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Partial stresses in heterogeneous media by a direct statistical approach

Paul Jouanna, Laurent Pèdesseau

*Équipe dynamique et thermodynamique des milieux complexes, UMR HSM 5569, MSE-ISTEEM, case 13,
Université Montpellier II, 34095 Montpellier cedex 5, France*

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Abstract

The total stress tensor in a structured or non-structured medium can be obtained by a direct statistical approach using the generalized virial theorem, without any reference to a potential function, as soon as positions, velocities and interactions of the particles are given by Molecular Dynamics. However, as shown here, it would be wrong to apply these results to a given class of particles in an heterogeneous medium without adding a cross internal virial tensor to the self internal virial tensor and the partial kinetic energy tensor relative to this class of particles. *To cite this article: P. Jouanna, L. Pèdesseau, C. R. Mecanique 332 (2004).*

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Résumé

Contraintes partielles en milieux hétérogènes par une approche statistique. Le tenseur total des contraintes dans un milieu structuré ou non-structuré peut être obtenu par une approche statistique directe à l'aide du théorème du viriel généralisé, sans référence aucune à une fonction potentiel, dès lors que positions, vitesses et interactions des particules sont connues en Dynamique Moléculaire. Cependant, comme montré ici, il serait erroné d'appliquer ces résultats à une classe de particules dans un milieu hétérogène sans l'ajout d'un tenseur viriel intérieur croisé, en plus du tenseur viriel intérieur propre et du tenseur énergie cinétique relatifs à cette classe de particules. *Pour citer cet article : P. Jouanna, L. Pèdesseau, C. R. Mecanique 332 (2004).*

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E-mail address: jouanna@msem.univ-montp2.fr (P. Jouanna).

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1. Introduction

1.1. Classical continuum approach of the stress tensor and partial stress tensor

In classical continuum mechanics, the stress tensor $\underline{\sigma}$ results from the first Euler's law [1] applied to the Cauchy's tetrahedron [2], in the classical non-polar case [3], section D. Stress, I and II, pp. 530–568. This tensor allows one to specify the stress vector $\mathbf{t}(\mathbf{n})$ which is applied at any point \mathbf{r} of the surface of any arbitrary volume. In heterogeneous media, in presence of Π different constituents π , attempts have been made to introduce the notion of partial stresses by Duhem, Reynolds, Jaumann, Prigogine, Truesdell and Toupin [3], section D. Stress, §215 and corresponding footnotes, pp. 567–568. These attempts were essentially applied to mixtures or to porous media. Finally, a generalised theory was developed for overcoming discrepancies when writing fundamental principles [4,5] in the most general case of heterogeneous media.

However, the use of partial stresses, as formally defined in the preceding theories, is facing in practice three levels of difficulties. Firstly, a quantification of partial stresses is not generally accessible to instrumentation and the experimental behaviour relationships of the different constituents cannot be established. Moreover, relationships relative to one constituent depend on all the other constituents. Finally the generation of behaviour laws, to be implemented in pure phenomenological models, appears to be a dream in complex heterogeneous media.

The above dilemma are fundamentally linked to the description of the matter as a black box. For penetrating this black box, homogenisation techniques are of great help. However, they face, at the microscopic level, the same difficulty, i.e., introducing the behaviour of the different constituents and are often based on assumed artificial model structures.

1.2. Alternative approach by statistical physics

A physical alternative approach, as proposed here, consists in starting deliberately from the discrete description of the matter at the atomic scale. To come back to coarser scales, the first step consists in converting atomic properties into average macroscopic entities by statistical physics. At this scale, physical experiments are today available, using for instance the Atomic Force Microscope; however they face again the same difficulty for investigating the behaviour of the different constituents.

At this stage, the breakthrough consists in replacing 'physical experiments' by 'numerical experiments', based on the knowledge of the atomic structure (X-ray, neutron diffraction, etc.) and the basic atomic interactions given by fundamental physics (Ab Initio). Such an approach is no more a dream due to the huge development in the late years of numerical computing capacities. The main issue is the possibility of *quantifying partial stresses* based on average positions and velocities of particles, as obtained by Molecular Dynamics.

This approach is based on the possibility of computing partial stress tensors at the atomic scale whatever the complexity of the matter may be. Basic statistical physics allows defining an average fluid pressure on a set of particles at the thermodynamic limit using the virial approach [6]. The stress tensor in a structured matter considered as homogeneous can be approached by the generalised virial approach [7]. However, it would be entirely wrong to extend directly the total stress expression to the partial stress of a subset of particles, without including an extra virial term, as developed hereunder.

