AN APPROACH TO BRIDGE ATOMIC- AND CONTINUUM-STRESS

J. Schjødt-Thomsen and R. Pyrz
Aalborg University, Dept. of Mech. Engng., Pontoppidanstraede 101, DK-9220 Aalborg East, Denmark

Keywords: *Atomic stress, Non-local, Strain gradient, Microdeformations*

Abstract

A framework for calculating the non-local, asymmetric atomic stress has been developed. The approach is based on the assumption that stress is derivable from an energy expression, i.e. an atomic force field. The atomic stress is linked to the first Brillouin zone or equivalently 3D Voronoi element surrounding the atom. Atomic displacements from e.g. MD simulations are used as input to the framework. The discrete nature of the atomic scale is linked to continuum theory through the Finite Element formalism using the interpolation functions of 3D Voronoi elements. The advantage of this approach compared to using the Clausius virial theorem is that the stresses from the present approach is defined in the same way as the non-local stress of traditional continuum mechanics so the relation of the present atomic stress and the traditional Cauchy stress is strongly anticipated but remains to be proved

1 Introduction

Materials reinforced with nano-sized structural elements have attracted very much attention after the publication of results indicating that these materials possessed tremendous potential compared to the bulk materials. Probably the most well known nano-element is the carbon nanotube, which with its perfect structure and excellent mechanical properties, created a tremendous focus on the possibility of using the carbon nanotubes as reinforcement in composite materials.

Addition of only a small fraction of nano-sized elements to a bulk material has shown to increase properties, such as thermal stability, tensile strength and stiffness. Only 4.2 weight percent of montmorillonite silicate embedded into the nylon-6 polymer increased the tensile modulus by a factor of 1.9, tensile strength by a factor of 1.6 and heat distortion temperature by a factor of 1.7, as compared to the neat bulk polymer [1]. For Epoxy composites the effect of embedding 15 weight percent of montmorillonite silicate caused a 10-fold increase of both stiffness and strength [2].

In [3] it was proved experimentally that micro- or nano-rotations occur in nano-scale materials and that these deformation mechanisms are especially important. As a direct consequence of these observations it is crucial that in order to exploit the potential of nano-materials, theoretical models must be formulated which take the actual deformation mechanisms into account. A continuum theory which deals with microdeformations, is the so-called micromorphic continuum theory proposed in a number of papers in the 1960'es and collected in [4].

Several approaches have been taken to determine continuum mechanics properties of nano elements and it seems that at a certain point a continuum quantity must be introduced in order to relate the measured quantities to traditional continuum mechanics [5,6].

Another challenge is the fact that the stresses obtained from the Clausius virial theorem is not directly related to either the Cauchy stress or the Piola--Kirchhoff stress of continuum mechanics since neither of these depend on velocity but merely on force [7,8].

An approach to link the nanolevel to continuum level is to apply the finite element method. This was done by [9]. The molecular structure is discretised using 3D tetrahedral elements. However, one drawback of this approach is that it becomes computationally intensive for large ensemble of atoms due to the large number of element nodes.

As a means to avoid using continuum measures on the nano-scale an alternative approach is taken in the present paper. A theoretical approach, considering the deformations on the atomic level, is derived to determine the stress on the atomic scale.

The stresses due to the deformations are obtained through derivatives of an atomic force field and integration over the volume of the first Brillouin zone (or Voronoi polyhedron). Thus, the stress is non-local since it involves an integration and the stress tensor may be non-symmetric in its indices and, in order to make this a continuous theory the interpolation functions from 3D Voronoi finite elements are applied. Using the Voronoi elements makes this approach strain gradient based as well, since it incorporates the strain measure proposed by [10].

