

The stress tensor in Thermodynamics and Statistical Mechanics

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Abstract

We prove that the stress tensor, τ^{ab} , of a molecular system with arbitrary, short-range interactions can be point-wisely expressed as the functional derivative of the partition function with respect to the local deformation tensor. In this approach the set of components of τ^{ab} has a simple interpretation as the set of Lagrangian multipliers which need to be introduced to enforce the conditions relating point particle displacements to the body local deformation tensor. The question of the non-uniqueness of the formula for τ^{ab} is discussed.

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1 Introduction

It has been shown in [1] that the invariance of the partition function of a molecular system under the change of variables induced by the (measure preserving) canonical transformation ¹

$$[\{\vec{r}\}, \{\vec{p}\}] \rightarrow [\{\vec{r}'\}, \{\vec{p}'\}], \quad (1)$$

$$r_i'^a = r_i^a + \epsilon^a(\vec{r}_i), \quad i = 1, 2, \dots, N, \quad (2)$$

$$p_i^a = \left. \frac{\partial r_i'^a(\vec{r})}{\partial r^b} \right|_{\vec{r}=\vec{r}_i} p_i'^b = \left[\delta^{ab} + \left. \frac{\partial \epsilon^a(\vec{r})}{\partial r^b} \right|_{\vec{r}=\vec{r}_i} \right] p_i'^b, \quad (3)$$

where $\vec{\epsilon}(\vec{r})$ represents the infinitesimal displacement of the body elements ² at the point \vec{r} , implies for a system with short-range interactions the local equilibrium condition [2]

$$\nabla^b \tau^{ab}(\vec{r}) + \mathcal{F}_{\text{ext}}^a(\vec{r}) = 0 \quad (4)$$

with $\tau^{ab}(\vec{r})$ the stress tensor at the point \vec{r} and $\mathcal{F}_{\text{ext}}^a(\vec{r})$ an external force (density). The local expression of $\tau^{ab}(\vec{r})$ in terms of the degrees of freedom (dof's) of the elementary constituents of the body was derived by explicitly computing the functional derivative of the partition function with respect to the particle displacement and comparing with eq. (4). The generality of the approach guarantees its validity in any statistical *ensemble*, for whichever type of (short-range) potential and boundary conditions, and in a classical as well in a quantum mechanical setting (see [1] for details).

The purpose of this brief note is twofold. First of all, after recalling how the equilibrium condition (4) can be deduced from purely thermodynamic considerations, we prove that to the set of stress tensor components can be given an elegant interpretation as the set of Lagrange multipliers that are needed to enforce the relation between the displacement vector, $\vec{\epsilon}(\vec{r})$, and the deformation tensor, $\eta^{ab}(\vec{r})$, given by the formula [2]

$$\eta^{ab}(\vec{r}) = \frac{1}{2} [\nabla^a \epsilon^b(\vec{r}) + \nabla^b \epsilon^a(\vec{r})]. \quad (5)$$

Secondly we rederive the local expression of the stress tensor for a molecular system (endowed with short-range interactions) by moving from the “passive” interpretation of the transformation (2) (followed in [1]) where eqs. (2) and (3) are seen as a mere change of variables, to an “active” one where we imagine that $\vec{\epsilon}(\vec{r})$ is the

¹A sum over repeated spatial indices ($a, b, \dots = 1, \dots, D$) is understood. We also frequently use the shorthand notation $\partial f(\vec{r})/\partial r^a = \nabla^a f(\vec{r})$.

²Boundary conditions matching those imposed to the body must be obeyed by the function $\vec{\epsilon}(\vec{r})$.

actual infinitesimal displacement of the body elementary constituents at the point \vec{r} .

As a fall-out of the approach we present in this paper the question of the uniqueness of the stress tensor [6] can be neatly addressed with the conclusion that no ambiguity affects the formula (23) below. We will show, in fact, that there is no freedom to add to this expression any arbitrary divergenceless, symmetric rank-two tensor, as *a priori* geometrically allowed by the structure of eq. (4).