2. Extending the generalized virial theorem to heterogeneous media

The generalized virial theorem valuable for an homogeneous structured medium can be extended to an heterogeneous medium considered as including Π different subsets π ($\pi = \pi_1, \pi_2, \dots, \pi_\Pi$) of particles, such as constituents, species or phases. The 'partial virial tensor' $\underline{\mathbf{V}}_\pi$ and the 'partial kinetic energy tensor' $\underline{\mathbf{E}}_{c\pi}$ relative to the subset π including N_π particles (i_π) are defined as follows:

$$\underline{\mathbf{V}}_{\pi} = \sum_{i\pi=1}^{N\pi} \mathbf{r}_{i\pi} \otimes \mathbf{f}_{i\pi} \quad \text{noted} \quad \sum_{i \in \pi} \mathbf{r}_i \otimes \mathbf{f}_i \quad (1)$$

$$\underline{\mathbf{E}}_{c\pi} = \sum_{i\pi=1}^{N\pi} \frac{\mathbf{p}_{i\pi} \otimes \mathbf{p}_{i\pi}}{2m_{i\pi}} \quad \text{noted} \quad \sum_{i \in \pi} \frac{\mathbf{p}_i \otimes \mathbf{p}_i}{2m_i} \quad (2)$$

with $\mathbf{r}_{i\pi}$ position of particle (i_{π}) at time t , $\mathbf{f}_{i\pi}$ force applied to particle (i_{π}) at time t , $\mathbf{p}_{i\pi}$ momentum of particle (i_{π}) at time t , $m_{i\pi}$ mass of particle (i_{π}).

Within a heterogeneous medium, the generalized virial theorem can be directly extended to any subset π of particles, stating that *the sum of the partial average virial tensor and twice the partial average kinetic tensor is equal to naught*:

$$\overline{\underline{\mathbf{V}}}_{\pi} + 2\overline{\underline{\mathbf{E}}}_{c\pi} = \mathbf{0} \quad (3)$$

This property can be verified considering the Hamilton–Jacobi equations of the microscopic movement of any particle belonging to the subset π given by:

$$\frac{d\mathbf{r}_{i\pi}}{dt} = \frac{\mathbf{p}_{i\pi}}{m_{i\pi}} \quad (4)$$

$$\frac{d\mathbf{p}_{i\pi}}{dt} = \mathbf{f}_{i\pi} \quad (5)$$

The material derivative of the tensorial product of the position vector $\mathbf{r}_{i\pi}$ by the momentum vector $\mathbf{p}_{i\pi}$ can be written:

$$\frac{d}{dt}(\mathbf{r}_{i\pi} \otimes \mathbf{p}_{i\pi}) = \mathbf{r}_{i\pi} \otimes \frac{d\mathbf{p}_{i\pi}}{dt} + \frac{d\mathbf{r}_{i\pi}}{dt} \otimes \mathbf{p}_{i\pi} = \mathbf{r}_{i\pi} \otimes \mathbf{f}_{i\pi} + \frac{\mathbf{p}_{i\pi} \otimes \mathbf{p}_{i\pi}}{m_{i\pi}} \quad (6)$$

Summing up on the N_{π} particles of the subset π leads to:

$$\sum_{i\pi=1}^{N\pi} \frac{d}{dt}(\mathbf{r}_{i\pi} \otimes \mathbf{p}_{i\pi}) = \sum_{i\pi=1}^{N\pi} \mathbf{r}_{i\pi} \otimes \mathbf{f}_{i\pi} + \sum_{i\pi=1}^{N\pi} \frac{\mathbf{p}_{i\pi} \otimes \mathbf{p}_{i\pi}}{m_{i\pi}} = \underline{\mathbf{V}}_{\pi} + 2\underline{\mathbf{E}}_{c\pi} \quad (7)$$

The time average value $\overline{\sum_{i\pi=1}^{N\pi} \frac{d}{dt}(\mathbf{r}_{i\pi} \otimes \mathbf{p}_{i\pi})}$ of the first member of this expression tends to zero for the same reason as in the case of a homogeneous medium [6] and, according to the assumption of ergodicity at the macroscopic equilibrium, time average and ensemble average are equal, leading to the extension of the generalized virial theorem to any subset π .