2 Theory

The basic working assumption is that the relation between stress σ_{ij} and strain ε_{ij}

$$\sigma_{ij}=\frac{1}{V}\frac{\partial W}{\partial \varepsilon_{ij}} \tag{1}$$

is applicable at atomic level also. In that case W is the atomic force field. Equation (1) is in fact what is used in many molecular mechanics simulations. However, the problem is that the volume V is not well defined, but is usually chosen as a bounding box surrounding the considered molecules. Furthermore, the atomic stress must be non-local and allow for asymmetry in the stress tensors indices. First the atomic potential, W, is rewritten as

$$\frac{W}{V}=\sum_{I}\frac{w}{\Omega^{I}} \tag{2}$$

where w is the potential for atom I occupying volume Ω^I.
This gives an expression for the atomic stress for atom I as

$$\sigma_{ij}^{(I)}=\frac{1}{\Omega^2}\int_{\Omega}\frac{\partial w}{\partial \varepsilon_{ij}}d\Omega \tag{3}$$

where Ω is the volume of the 3D Voronoi polyhedron surrounding atom I and the integration is introduced to make the stress nonlocal. The asymmetry of the stress tensor is ssured if the derivative of the potential is taken with respect to the displacement gradient, D_{ij}

$$D_{ij}=\frac{\partial u_i}{\partial x_j}=u_{i,j} \tag{4}$$

since

$$\varepsilon_{ij}=\frac{1}{2}\left(D_{ij}+D_{ji}\right) \tag{5}$$

Thus, the final expression for the stress of atom I becomes

$$\sigma_{ij}^{(I)}=\frac{2}{\Omega^2}\int_{\Omega}\frac{\partial w}{\partial D_{ij}}d\Omega \tag{6}$$

which is non-local and may be asymmetric in its indices. However, it is easily seen that replacing $D_{ij}/2$ with ε_{ij} gives $(\sigma_{ij}+\sigma_{ji})/2$ which is clearly the symmetric part of the stress tensor.

2.1 Atomic Force Field

Depending on the material under study, the atomic force field may not be the same in all cases, but Eq. 6 is considered to be generally applicable and most importantly not restricted to a specific force field.

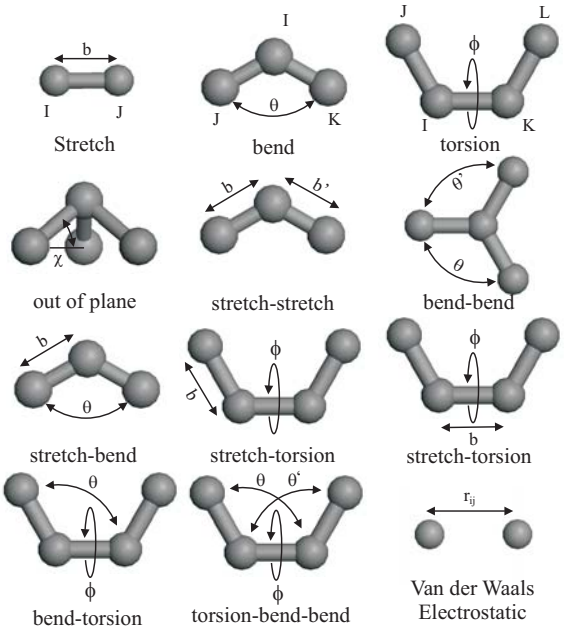

Fig. 1. Deformation modes.

However, in the present study the "COMPASS" force field, [11], is taken as a starting point to illustrate the applicability of the method. The deformation modes are shown in Fig. 1 and the COMPASS force field is given as

$$
\begin{aligned}
w=&\sum_b \begin{bmatrix} k_2(b-b_0)^2+k_3(b-b_0)^3 \\ +k_4(b-b_0)^4 \end{bmatrix} \\
&+\sum_\theta \begin{bmatrix} k_2(\theta-\theta_0)^2+k_3(\theta-\theta_0)^3 \\ +k_4(\theta-\theta_0)^4 \end{bmatrix}+ \\
&\sum_\phi \begin{bmatrix} k_1(1-\cos\phi)+k_2(1-\cos 2\phi) \\ +k_3(1-\cos 3\phi) \end{bmatrix} \\
&+\sum_\chi k_2\chi^2+ \\
&\sum_{b,b'} k\,(b-b_0)(b'-b'_0) \\
&+\sum_{b,\theta} k\,(b-b_0)(\theta-\theta_0)+ \\
&\sum_{b,\phi}(b-b_0)\begin{bmatrix} k_1(1-\cos\phi)+k_2(1-\cos 2\phi) \\ +k_3(1-\cos 3\phi) \end{bmatrix}+ \\
&\sum_{\theta,\phi}(\theta-\theta_0)\begin{bmatrix} k_1(1-\cos\phi)+k_2(1-\cos 2\phi) \\ +k_3(1-\cos 3\phi) \end{bmatrix} \\
&+\sum_{\theta,\theta'} k\,(\theta-\theta_0)(\theta'-\theta'_0) \\
&+\sum_{\theta,\theta',\phi} k\,(\theta-\theta_0)(\theta'-\theta'_0)\cos\phi \\
&\sum_{i,j}\frac{q_i q_j}{r_{ij}}+\sum_{i,j} e_{ij}\left[2\left(\frac{r_{ij}^0}{r_{ij}}\right)^9-3\left(\frac{r_{ij}^0}{r_{ij}}\right)^6\right]
\end{aligned}
\qquad (7)
$$