2 Mechanics and thermodynamics

Let us start with a discussion of the physics of local body deformations. Assuming that the system is at mechanical equilibrium at fixed temperature, the principle of virtual works [3] ensures us that the work done by the body under an infinitesimal local deformation is zero. Furthermore, if the deformation transformation is reversible, the variation of the free energy will be equal to minus the work done by the body [4]. In these circumstances one can write the variation of the free energy of the system under an infinitesimal (reversible) deformation, as a function of the particle displacement vector and deformation tensor, in the form

$$d\mathcal{A}(\eta, \epsilon) = -\delta_{rev}L(\eta, \epsilon) = \int_V d^3r \tau^{ab}(\vec{r})\eta^{ab}(\vec{r}) - \int_V d^3r \mathcal{F}_{\text{ext}}^a(\vec{r})\epsilon^a(\vec{r}), \quad (6)$$

where the first term in the last equality corresponds to the work done by the body deformation and the second to the work done by the external force (if there is one). As recalled above, the sum of the two contribution vanishes provided the displacement vector and the deformation tensor are related as in eq. (5).

The way to see what the condition of thermodynamic equilibrium implies for this constrained system, is to introduce Lagrange multipliers, λ^{ab} , to enforce eqs. (5), and define the “unconstrained” variation of \mathcal{A}

$$d\mathcal{A}_{\text{uncon}}(\eta, \epsilon; \lambda) = \int_V d^3r \tau^{ab}(\vec{r})\eta^{ab}(\vec{r}) - \int_V d^3r \mathcal{F}_{\text{ext}}^a(\vec{r})\epsilon^a(\vec{r}) + \\ - \int_V d^3r \lambda^{ab}(\vec{r}) \left[\eta^{ab}(\vec{r}) - \frac{1}{2}[\nabla^a \epsilon^b(\vec{r}) + \nabla^b \epsilon^a(\vec{r})] \right]. \quad (7)$$

Imposing the vanishing of $d\mathcal{A}_{\text{uncon}}(\eta, \epsilon; \lambda)$ immediately yields the relations

$$\tau^{ab}(\vec{r}) - \lambda^{ab}(\vec{r}) = 0, \quad (8)$$

$$\mathcal{F}_{\text{ext}}^a(\vec{r}) + \nabla^b \lambda^{ab}(\vec{r}) = 0. \quad (9)$$

Eqs. (8) provide the announced interpretation of the set of stress tensor components as the set of Lagrange multipliers which enforce the constraints (5). Eliminating λ^{ab} between eqs. (8) and (9) gives back the body equilibrium condition (4).

3 Statistical Mechanics

We now want to get an explicit expression of the stress tensor in terms of the elementary dof's of the system. To this end we need to display the functional dependence of the free energy on η^{ab} and ϵ^a . Upon comparing with the form of eq. (6), one can derive the desired formula for $\tau^{ab}(\vec{r})$.

The procedure outlined above can be straightforwardly implemented in Statistical Mechanics. Let us consider, in fact, a system interacting through the short-range potential $\mathcal{U}[\{q\}]$ and let $\mathcal{U}_{\text{ext}}[\{q\}]$ be a generic external potential. Working, for concreteness, in the *canonical ensemble* (but the argument that follows would similarly go through in the *micro-canonical ensemble* [1]), one has for the free energy the formulae

$$\mathcal{A} = -\frac{1}{\beta} \log \mathcal{Z}_c^0, \quad (10)$$

$$\mathcal{Z}_c^0 = \int \prod (d^D p) \int_V \prod (d^D q) \exp \left(-\beta \mathcal{H}_{\text{ext}}^0[\{q\}, \{p\}] \right), \quad (11)$$

$$\mathcal{H}_{\text{ext}}^0[\{q\}, \{p\}] = \mathcal{H}^0[\{q\}, \{p\}] + \mathcal{U}_{\text{ext}}[\{q\}], \quad (12)$$

$$\mathcal{H}^0[\{q\}, \{p\}] = \sum_{i=1}^N \frac{(\vec{p}_i)^2}{2m} + \mathcal{U}[\{q\}]. \quad (13)$$

In eq. (11) the symbol $\prod^N (d^D p) \prod^N (d^D q)$ is a short-hand notation for the D -dimensional integration measure over the system phase space and V is the volume of the box in which the system is contained. The superscript “0” in the previous equations is to recall that they refer to the undeformed body in equilibrium.