3. Internal and external decomposition of the virial tensor relative to a subset π

In the case of a structured heterogeneous medium, the force applied to a particle $i \in \pi$, belonging to the subset π within the volume v , can be subdivided into:

- an *external force* $\boldsymbol{\varphi}_i$ applied by external atoms of the volume v ,
- ‘*self*’ *internal forces* \mathbf{f}_{ij} applied to the particle $i \in \pi$ by the $N_{\pi} - 1$ particles $j \in \pi$ belonging to the same subset π within the volume v ,
- ‘*cross*’ *internal forces* \mathbf{f}_{ik} applied to the particle $i \in \pi$ by particles $k \notin \pi$ belonging to other subsets within the volume v .

The total force applied to particle $i \in \pi$ can be written:

$$\mathbf{f}_i = \boldsymbol{\varphi}_i + \sum_j \mathbf{f}_{ij} + \sum_k \mathbf{f}_{ik} \quad (\text{with the convention } \mathbf{f}_{ii} = \mathbf{0}) \quad (8)$$

Thus, the virial tensor in a heterogeneous medium can be split into three tensors:

$$\sum_{i \in \pi} \mathbf{r}_i \otimes \mathbf{f}_i = \sum_{i \in \pi} \mathbf{r}_i \otimes \boldsymbol{\varphi}_i + \sum_{i \in \pi} \sum_{j \in \pi} \mathbf{r}_i \otimes \mathbf{f}_{ij} + \sum_{i \in \pi} \sum_{k \notin \pi} \mathbf{r}_i \otimes \mathbf{f}_{ik} \quad (9)$$

short notations $\sum_{i \in \pi}$ or $\sum_{j \in \pi}$ being used for summations on particles belonging to the subset π and short notation $\sum_{k \notin \pi}$ for a summation on all particles, except for particles belonging to the subset π .

This expression leads to defining the ‘partial external virial tensor’ $\underline{\mathbf{V}}_{\pi \text{ ext}}$, the ‘partial self internal virial tensor’ $\underline{\mathbf{V}}_{\pi \pi \text{ int}}$ and the ‘partial cross internal virial tensor’ $\underline{\mathbf{V}}_{\pi \pi' \text{ int}}$ as follows:

$$\underline{\mathbf{V}}_{\pi \text{ ext}} \hat{=} \sum_{i \in \pi} \mathbf{r}_i \otimes \boldsymbol{\varphi}_i \quad (10)$$

$$\underline{\mathbf{V}}_{\pi \pi \text{ int}} \hat{=} \sum_{i \in \pi} \sum_{j \in \pi} \mathbf{r}_i \otimes \mathbf{f}_{ij} \quad (11)$$

$$\underline{\mathbf{V}}_{\pi \pi' \text{ int}} \hat{=} \sum_{i \in \pi} \sum_{k \notin \pi} \mathbf{r}_i \otimes \mathbf{f}_{ik} \quad (12)$$

Thus the generalized virial theorem relative to one subset π of a heterogeneous medium can be written:

$$\overline{\underline{\mathbf{V}}_{\pi \text{ ext}}} + \overline{\underline{\mathbf{V}}_{\pi \pi \text{ int}}} + \overline{\underline{\mathbf{V}}_{\pi \pi' \text{ int}}} + 2\overline{\underline{\mathbf{E}}_{\pi c}} = \overline{\underline{\mathbf{V}}_{\pi \text{ ext}}} + \overline{\underline{\mathbf{V}}_{\pi \pi \text{ int}}} + \overline{\underline{\mathbf{V}}_{\pi \pi' \text{ int}}} + 2\overline{\underline{\mathbf{E}}_{\pi c}} = 0 \quad (13)$$

with:

$$\overline{\underline{\mathbf{V}}_{\pi \text{ ext}}} \hat{=} \left\langle \sum_{i \in \pi} \mathbf{r}_i \otimes \boldsymbol{\varphi}_i \right\rangle \quad (\text{average external virial tensor relative to } \pi) \quad (14)$$

$$\overline{\underline{\mathbf{V}}_{\pi \pi \text{ int}}} \hat{=} \left\langle \sum_{i \in \pi} \sum_{j \in \pi} \mathbf{r}_i \otimes \mathbf{f}_{ij} \right\rangle \quad (\text{average self internal virial tensor relative to } \pi) \quad (15)$$

