator we have

$$\frac{\partial A(\mathbf{r})}{\partial t} = \frac{i}{2\hbar}\left(\{[H,A], \delta(\hat{\mathbf{R}} - \mathbf{r})\} + \{A, [H, \delta(\hat{\mathbf{R}} - \mathbf{r})]\} \right) \tag{59}$$

It is interesting to draw an analogy between Equation (59) and the generalized continuity equation from classical mechanics

$$\frac{dp_i}{dt} + \frac{\partial}{\partial x_j}\Pi_{ij} = S_i \tag{60}$$

Notice that if H and A commute, then the first term on the right hand side of Equation (59) vanishes. That is why we can identify this term to correspond to the source term S_i in its classical counterpart. After some manipulation, Equation (59) can be re-written as

$$\frac{\partial}{\partial t} A(\mathbf{r}) + \frac{1}{4} \nabla_{r,i} \left\{ A, \left\{ \frac{p_i}{m}, \delta(\hat{\mathbf{R}} - \mathbf{r}) \right\} \right\} = \frac{1}{2} \left\{ \frac{\partial}{\partial t} A, \delta(\hat{\mathbf{R}} - \mathbf{r}) \right\} \qquad (61)$$

From Equation (61), the flux density operator corresponding to the operator A can be written as

$$T_i^A(\mathbf{r}) = \frac{1}{4} \left\{ A, \left\{ \frac{p_i}{m}, \delta(\hat{\mathbf{R}} - \mathbf{r}) \right\} \right\} \qquad (62)$$

For example, in order to find the flux density of particles, we can substitute the identity operator in place of A to obtain:

$$T_i^{(N)}(\mathbf{r}) = \frac{h}{m} \text{Im}(\psi^* \nabla_i \psi) \qquad (63)$$

Equation (62) is recognizable as the expression for the well-known particle current density from quantum mechanics. Now, in order to find the kinetic contribution of stress, we substitute the momentum operator in place of A in Equation (62) to obtain,

$$\left\langle T_{ij}^{kin}(\mathbf{r}) \right\rangle = \frac{h^2}{4m} \left[\frac{\partial \psi^*}{\partial r_i} \frac{\partial \psi}{\partial r_j} + \frac{\partial \psi^*}{\partial r_j} \frac{\partial \psi}{\partial r_i} - \frac{\partial^2 \psi^*}{\partial r_i \partial r_j} \psi - \psi^* \frac{\partial^2 \psi}{\partial r_i \partial r_j} \right] \qquad (64)$$

To find the interaction contribution to the stress, we have to focus on the source term in Equation (61). Simple inspection shows that a form of stress due to Kugler 1967 satisfies Equation (61), in the sense that its divergence yields the source term in Equation (61). Kugler's stress definition however contains some objectionable features. Even if the interactions defined by *V* are short-ranged, the curl-free nature of the potential term renders the Kugler stress inherently long-ranged and thus nonlocal. In particular, the long-range character of the Kugler stress derives from the term,

$$T_{\alpha\beta}^{pot}(\mathbf{r}) = \frac{1}{4\pi} \nabla_{i\alpha}(V) \frac{(\mathbf{r} - \hat{\mathbf{R}})_\beta}{|\mathbf{r} - \hat{\mathbf{R}}|^3} \qquad (65)$$

The Kugler stress corresponding to the interaction between two particles A and B can be visualized as a radial flow of momentum from A to infinity, superimposed on a radial flow from infinity to B. This makes it possible to assign a distribution of sources at infinity which need not bear any relation to the actual physical sources. The issue of the long-ranged character of the Kugler stress may be partially circumvented by computing stress by summing over pairs of interacting particles thereby resulting in a dipole-like long-range distance dependence of the form. However, this form of stress field is still long-ranged albeit of a somewhat weaker form than the original one. When the interaction is Coulombic, the Kugler's form of stress results in severe anomalies and a different form of the stress tensor called the Maxwell form (Feynman 1939; Jackson 1999) is employed. The latter is applicable for particles interacting via Coulombic forces. In the static limit (in the absence of magnetic effects), Maxwell's stress field is given as:

$$T_{\alpha\beta}^{Max}(\mathbf{r}) = \frac{1}{4\pi}\left\langle E_\alpha(\mathbf{r})E_\beta(\mathbf{r}) - \frac{1}{2}\delta_{\alpha\beta}\mathbf{E}^2(\mathbf{r})\right\rangle$$

$$E_\alpha(\mathbf{r}) = \sum_i Z_i \frac{\left(\mathbf{r}-\hat{\mathbf{R}}_i\right)}{\left|\mathbf{r}-\hat{\mathbf{R}}_i\right|^3}$$

