Physical Interpretation of the Virial Stress

By Leon van Dommelen

FAMU-FSU College of Engineering
Tallahassee, FL 32303, USA

The virial stress is rederived using only fundamental physics, in order to better understand its meaning. Despite recent claims to the contrary, it is found that when properly applied, the virial stress produces the desired macroscopic stress, and that the dynamical term in it does represent physical forces between adjacent material regions.

1. Introduction

The virial stress is commonly used to find the macroscopic (continuum) stress in molecular dynamics computations. The macroscopic stress tensor in a macroscopically small, but microscopically large, volume Ω is typically taken to be:

$$\sigma_{\alpha\beta} = \frac{1}{\Omega} \sum_{i \text{ in } \Omega} \left(-m^{(i)}(u_\alpha^{(i)} - \bar{u}_\alpha)(u_\beta^{(i)} - \bar{u}_\beta) + \tfrac{1}{2}\sum_j (x_\alpha^{(j)} - x_\alpha^{(i)})f_\beta^{(ij)} \right) \qquad (1.1)$$

where $m^{(i)}$ is the mass of the i-th molecule in Ω, $\vec{x}^{(i)}$ its position, with Cartesian components $(x_1^{(i)}, x_2^{(i)}, x_3^{(i)}) = (x^{(i)}, y^{(i)}, z^{(i)})$, $\vec{u}^{(i)}$ its velocity, $\bar{\vec{u}}$ the local average velocity, and $\vec{f}^{(ij)}$ is the force on molecule i exerted by another molecule j.

This stress was found by Irving & Kirkwood (1950) for the ensemble-averaged equations of hydrodynamics, though they did not write down the local volume-averaged version above. The version that will be adopted here was derived by Cormier *et al.* (2001), based on the work of Lutsko (1988). Similar expressions have been derived by earlier authors, for example based on the virial of Clausius (1870).

Recently Zhou (2003*a,b*) has cast doubt on the validity of the first, dynamical, term in the virial formula since the desired Cauchy stress is supposed to represent mechanical forces only. In this paper we will examine the proper stress from the most basic ideas, in order to determine the physical meaning of both terms unambiguously.

We will be concentrating on the molecular dynamics simulation of a solid. We assume the solid is at rest on the macroscopic scale, so that the average velocity vanishes, and that the solid is homogeneous on all but the microscopic level.

Figure 1 shows a direct attempt to evaluate the stress on a surface AA' by finding the force exerted on the set I of atoms below AA' by the set J above AA'. For convenience, we have taken the y-axis normal to the surface AA', which extends distances Δx and Δz in the other two directions.
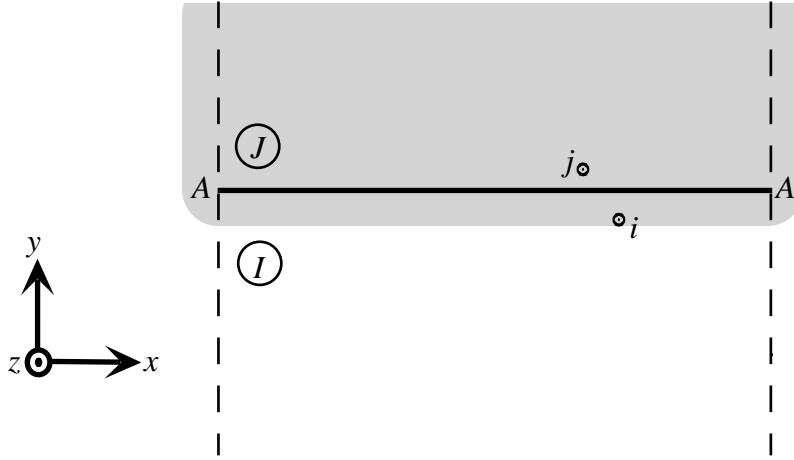
Figure 1. Straightforward evaluation of the macroscopic stress.

We assume that while the surface is macroscopically small, it extends over a large enough microscopic area that microscopic variations are averaged away; (compare Nakane 2000). In addition we assume it is large enough compared to the molecular interaction distance (sketched as grey) that edge effects on the computed net force are negligible. By its very definition, our macroscopic stress becomes:

$$\vec{\sigma}_2 = \frac{1}{\Delta x \Delta z} \sum_{i \text{ in } I} \sum_{j \text{ in } J} \vec{f}^{(ij)} \tag{1.2}$$

Of course, to reduce random fluctuations, in addition to averaging over the spatial intervals Δx and Δz, one might want to average further over a macroscopically small time interval around the desired time of the stress. However, a purely spatial average tends to be more convenient in a time-marching computation, and one expects the ergodic assumption to be valid that averaging short scale processes over time can be simulated by averaging different stages of those processes over space.