This force field contains basically two categories of terms, i. e. valence- and nonbond interaction terms. Terms containing b represent stretching of bonds, terms with θ represents bending of bonds, terms with φ represents torsion of bonds and terms with χ represents out of plane bending ("wagging"). Additionally, there are 6 cross coupling terms where terms with (b,b_0) represent stretch–stretch, terms with (θ, θ_0) represent bend–bend, terms with (b, θ) represent stretch–bend, terms with (b, φ) represent stretch–torsion, terms with (θ; φ) and (θ, θ', φ) represent bend–torsion modes. Finally, the term involving q_i represents Coulombic electrostatic interaction and the last terms is the Lennard–Jones potential for van der Waals interaction.

Since the atomic force field, w, is not an explicit function of the displacement gradient, Eq. 7 needs reformulation in terms of quantities related to the displacement gradient in order to calculate the derivatives according to Eq. 6.

Terms involving b and b' correspond to a change of distance and can be related to the strain tensor as

$$b-b_0=\varepsilon_{ij}\,n_i\,n_j\,\mathrm{d}s=\varepsilon_{ij}\,n_i^{0,IJ}\,n_j^{0,IJ}\left|\mathbf{r}^{0,I}-\mathbf{r}^{0,J}\right| \qquad (8)$$

where $\mathbf{r}^{0,I}$ and $\mathbf{r}^{0,J}$ are the position vectors of atom I and J, respectively, $n_i^{0,IJ}$ is component i of the unit vector connecting atom I and J in the undeformed state and |.| denotes the length of a vector. Eq. 8 in terms of displacement gradients, is then

$$b-b_0=\frac{1}{2}\left(u_{i,j}+u_{j,i}+u_{k,i}\,u_{k,j}\right)n_i^{0,IJ}\,n_j^{0,IJ}\left|\mathbf{r}^{0,I}-\mathbf{r}^{0,J}\right| \qquad (9)$$

For the bending terms the same approach is used as for the derivation of shear strain, but without the assumption of an initial right angle, i.e.

$$
\begin{aligned}
&\cos\theta=\left(2\varepsilon_{ij}+\delta_{ij}\right)n_i\,m_j \quad \Rightarrow \\
&\cos\theta=\left[\left(u_{i,j}+u_{j,i}+u_{k,i}\,u_{k,j}\right)+\delta_{ij}\right]n_i^{0,IJ}\,n_j^{0,IK}
\end{aligned}
\qquad (10)
$$

Now, since it is θ which enters the atomic force field, then a MacLaurin series, [12], is used, i.e.

$$
\begin{aligned}
&\cos\theta=\psi \quad \Rightarrow \\
&\theta=\frac{\pi}{2}-\psi-\frac{1}{2\cdot 3}\psi^3+\frac{1\cdot 3}{2\cdot 4\cdot 5}\psi^5+\frac{1\cdot 3\cdot 5}{2\cdot 4\cdot 6\cdot 7}\psi^7 \\
&+\frac{1\cdot 3\cdot 5\cdot 7}{2\cdot 4\cdot 6\cdot 8\cdot 9}\psi^9+\ldots
\end{aligned}
\qquad (11)
$$

which makes the stress nonlinear in $u_{i,j}$.