(66)

However, if the potential is a pair potential of the form V then, a Hardy stress like operator can be derived for the potential part of the stress as follows

$$T_{\alpha\beta}^{pot}(\mathbf{r}) = -\frac{1}{2}\sum_{i,j}\int_0^1 d\lambda\,\delta\left[\mathbf{r}-\hat{\mathbf{R}}_i - \lambda\left(\hat{\mathbf{R}}_i - \hat{\mathbf{R}}_j\right)\right]\left(\hat{R}_{i,\alpha} - \hat{R}_{j,\alpha}\right)\frac{\partial w}{\partial \hat{R}_{i,\beta}}$$

(67)

Similarly, a Noll like stress can also be derived. Both of these forms do not possess the long-ranged character of Kugler's potential and are more generally applicable than the Maxwell stress.

4. Revisiting the Virial Stress

The original virial theorem due to Clausius provides a relation connecting the time-averaged translational kinetic energy of a stationary dynamical system of particles to the time-average of the so-called virial of the forces acting on the particles. It can be extended to statistical mechanics by replacing the time-averages by ensemble averages. We discussed a scaling type approach to prove the virial theorem in the quantum mechanical case in the previous section. It is intriguing to see if a similar scaling approach will work for the classical/statisitical mechanical case---arguably making the analogy to quantum mechanical global stress more transparent.

In a canonical ensemble, we have

$$F(T,V) = -K_B T \ln Z(T,V)$$

(68)

Here, F is the Helmholtz free energy and Z is the partition function. From thermodynamics we can express the pressure P as,

$$P = -\left(\frac{\partial F}{\partial V}\right)_T$$

(69)

Simplifying, we have

$$P = K_B T\left(\frac{\partial \ln Z(T,V)}{\partial V}\right)_T = K_B T\left(\frac{1}{Z}\frac{\partial Z}{\partial V}\right)_T$$

$$= -\frac{\left(\int \frac{\partial H}{\partial V}e^{-H/K_B T}d\tau\right)}{\int e^{-H/K_B T}d\tau} = -\left\langle\frac{\partial H}{\partial V}\right\rangle$$

(70)

Consider a set of particles with coordinates {$\mathbf{r}_i$} and conjugate momenta {$\mathbf{p}_i$} enclosed within a container in thermal equilibrium at temperature T. Consider the container to be

a cubical box of volume V with rigid walls such that the potential due to the wall is of the form

$$U'(\mathbf{r}_i) = 0, \text{ all } \mathbf{r}_i \text{ inside box}$$
$$= \infty, \text{ any } \mathbf{r}_i \text{ outside box}$$

(71)

The pressure in statistical mechanics is written as

$$P = -\left\langle \frac{\partial H}{\partial V} \right\rangle$$

(72)

Here, the brackets denote an ensemble average.
In order to evaluate this quantity, we assume a form for our Hamiltonian,

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + U(\mathbf{r}_1, \ldots, \mathbf{r}_N)$$

(73)

We now scale the Hamiltonian using a simple canonical transformation of the form

$$\mathbf{r}_i' = L\mathbf{r}_i; \mathbf{p}_i' = L^{-1}\mathbf{p}_i$$

(74)

Here, L = V $^{1/3}$. Therefore, the scaled cube is a cube of unit dimensions.
From Equations (72-73) we have,

$$P = -\left\langle \frac{\partial H}{\partial V} \right\rangle = -\frac{1}{N!h^{3N}} \frac{\int \exp[-\beta H_L] \frac{\partial H_L}{\partial V} d\mathbf{p}_1 \ldots d\mathbf{p}_N d\mathbf{r}_1 \ldots d\mathbf{r}_N}{Z_L}$$

(75)

We now assess how the partition function Z scales under the canonical transformation given by Equation (74).

The partition function Z for a system of N classical particles can be written as

$$Z = \frac{1}{N!h^{3N}} \int \exp\left[-\beta H(\mathbf{p}_1 \ldots \mathbf{p}_N; \mathbf{r}_1 \ldots \mathbf{r}_N)\right] d\mathbf{p}_1 \ldots d\mathbf{p}_N d\mathbf{r}_1 \ldots d\mathbf{r}_N$$

(76)

The rescaled Hamiltonian becomes

$$H_L = H(\mathbf{p}_1 / L, \ldots \mathbf{p}_N / L, L\mathbf{x}_1, \ldots L\mathbf{x}_N)$$

(77)

The rescaled partition function $Z[H_L]$ becomes

$$Z[H_L] = \frac{1}{N!h^{3N}} \int \exp[-\beta H_L] d\mathbf{p}_1 \ldots d\mathbf{p}_N d\mathbf{r}_1 \ldots d\mathbf{r}_N$$

(78)

By substituting $\mathbf{p}_i \to L\mathbf{p}_i; \mathbf{r}_i \to L^{-1}\mathbf{r}_i$ in the above equation, we have

$$Z[H_L] = \frac{1}{N!h^{3N}} \int \exp[-\beta H] L d\mathbf{p}_1 \ldots L d\mathbf{p}_N L^{-1} d\mathbf{r}_1 \ldots L^{-1} d\mathbf{r}_N = Z[H]$$

(79)

Therefore the partition function Z remains invariant under the canonical scaling.