$$\overline{\underline{\mathbf{V}}_{\pi \pi' \text{ int}}} \hat{=} \left\langle \sum_{i \in \pi} \sum_{k \notin \pi} \mathbf{r}_i \otimes \mathbf{f}_{ik} \right\rangle \quad (\text{average cross internal virial tensor relative to } \pi) \quad (16)$$

$$\overline{\underline{\mathbf{E}}_{\pi c}} \hat{=} \left\langle \sum_{i \in \pi} \frac{\mathbf{p}_i \otimes \mathbf{p}_i}{2m_i} \right\rangle \quad (\text{average kinetic energy tensor relative to } \pi) \quad (17)$$

Applied to the whole set of the N particles, the total virial tensor becomes identical to the virial tensor of an homogeneous medium, because in that case the set of particles $k \notin (\pi_1 \cup \pi_2 \cup \dots \cup \pi_\Pi)$ is empty and the total cross virial tensor vanishes.

4. External virial tensor and partial stress tensor

The external forces $\boldsymbol{\varphi}_{i\pi}$ due to external atoms on particles belonging to the subset π can be divided into ‘contact forces $\boldsymbol{\varphi}_{i\pi \text{ cont}}$ ’ applied to internal atoms $i \in (\pi \text{ cont})$ in the vicinity of the boundary, and ‘volume forces $\boldsymbol{\varphi}_{j\pi \text{ vol}}$ ’ applied by long range forces to internal atoms $j \in (\pi \text{ vol})$ within volume v . Thus the average external virial tensor can be split into an average external virial tensor $\overline{\underline{\mathbf{V}}_{\text{ext cont}}}$ due to contact forces and an average external virial tensor $\overline{\underline{\mathbf{V}}_{\text{ext vol}}}$ due to long range forces:

$$\bar{V}_{\pi \text{ ext tot}} = \bar{V}_{\pi \text{ ext cont}} + \bar{V}_{\pi \text{ ext vol}} \hat{=} \left\langle \sum_{i \in \pi \text{ cont}} \mathbf{r}_{i\pi} \otimes \boldsymbol{\varphi}_{i\pi \text{ cont}} \right\rangle + \left\langle \sum_{i \in \pi \text{ vol}} \mathbf{r}_{i\pi} \otimes \boldsymbol{\varphi}_{i\pi \text{ vol}} \right\rangle \quad (18)$$

Let us consider the $\mathbf{n} ds$ element on the boundary of the whole set of particles, \mathbf{n} being the external normal vector at position \mathbf{r} and ds the element surface. In the heterogeneous medium, the internal particles belonging to the particles of the subset π being in the vicinity of the boundary apply an average force $\langle \boldsymbol{\varphi}_{i\pi} \rangle$ on the boundary element $\mathbf{n} ds$, given by:

$$\langle \boldsymbol{\varphi}_{i\pi} \rangle \hat{=} \underline{\boldsymbol{\sigma}}_{\pi} \mathbf{n} ds \quad (19)$$

where $\underline{\boldsymbol{\sigma}}_{\pi}$ is by definition the partial stress tensor relative to the subset π , with the usual sign conventions.

The expression of $\bar{V}_{\pi \text{ ext cont}}$ can thus be written:

$$\bar{V}_{\pi \text{ ext cont}} \hat{=} \left\langle \sum_{i \in \pi \text{ cont}} \mathbf{r}_{i\pi} \otimes \boldsymbol{\varphi}_{i\pi \text{ cont}} \right\rangle = \oint_s \mathbf{r}_{i\pi} \otimes \underline{\boldsymbol{\sigma}}_{\pi} \mathbf{n} ds \quad (20)$$

A demonstration similar to the demonstration used in the case of a homogeneous medium [7], Subsection 3.2, leads to:

$$v \underline{\boldsymbol{\sigma}}_{\pi}^T = \left\langle \sum_{i \in \pi \text{ cont}} \mathbf{r}_{i\pi} \otimes \boldsymbol{\varphi}_{i\pi \text{ cont}} \right\rangle \quad (21)$$

Finally,

$$\bar{V}_{\pi \text{ ext tot}} = \bar{V}_{\pi \text{ ext cont}} + \bar{V}_{\pi \text{ ext vol}} = v \underline{\boldsymbol{\sigma}}_{\pi}^T + \left\langle \sum_{i \in \pi \text{ vol}} \mathbf{r}_{i\pi} \otimes \boldsymbol{\varphi}_{i\pi \text{ vol}} \right\rangle \quad (22)$$