In section 3, it will be seen that the sum of forces (1.2) is directly evaluated using the second term in the virial sum (1.1), begging the question what the first term is doing. Certainly, as Zhou (2003a,b) very correctly explains, if the sets I and J are Lagrangian sets, (i.e. they contain the same atoms at different times,) *the sum of forces (1.2) is all there is; absolutely no additional dynamical terms should be added.*

2. Cross-overs

The derivation of the previous section, though giving the most direct evaluation of the stress, is too constraining in practice. While in a crystal structure it may be possible to define special planes AA' that properly separate Lagrangian sets, for arbitrary solids and arbitrary planes at least some atoms will be close to the plane AA' and heat motion will push them periodically across the plane. Note that from here on, set I stands more precisely for the Lagrangian set of atoms whose *nominal* position is in region I, below plane AA'.
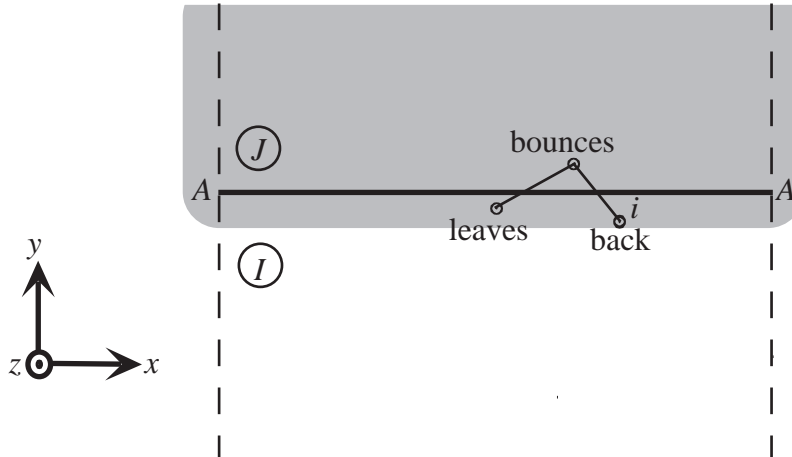
Figure 2. The cross-over problem.

Consider the example situation sketched in figure 2, in which a molecule from set I crosses the plane AA' into the region J, bounces off the atoms there, and returns to region I. The forces that bounce atom i are clearly *physical* forces exerted by atoms in set J on an atom in set I. They should be included in our stress force: they add to the changes of momentum of Lagrangian set I. Alternately, they add to the forces that must be exerted on set I elsewhere to keep it at rest. Yet our sum of forces (1.2) completely ignores these forces as soon as the atom i temporarily crosses the plane AA'.

So, to get the proper sum of the *physical* forces of the set J on the set I, the sum of forces (1.2) has to be augmented by forces on atoms i that are temporarily on the other side of the plane. To actually track atoms through the plane and back is of course very inconvenient, especially in a purely spatial average, and the standard trick is to instead substract the momentum of the atom i when it leaves and add the new momentum back when it returns through the plane. The net effect is the same as including the integrated force on atom i while it was at the other side.

Note that the atoms are not normally billiard balls as suggested above, and atom i will probably be pulled back by its fellow atoms in I as well as bounced back by the atoms in J. Fortunately, due to Newton's third law, the part of the momentum change of atom i due to its fellows in I exactly cancels falsely counting the reaction forces by i on its fellows as forces exerted by set J on set I. The same story holds in reverse for atoms j wandering into region I.

Thus, to get the correct stress, we need to add the net momentum flux of atoms through the surface AA' to the sum of the forces (1.2). This dynamical term is not an artificial addition, but represents actual *mechanical* forces of the Lagrangian set J on the set I that are not correctly accounted for in the sum (1.2). (Compare Todd *et al.* 1995).

The above seems to be the key point missed by Zhou, who assumes the force term in the virial stress to be the correct evaluation of the forces and the dynamical term to be an addition (which cannot be zero since it involves squares.) In fact, as seen in the next section, the first term in the virial stress is exactly the correction

for the physical forces on cross-overs missed by the force sum (1.2). This invalidates the central point made by Zhou; for example, in his abstract: "The virial stress is not a measure for mechanical force between material points and cannot be regarded as a measure for mechanical stress in any sense." The discussion above shows that it does describe mechanical force, with the first dynamical term describing the mechanical force when atom i is at the other side of plane AA', and the second force term describing the part when it is not.