Now considering the torsional deformation mode in Fig. 1, the torsion terms are obtained as follows, see Fig. 2. The vectors $\mathbf{r}^{IJ}$ and $\mathbf{r}^{KL}$ are projected onto a plane orthogonal to the vector connecting atom I and atom K. These projections are denoted as $\mathbf{p}^{IJ}$ and $\mathbf{p}^{KL}$, respectively. The angles θ_1 and θ_2 are obtained as

$$\cos\theta_1=\frac{\mathbf{r}^{IJ}\cdot\mathbf{r}^{IK}}{|\mathbf{r}^{IJ}||\mathbf{r}^{IK}|} \text{ and}$$

$$\cos\theta_2=\frac{\mathbf{r}^{KL}\cdot\mathbf{r}^{KI}}{|\mathbf{r}^{KL}||\mathbf{r}^{KI}|}$$

The projections $\mathbf{p}^{IJ}$ and $\mathbf{p}^{KL}$ are obtained as

$$\begin{aligned}\mathbf{p}^{IJ}&=\mathbf{r}^{IJ}\cos\left(\theta_1-\frac{\pi}{2}\right)\\ \mathbf{p}^{KL}&=\mathbf{r}^{KL}\cos\left(\theta_2-\frac{\pi}{2}\right)\end{aligned} \tag{12}$$

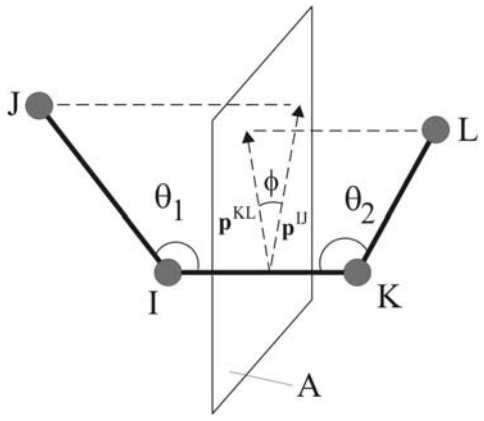

Fig. 2. Projection of vectors $\mathbf{r}^{IJ}$ and $\mathbf{r}^{KL}$ onto plane A.

Now the torsional angle which lies in plane A is obtained as the angle between $\mathbf{p}^{IJ}$ and $\mathbf{p}^{KL}$. cosφ is then found in a manner analogous to the bending terms, i.e.

$$\cos\varphi=\left(u_{i,j}+u_{j,i}+u_{k,i}\,u_{k,j}+\delta_{ij}\right)\frac{p_i^{IJ}}{|\mathbf{p}^{IJ}|}\frac{p_j^{KL}}{|\mathbf{p}^{KL}|} \tag{13}$$

where p_i^{IJ} is component "i" of vector $\mathbf{p}^{IJ}$. Subsequently using the trigonometric multiple angle relations

$$\begin{aligned}\cos2\varphi&=2\cos^2\varphi-1\\ \cos3\varphi&=4\cos^3\varphi-3\cos\varphi\end{aligned} \tag{14}$$

The other "mixed" terms are obtained using the expressions derived previously. So the term to be dealt with now is the Lennard—Jones potential. The ratios of distances can be rewritten as

$$\begin{aligned}\frac{r_{ij}^0}{r_{ij}}&=\frac{r_{ij}^0}{r_{ij}^0+\Delta r_{ij}}=\frac{1}{1+\varepsilon_{ij}\,n_i^{0,IJ}\,n_j^{0,IJ}}\\ &=\frac{1}{1+\left(u_{i,j}+u_{j,i}+u_{k,i}\,u_{k,j}\right)n_i^{0,IJ}\,n_j^{0,IJ}}\end{aligned} \tag{15}$$

Finally, the Coulomb electrostatic interaction is taken into account using the same approach as for the Lennard—Jones potential, i.e.