5. Expression of the internal virial tensor and stresses

5.1. Partial self internal virial tensor of a subset π

The partial self internal virial tensor, relative to the particles belonging to a subset π , is given in the case of 2-body interactions by:

$$\mathbf{V}_{\pi\pi \text{ int}} \hat{=} \sum_{i \in \pi} \sum_{j \in \pi} \mathbf{r}_i \otimes \mathbf{f}_{ij} = \frac{1}{2} \sum_{i \in \pi} \sum_{j \in \pi} \overline{(\mathbf{r}_i - \mathbf{r}_j) \otimes \mathbf{f}_{ij}} \quad (23)$$

The expression of the partial internal tensor does not depend on the origin of the co-ordinates of the reference frame, because this tensor depends on the relative position of particles.

5.2. Partial cross internal virial

The preceding treatment cannot be applied to the partial cross internal virial as defined by (16) because indices i and k are assigned to distinct sets of particles and \mathbf{r}_k never appears in the first summation on i . Thus the expression of the cross internal virial tensor cannot be written in function of the relative co-ordinates $(\mathbf{r}_i - \mathbf{r}_j)$ of the particles and remains in the definition form:

$$\bar{\mathbf{V}}_{\pi\pi' \text{ int}} \hat{=} \sum_{i \in \pi} \sum_{k \notin \pi} \overline{\mathbf{r}_i \otimes \mathbf{f}_{ij}} \quad (24)$$

The partial cross internal tensor appears to depend on the origin of the co-ordinates. Indeed, if the reference frame $Oxyz$ becomes $O'x'y'z'$, the position vector \mathbf{r}_i of a particle becomes \mathbf{r}'_i and a virial tensor $\underline{\mathbf{V}}$ is modified to $\underline{\mathbf{V}'}$ as follows:

$$\underline{\mathbf{V}'} = \sum_i \mathbf{r}'_i \otimes \mathbf{f}_i = \sum_i \mathbf{r}_i \otimes \mathbf{f}_i + \sum_i \overrightarrow{O'O} \otimes \mathbf{f}_i = \underline{\mathbf{V}} + \overrightarrow{O'O} \otimes \sum_i \mathbf{f}_i \quad (25)$$

However if the inertia center of the particles considered is statistically at rest or in a steady movement, as assumed in standard statistical physics, the average value $\overline{\sum_i \mathbf{f}_i} = \mathbf{0}$. Thus $\overline{\underline{\mathbf{V}'}} = \overline{\underline{\mathbf{V}}}$, i.e., the average virial tensor becomes independent of the origin of co-ordinates in the chosen inertial frame.

The above statement can be applied to the cross internal virial tensor, considering that if the average expression $\overline{\sum_i \mathbf{f}_i} = \mathbf{0}$ on the total medium, then statistically the center of inertia of a subset of particles belonging to a subset π remains at rest or in a steady movement, i.e., $\overline{\sum_{i \in \pi} \mathbf{f}_i} = \mathbf{0}$. Thus according to the above assumptions, the average partial cross virial tensor does not depend on the choice of the origin of co-ordinates.

5.3. Computation of the partial stress relative to a subset π

Thus the generalized virial theorem extended to a subset π as expressed by (3), with the expression (11) of $\underline{\mathbf{V}}_{\pi\pi \text{ int}}$, plus the expression (12) of $\underline{\mathbf{V}}_{\pi\pi' \text{ int}}$ and the expression (22), leads to the following expression of the transpose stress tensor:

$$\underline{\boldsymbol{\sigma}}_{\pi}^T = \frac{1}{v} \left[\frac{1}{2} \sum_{i \in \pi} \sum_{j \in \pi} \overline{(\mathbf{r}_i - \mathbf{r}_j) \otimes \mathbf{f}_{ij}} + \sum_{i \in \pi} \sum_{k \notin \pi} \overline{\mathbf{r}_i \otimes \mathbf{f}_{ik}} + \sum_{i \in \pi} \frac{\overline{\mathbf{p}_i \otimes \mathbf{p}_i}}{m_i} \right] - \frac{1}{v} \left\langle \sum_{i \in \pi \text{ vol}} \mathbf{r}_{i\pi} \otimes \boldsymbol{\varphi}_{i\pi \text{ vol}} \right\rangle \quad (26)$$