3. The virial average

While, as we noted in the introduction, time-averaging the force sum (1.2) from set J on set I is a logical way to reduce statistical fluctuations, the virial stress is based on an average that is diabolically more clever. Since it was assumed that the macroscopic stress has negligible variation over the stress plane $\Delta x \Delta z$, it will normally also have negligible variation over a similar linear extent in the y-direction. (Note that this might not always be desirable, for example near walls, (Todd *et al.* 1995), but we will assume it is.) We can therefore average over an infinitely dense set of equivalent planes AA' in a vertical region Δy, as sketched in figure 3.
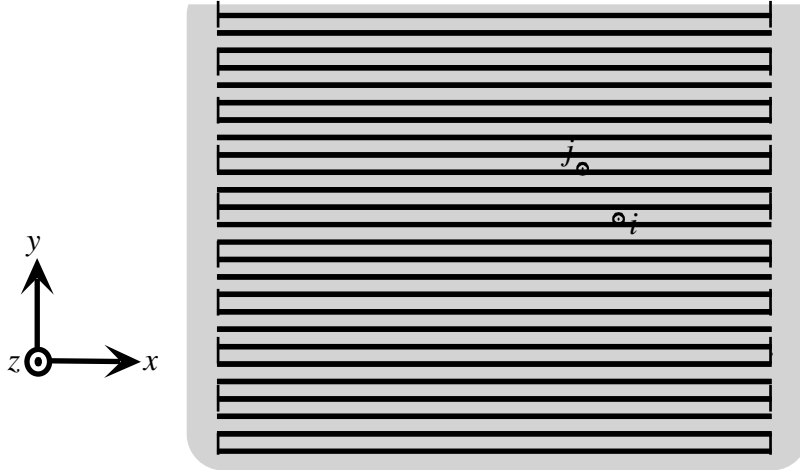

Figure 3. Averaging in the y-direction.

The mathematics of the averaging is simple. For a given pair of atoms i and j as shown, the relative fraction of planes that have i below and j above them is obviously $\left(y^{(j)} - y^{(i)} \right) / \Delta y$. Thus our sum of the forces through a single plane (1.2) becomes exactly the second term in the virial stress theorem (1.1). The factor $1/2$ comes in since only pairs with $y_j > y_i$ should be counted, and the virial theorem counts them all. (Because of Newton's third law, $\vec{f}^{(ji)} = -\vec{f}^{(ij)}$.)

Following Cormier *et al.* (2001), for pair i and j not both inside the volume, it is desirable to reduce the contribution of that pair by the fraction of their bond that is actually inside, since this gives a straight average of the stress of Irving & Kirkwood, (Irving & Kirkwood, 1950, Appendix).

The diabolical part of this averaging is that it makes undercounting cross-overs unavoidable: not all these planes can be away from nominal atom positions. Fortunately, the amount that needs to be added to fix things is simple. In an infinitesimal time interval δt, (that can be much smaller than even the microscopic time scales,) the relative fraction of planes crossed by an atom i is $u_2^{(i)} \delta t / \Delta y$ and the corresponding momentum that must be substracted (becoming added if $u_2^{(i)}$ is negative) from these planes to correct for uncounted physical forces is an amount $m_i \vec{u}^{(i)}$ larger. This exactly produces the first term in the virial stress.

Thus the dynamical term in the virial stress becomes simply the proper sum of all the *mechanical* forces missed in the second term, and nothing more.

4. Final remarks

Most of the examples that Zhou (2003a) uses to argue the incorrectness of the virial stress suffer from the problem that the macroscopic motion is not substracted out. We have absolutely no issue with the claim that the macroscopic motion part does not corresponds to *physical* forces. This is, after all, immediately clear from doing a Gallilean transform. Nor does it seem that there has been much misconception about this; it is very clearly shown in Irving & Kirkwood (1950), and authors that needed to substract the mean motion seem to have done so, eg Hardy (1982).

(Yet, as a fluid dynamicist, the author wants to point out that the Lagrangian description, following the motion of the fluid, is most times highly inconvenient for us. In a fixed coordinate frame, the additional terms in the virial stress become simply the convective terms that must be added to the Eulerian conservative equations. The author is, however, unaware of claims that the convective terms would be physical forces.)

Figure 11 in Zhou (2003a) does include the thermal motion, but it is assumed to be negligible. Only the example of figure 5 actually addresses a valid case of thermal motion effects. It is no more than a symmetric two-atom system were the atoms i and j, connected by a linear or nonlinear spring, vibrate along the y-axis (his x-axis) according to $y^{(j)} = -y^{(i)}$. One can fill space with such pairs to create a macroscopic continuum. Obviously, this does not support any macroscopic force.