$$\frac{q_i\,q_j}{r_{ij}}=\frac{q_I\,q_J}{r_{IJ}^0+\left(u_{i,j}+u_{j,i}+u_{k,i}\,u_{k,j}\right)n_i^{0,IJ}\,n_j^{0,IJ}} \tag{16}$$

with $r_{IJ}^0=\left|\mathbf{r}^{0,I}-\mathbf{r}^{0,J}\right|$

Now all the terms of Eq. 7 have been expressed through the displacement gradient. Then the differentiation must be carried out with respect to the displacement gradient according to Eq. 6, to give the stress of atom *I*. The differentiations are rather straight forward, bearing in mind that

$$\frac{\partial\left(u_{i,j}\right)}{\partial\left(u_{k,l}\right)}=\frac{\partial\left(D_{ij}\right)}{\partial\left(D_{kl}\right)}=\delta_{ik}\,\delta_{jl} \tag{17}$$

from which

$$\begin{aligned}&\frac{\partial\left(u_{k,l}+u_{l,k}+u_{r,k}\,u_{r,l}\right)}{\partial\left(u_{i,j}\right)}=\\ &=\delta_{ik}\,\delta_{lj}+\delta_{il}\,\delta_{jk}+\delta_{ir}\,\delta_{jk}\,u_{r,l}+\delta_{ir}\,\delta_{jl}\,u_{r,k}\end{aligned} \tag{18}$$

2.2 Discrete/Continuous

In order to link the discrete nature of the atoms with continuum mechanics the Finite Element formalism is used. The continuous displacements, $\{\mathbf{u}\}$ are replaced by their discrete displacements, $\{\mathbf{d}\}$, via the elements interpolation functions, $[\mathbf{N}]$, as

$$\{\mathbf{u}\}=[\mathbf{N}]\{\mathbf{d}\} \tag{19}$$

In the present study the molecular structure is discretised into 3D Voronoi elements. This approach enables morphological characterization of the structure and provides the volume for the integration of Eq. 6. Using the FE formalism in conjunction with Eq. 6, requires the derivatives of the shape functions with respect to spatial coordinates

$$\frac{\partial u_i}{\partial x_j}=\frac{\partial N_{ik}}{\partial x_j}d_k \tag{20}$$

which are used to replace $u_{i,j}$ in Eq. 6.

The shape functions of the 3D Voronoi elements are expressed in terms of geometric quantities of the elements, see Fig. 3. For illustrative purposes, it suffices to consider the 2D element. The interpolation functions are

$$N_p=\frac{\Phi_p}{\sum_q \Phi_q} \tag{21}$$

where Φ_p is given as

$$\Phi_p=\frac{s_p}{h_p} \tag{22}$$

where s_p is the length (area in 3D) of edge F_p (face in 3D) of the element and h_p is the distance between point **x** within the element and node n_p.

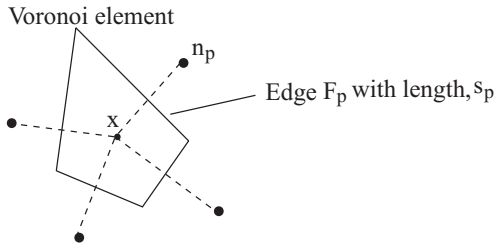

Fig. 2. 2D Voronoi element.

Using this approach introduces quantities related to those used in the atomic interaction cell strain, ε_{ij}^c, of [10], which is based on the vector, **h**, collinear with the line joining point **x** within the element and node n_p. The length of this vector, **h**, is equal to s_p. The atomic interaction cell strain is the dyadic product of the displacement vector and **h**, i.e.

$$\varepsilon_{ij}^c=\frac{1}{V^c}h_i^c u_j^c \tag{23}$$

this shows that the present approach to some extent incorporates the atomic interaction cell strain and makes it strain gradient based as well.

Finally, when the stress from atom I is obtained the stress for larger domains may simply be obtained as a volume averaging over the volume considered i. e.

$$\langle\sigma_{ij}\rangle=\frac{1}{V}\sum_{I=1}^{N}\sigma_{ij}^{(I)} \tag{24}$$

Consequently the continuum stress can be thought of as a volume average of the atomic stress.

3 Conclusions

In the present paper a framework for calculating the non-local, strain gradient based, asymmetric atomic stresses has been developed. The approach is based on the assumption that the stress is derivable from an energy expression, which is based on a general atomic force field. The atomic force field differentiated with respect to the displacement gradient, consequently allowing for an asymmetric stress tensor.