Discussion:

- (i) The second term in the right-hand side member $(1/v) \sum_{i \in \pi} \sum_{k \notin \pi} \overline{\mathbf{r}_i \otimes \mathbf{f}_{ik}}$ is a term which does not appear in the expression of the total stress. Forgetting this term could generate totally wrong results, because it can be of first order as compared to other terms. For instance in a partially dried clay, the partial pressure of water can be of hundreds of bars, even if the total pressure is negligible.
- (ii) The last term of the right hand side member $-(1/v) \langle \sum_{i \in \pi \text{ vol}} \mathbf{r}_{i\pi} \otimes \boldsymbol{\varphi}_{i\pi \text{ vol}} \rangle$ is related to long range external forces $\boldsymbol{\varphi}_{i\pi \text{ vol}}$. If this term is neglected, the transpose of the partial tensor $\underline{\boldsymbol{\sigma}}_{\pi}^T$ relative to the subset π is given when positions, velocities and interactions \mathbf{f}_{ij} and \mathbf{f}_{ik} of the particles are given by a standard Molecular Dynamics. However, it must be emphasized that neglecting this last term may be incorrect in a molecular simulation, for instance in presence of long range Coulomb interactions, for instance evaluated by Ewald sums using a periodic boundary technique. In that case the cluster, where the stress is computed, is limited to the central box and long range forces, issued from atoms of periodically duplicated boxes, act as external volume forces.

5.4. Total stress

Applying (26) to the N particles of the total medium gives the total stress of the heterogeneous medium. This expression is similar to the expression of the stress obtained for a homogeneous medium, because the summation on the total medium of the second term in the right-hand side member of (26) is equal to zero, the set of particles $k \notin (\pi_1 \cup \pi_2 \cup \dots \cup \pi_N)$ becoming empty.

Assuming the long range forces to be negligible, it comes:

$$\underline{\boldsymbol{\sigma}}^T = \frac{1}{v} \left[\frac{1}{2} \sum_{i \in (\pi_1 \cup \pi_2 \cup \dots \cup \pi_N)} \sum_{j \in (\pi_1 \cup \pi_2 \cup \dots \cup \pi_N)} \overline{(\mathbf{r}_i - \mathbf{r}_j) \otimes \mathbf{f}_{ij}} + \sum_{i \in (\pi_1 \cup \pi_2 \cup \dots \cup \pi_N)} \frac{\overline{\mathbf{p}_i \otimes \mathbf{p}_i}}{m_i} \right] \quad (27)$$

5.5. Additivity of partial stresses

Summing up on all the subsets π ($\pi = 1, \dots, \Pi$) the partial stresses (26), assuming here long range forces to be negligible, leads to:

$$\sum_{\pi=1}^{\pi=\Pi} \underline{\sigma}_{\pi}^T = \sum_{\pi=1}^{\pi=\Pi} \left\{ \frac{1}{v} \left[\frac{1}{2} \sum_{i \in \pi} \sum_{j \in \pi} \overline{(\mathbf{r}_i - \mathbf{r}_j) \otimes \mathbf{f}_{ij}} + \sum_{i \in \pi} \sum_{k \notin \pi} \overline{\mathbf{r}_i \otimes \mathbf{f}_{ik}} + \sum_{i \in \pi} \frac{\overline{\mathbf{p}_i \otimes \mathbf{p}_i}}{m_i} \right] \right\} \quad (28)$$

According to the identity:

$$\sum_{\pi=1}^{\pi=\Pi} \sum_{i \in \pi} \sum_{k \notin \pi} \overline{\mathbf{r}_i \otimes \mathbf{f}_{ik}} = 0 \quad (29)$$

it comes:

$$\begin{aligned} \sum_{\pi=1}^{\pi=\Pi} \underline{\sigma}_{\pi}^T &= \sum_{\pi=1}^{\pi=\Pi} \left\{ \frac{1}{v} \left[\frac{1}{2} \sum_{i \in \pi} \sum_{j \in \pi} \overline{(\mathbf{r}_i - \mathbf{r}_j) \otimes \mathbf{f}_{ij}} + \sum_{i \in \pi} \sum_{k \notin \pi} \overline{\mathbf{r}_i \otimes \mathbf{f}_{ik}} + \sum_{i \in \pi} \frac{\overline{\mathbf{p}_i \otimes \mathbf{p}_i}}{m_i} \right] \right\} \\ &= \frac{1}{v} \left[\frac{1}{2} \sum_{i \in (\pi_1 \cup \pi_2 \cup \dots \cup \pi_{\Pi})} \sum_{j \in (\pi_1 \cup \pi_2 \cup \dots \cup \pi_{\Pi})} \overline{(\mathbf{r}_i - \mathbf{r}_j) \otimes \mathbf{f}_{ij}} + \sum_{i \in (\pi_1 \cup \pi_2 \cup \dots \cup \pi_{\Pi})} \frac{\overline{\mathbf{p}_i \otimes \mathbf{p}_i}}{m_i} \right] \end{aligned} \quad (30)$$

which proves that the summation of the partial stresses leads, under the above assumption, to the total stress:

$$\sum_{\pi=1}^{\pi=\Pi} \underline{\sigma}_{\pi}^T = \underline{\sigma}^T \quad (31)$$

This is consistent with physical intuition. The total stress is by definition the action on the box wall of particles N_1 of subset 1, N_2 of subset 2, ..., N_{π} of subset π , ..., N_{Π} of subset Π . Thus the total stress is equal to the sum of the action of all the particles. As the action of the different particles is defined here as the partial stress, the total stress must be equal to the sum of the partial stresses.

The apparent obviousness of this result is worth thinking over. The first comment is that partial stresses can be different from zero, even if the total stress is equal to zero. Such a situation is the case of a structured cluster placed in the void for instance.

The second comment concerns fluids. It is classical to define the so-called ‘partial pressure’ q_{π} of the species π as the product of the total pressure P_t by the mole fraction x_{π} of the species π .

$$q_{\pi} = x_{\pi} P_t \quad (32)$$

Except in the case where particles have no mutual interactions, this so-called ‘partial pressure’ q_{π} is different from the partial pressure p_{π} , which is defined here as a particular case of the tensor $\underline{\sigma}_{\pi}$ in the case of a fluid. Owing to the identity:

$$x_1 + x_2 + x_{\pi} + \dots + x_{\Pi} = 1 \quad (33)$$

summing up these so-called ‘partial pressures’ leads also to the total pressure:

$$\sum_{\pi} q_{\pi} = P_t \quad (34)$$

Even if this relation looks like a special case of (31), its proof and its meaning are, in general, entirely different.

6. Conclusion

The generalised virial theorem extended to structured heterogeneous media leads to the transpose partial stress tensor, relative to any subset of constituents, by adding, in a unit volume, the average partial self internal virial tensor, twice the average partial kinetic energy tensor, the average partial cross internal virial tensor and a possible long range forces term. For the sake of simplicity, 2-body interactions are assumed in all the above developments. However an extension of these concepts is possible in the presence of 3-body interactions [8].

The main issue here is to give to partial stresses a physical meaning via a Molecular Dynamics numerical experiment, when a phenomenological approach poses only their formal definition and when a physical experimentation is not possible. If necessary, these partial stresses can feed an homogenisation process to come back to a macro scale. Partial stresses are computed under the equilibrium assumption of statistical physics, this restriction being consistent with their status of state variable, but their expression is not affected by a macroscopic evolution which is very slow as compared to the motion of particles. Their divergence, as stated in a classical momentum balance equation, gives in fact a macroscopic information on momentum exchanges between particles at the atomic scale. However, this contribution has not to be confused, in the same balance equation, with the volumetric rate of momentum exchanges between constituents, occurring in a non-equilibrium macroscopic diffusion movement. Briefly, the divergence of partial stresses obtained by statistical physics gives a global information on momentum exchanges between constituents at the atomic scale, in the same manner as temperature does for the kinetic energy of particles.

In practice, quantified partial stresses can be used as criteria in heterogeneous media, as total stress in homogeneous media. For instance, the cohesion of a structured medium in presence of a fluid with additives can be quantified using the partial tensor relative to the solid. Similarly the degree of interaction between different species in an alloy can be quantified by their partial tensors. The consistency of a gel depending on additives can be estimated in the same manner, etc.

Finally, instead of being a competitive treatment, statistical physics becomes today a fully complementary approach to classical mechanics, bringing information from ‘numerical experiments’ at the atomic level, possibly through homogenisation techniques, up to the phenomenological level.

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