Zhou's error in this example seems to be simple sloppy math. He finds the macroscopic virial stress by time-averaging over a period τ, which is appropriate for his assumption that all pairs are in the same phase, (the assumption of random phases would allow a more appealing space average, and would not change the results here.) His error, in his equation (31), is in assuming that the average of the second term in the virial stress is zero. In fact, the average of $\left(y^{(j)} - y^{(i)}\right) f_y^{(ij)}$ is not just the average of $\left(y^{(j)} - y^{(i)}\right)$ times the average of $f_y^{(ij)}$, which would be zero, but also includes the average of $\left(y'^{(j)} - y'^{(i)}\right) f'_y^{(ij)}$, where primes indicate instantaneous deviation from the average. The last term is always positive: when the atoms are closer together than nominal the force between them will be repulsive and when they are farther apart, attractive. The correct average of the second term in the virial stress is in fact easily found as

$$\frac{1}{\tau \Omega} \int_\tau -2y^{(i)} f_y^{(ij)} \mathrm{d}t = \frac{1}{\tau \Omega} \int_\tau -2y^{(i)} m \ddot{y}^{(i)} \mathrm{d}t = \frac{1}{\tau \Omega} \int_\tau 2m \dot{y}^{(i)2} \mathrm{d}t, \qquad (4.1)$$

using integration by parts and periodicity. This, of course, is just what is needed to balance the first, dynamical term, and the stress is correctly evaluated to be zero as it should, and is not a negative value as Zhou claims.

This author feels that it is also misleading to claim that for a gas, the dynamical term in the virial stress corresponds to a physical force at the wall only. While this, obviously, is true for the physics-book model of an ideal gas as a system of noninteracting point masses, a system at such a Knudsen number does not truly act as a simple continuum on macroscopically small scales. The gasses that ordinary fluid mechanics deals with have a free path length that is small compared to macroscopic scales. We propose that the discussion of section 2 can then be changed to read that atom i wanders into the J region to lose its momentum in collisions with the atoms there and becomes anonymous within its new surroundings at a distance that scales with the free path length. To maintain the statistical mass distribution, an *other* atom will come wandering out of that region to cross back into region i. One might, with some justification, object that due to the atom swap, the region I is no longer representative of any Lagrangian set. We submit however that Newton's laws for systems are not at all affected if we swap two identical particles with the same momentum. However one might think about that, it is obviously unjustified to say that the collision forces that make atom i anonymous in set J and the ones that kick the new atom back to set I are not internal *mechanical* forces "in any sense." Assuming that the atoms only fill a small fraction of space, so that collisions with the atoms at opposite sides of the plane AA' are rare, most of those physical forces will be represented by the dynamical term.

A note on the virial averaging might also be in order. The straight Cormier *et al.* average of the Kirkwood & Irving stress has the disadvantage that it also affects the macroscopic scales to second order in averaging size. Thus it seems that it may in many cases be more desirable to use the higher order operators commonly used in discrete vortex methods (eg, Shankar & Van Dommelen 1996). The advantage would be that for given error in smoothing macroscopic scales, one can average over a larger region in space, reducing microscopic variations. This seems to be equivalent to the expressions derived by Hardy (1982), though higher order averaging functions are not uniformly positive. In any case, now that we understand the relevance of the virial stress, we propose to concentrate on how to evaluate it best.

References

Clausius, R. 1870 On a mechanical theory applicable to heat. *Philosophical Magazine* **40**, 122-127.

Cormier, J., Rickman, J. M. & Delph, T. J. 2001 Stress calculation in atomistic simulations of perfect and imperfect solids. *J. Appl. Phys.* **89**, 99-104.

Hardy, R. J. 1982 Formulas for determining local properties in molecular dynamics simulations: shock waves. *J. Chem. Phys.* **76**, 622-628.

Irving, J. H. & Kirkwood, J. G. 1950 The statistical mechanical theory of transport processes, IV. The equations of hydrodynamics. *J. Chem. Phys.* **18**, 817-829.

Lutsko, J. F. 1988 Stress and elastic constants in anisotropic solids: molecular dynamics techniques. *J. Appl. Phys.* **64**, 1152-1154.

Nakane, M., Shizawa, K., & Takahashi, K. 2000 Microscopic discussions of macroscopic balance equations for solids based on atomic configurations. *Arch. Appl. Mech.* **70**, 533-549.

Shankar, S. & Van Dommelen, L. L., 1996 A New Diffusion Procedure for Vortex Methods. *J. Comput. Phys.* **127**, 88-109.

Todd, B. D., Evans, D. J. & Daivis, P. J. 1995 Pressure tensor of inhomogeneous fluids. *Phys. Rev.* E **52**, 1627-1638.

Zhou, M. 2003*a* A new look at the atomic level virial stress - on continuum-molecular system equivalence. *Proc. R. Soc.* A, to appear. http://diva.me.gatech.edu/publications.shtml

Zhou, M. 2003*b* The virial stress is no stress. Submitted to *Phys. Rev. B.* http://diva.me.gatech.edu/publications.shtml