The atomic stress in the present approach is linked to the first Brillouin zone or equivalently the Voronoi cell surrounding the atom, so no averaging over an arbitrary volume is carried out.

To illustrate the principle of the framework the versatile force field - the COMPASS force field - has been used. However, it should be emphasized that the theory itself is general and not limited by choice of force field. The atomic displacements for the stress calculations can be obtained from e.g. a molecular dynamics simulation.

This approach is clearly discrete due to the discrete nature of the atoms, however, the link to a continuum theory is established through the finite element formalism using the interpolation functions of 3D Voronoi elements. The elements have the

advantage that their interpolation functions only depend on the positions of the nodes of the elements and not on the shape and the principal forms of the interpolation functions are the same no matter how many nodes the element contains. Finally, the advantage of this approach compared to using the Clausius virial theorem is that the stress from this approach is defined exactly as the non-local stress of traditional continuum mechanics so the relation between the present atomic stress and the traditional Cauchy stress is strongly anticipated, but remains to be proved.

References

[1] Kojima Y., Usuki A., Kawasumi M., Okada A., Fukushima Y., Kurauchi T., and Kamigaito O. "Mechanical Properties of Nylon-6 Clay Hybrid". *J. Mater. Res.*, Vol. 8, No. 5, pp 1185-1189, 1993.

[2] Lan T., and Pinnavaia T. "Clay-Reinforced Nanocomposites". *Chem. Mater.*, Vol. 6, pp 2216-2219, 1994.

[3] Murayama M., Howe J. M., Hidaka H. and Takaki S. "Atomic--Level Observation of Disclination Dipoles in Mechanically Milled Nanocrystalline Fe". *Science*, Vol. 295, pp 2433-2435, 2002.

[4] Eringen A. C. *"Microcontinuum Field Theories - I: Foundations and Solids"*. Springer, 1999.

[5] Odegard G. M., Gates T. S., Nicholson L. M. and Wise K. E. "Equivalent--Continuum Modeling of Nano-Structured Materials". *Comp. Sci. Tech.,* Vol. 62, pp 1869-1880, 2002.

[6] Natsuki T., Tantrakarn K. and Endo M. "Prediction of Elastic Properties for Single--Walled Carbon Nanotubes", *Carbon*, Vol. 42, pp 39-45, 2004.

[7] Constanzo F., Gray G. L. and Andia P. C. "On the definitions of effective stress and deformation gradient for use in MD: Hill's macro--homogeneity and the virial theorem", *Int. J. Engng. Sci.*, Vol. 43, pp 533-555, 2005.

[8] Zhou M. "A new look at the atomic level virial stress: On continuum – molecular system equivalence", *Proc. R. Soc. Lond. A*, Vol. 459, pp 2347--2392, 2003.

[9] Zhou M. and McDowell D. L. "Equivalent continuum for dynamically deforming atomistic particle systems", *Phil. Mag. A*, Vol. 82, No. 13, pp 2547--2574, 2002.

[10] Pyrz, R. "The concept of strain tensor at atomic level" *Proceedings of the 2006 Multifunctional Nanocomposites International Conference (CD-Rom)*, Honolulu, Hawaii, U.S.A, paper no. 17026, 2006.

[11] Sun, H., "Compass: An ab initioforce–field optimized for condensed phase applications – overview with details on alkane and benzene compounds". *J. Phys. Chem.B,* Vol. 102, pp. 7338–7364, 1998.

[12] Gradshteyn, L. S., and Ryzhik, I. M., *Table of Integrals Series and Products, 6th. Ed.* Academic Press, 2000.

[13] Calvo, N., Idelsohn, S. R., and Onate, E. "The extended Delaunay tessellation". *Engineering Communications*, Vol. 20, No. 5/6, pp. 583-600, 2003.

[14] Idelsohn, S. R., Onate, E., Calvo, N., and Pin, F. D., "The meshless finite element method", *Int. J. Num. Meth. Engng.,* Vol. 58, pp. 893-912, 2003.