Now consider

$$P = -\left\langle \frac{\partial H}{\partial V} \right\rangle = -\frac{1}{N!h^{3N}} \frac{\int \exp[-\beta H_L] \frac{\partial H_L}{\partial V} d\mathbf{p}_1...d\mathbf{p}_N d\mathbf{r}_1...d\mathbf{r}_N}{Z_L} \tag{80}$$

Further,

$$\frac{\partial H}{\partial V} = \frac{2}{3} L^{-5} \sum_i \frac{p_i'^2}{2m_i} - \frac{1}{3} L^{-2} \sum_i \mathbf{x}_i'.\nabla_i U$$

$$\frac{2}{3V} \sum_i \frac{p_i^2}{2m_i} - \frac{1}{3V} \sum_i \mathbf{x}_i.\nabla_i U \tag{81}$$

So, from Equations (80-81) and the invariance of the partition function, we have

$$3PV = \left\langle 2 \sum_i \frac{p_i^2}{2m_i} \right\rangle - \left\langle \sum_i \mathbf{x}_i.\nabla_i U \right\rangle \tag{82}$$

Equation (82) is the Clausius form of the Virial theorem. If the particles are bound under the influence of their own internal interactions (say there is no box enclosing the particles), then the pressure P goes to zero.

The tensor form of the virial theorem can be obtained in an analogous manner by scaling the Hamiltonian using transformation of the form

$$r_{i,\alpha}' = h_{\alpha\beta} r_{i,\beta}; \, p_{i,\alpha}' = h^{-1}{}_{\alpha\beta} p_{i,\beta} \tag{83}$$

Here, the tensor **h** is represented as a matrix consisting of the vectors which make the sides of the box enclosing the N-particle system. The volume of this box is given by det(**h**).

A uniform strain applied to the whole box can be thought of as a rescaling of the metric tensor **h**. The macroscopic stress is then simply given as:

$$\sigma_{\alpha\beta} = -\left\langle \frac{\partial H}{\partial h_{\alpha\beta}} \right\rangle = -\frac{1}{N!h^{3N}} \frac{\int \exp[-\beta H'] \frac{\partial H'}{\partial h_{\alpha\beta}} d\mathbf{p}_1...d\mathbf{p}_N d\mathbf{r}_1...d\mathbf{r}_N}{Z'} \tag{84}$$

From this, the tensor form of the virial theorem is easily recovered.

5. Discussion

The present paper provides a unified setting that connects continuum, empirical molecular dynamics and quantum mechanical stress concepts. The essential tool is provided by Murdoch's formalism (2007) of arriving at a spatially varying stress field in a discrete setting. Analogous to molecular dynamics, Hardy stress and Noll stress like operators can represent the microscopic stress measures in quantum mechanics. The major challenge that remains is to cast our formalism in a computationally favorable

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framework like Density Functional Theory (DFT) and observe how well the microscopic stress measures compare with the Maxwell's stress that is the gauge of choice for Columbic systems. Our formalism is not restricted to Columbic potentials so non-coulomb like potentials which often occur in pseudo-potentials used in DFT calculations can be included as well.

The issue of the uniqueness of the quantum mechanical stress is still open to debate. The reader is referred to a recent review by us and references therein for further discussion (Maranganti et al. 2006). It remains to be seen if the non-uniqueness of the quantum mechanical stress is of any physical consequence. One viewpoint that can be taken is that the force is the physical quantity that is transmitted across scales and since all stress measures when integrated over a surface yield the same force, the choice of the quantum stress definition (whether Noll's, Hardy's or some other) is a matter of convenience. In fact, the form of quantum stress derived by us (which does not solely depend upon the charge density) does not appear to be an observable in quantum mechanics. An arbitrary divergence free non-Hermitian operator may be added to any permissible quantum mechanical stress operator which will still satisfy the continuity equations. Accordingly, our belief is that in the quantum mechanical context, the spatially varying stress is a non-observable. This strengthens the viewpoint that in multiscale modeling, passing information about the forces across multiple length scales may be more physical then stress.

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