To find the functional dependence of the free energy upon η^{ab} and ϵ^a , we have to provide the expression of the Hamiltonian of a system subjected to a local deformation (of the type indicated in eq. (2)). To this end we first notice that under the infinitesimal displacement $\vec{\epsilon}(\vec{q})$ the line element squared changes according to the formula [2]

$$dq^a dq^a \rightarrow dq^a dq^a + 2\eta^{ab}(\vec{q}) dq^a dq^b, \quad (14)$$

with $\eta^{ab}(\vec{q})$ related to $\epsilon^a(\vec{q})$ as in eq. (5). Consequently also the kinetic energy of the system will get modified because of the addition of the extra contribution coming from the second term in eq. (14). In fact, from eq. (14) one formally gets for the modulus square of the velocity

$$\frac{dq^a}{dt} \frac{dq^a}{dt} \rightarrow \frac{dq^a}{dt} \frac{dq^a}{dt} + 2\eta^{ab}(\vec{q}) \frac{dq^a}{dt} \frac{dq^b}{dt}. \quad (15)$$

The Hamiltonian of the deformed system will thus read

$$\begin{aligned} \mathcal{H}_{\text{ext}}[\{q\}, \{p\}; \eta, \epsilon] &= \mathcal{H}_{\text{ext}}^0[\{q\}, \{p\}] + \\ &- \sum_{i=1}^N \eta^{ab}(\vec{q}_i) \frac{p_i^a p_i^b}{m} - \frac{1}{2} \sum_{j \neq i=1}^N \eta^{ab}(\vec{q}_i) q_{ij}^a \mathcal{F}_{ij}^b[\{q\}] - \sum_{i=1}^N \epsilon^a(\vec{q}_i) \mathcal{F}_{i,\text{ext}}^a[\{q\}], \end{aligned} \quad (16)$$

where we have introduced the definitions

$$\mathcal{F}_{ij}^a[\{q\}] = -\frac{\partial \mathcal{U}[\{q\}]}{\partial q_{ij}} \cdot \frac{q_{ij}^a}{q_{ij}}, \quad \mathcal{F}_{i,\text{ext}}^a[\{q\}] = -\frac{\partial \mathcal{U}_{\text{ext}}[\{q\}]}{\partial q_i^a}, \quad (17)$$

$$\vec{q}_{ij} = \vec{q}_i - \vec{q}_j, \quad q_{ij} = \sqrt{\vec{q}_{ij}^2}. \quad (18)$$

The first term in the second line in the r.h.s. of eq. (16) comes directly from eq. (15) after passing from velocities to canonical momenta. The second and third term arise as a consequence of the particle displacement $q^a \rightarrow q_i^a + \epsilon^a(\vec{q}_i)$ (eq. (2)) in $\mathcal{U}[\{q\}]$ and $\mathcal{U}_{\text{ext}}[\{q\}]$, respectively. While the structure of the third term is obvious, the form of the second needs some explanation. First of all, we observe that we can always consider a translationally invariant interaction potential as a function of the set of the two-particle distances $\{q_{ij}\}$. Secondly, since \mathcal{U} is assumed to be short-range on the macroscopic scale over which $\vec{\epsilon}$ can appreciably vary, we conclude that one can get non-vanishing contributions to the r.h.s. of eq. (16) only from terms where all particle distances are very small (smaller than some typical microscopic length). In computing the variation of q_{ij} under a particle displacement, we are then justified in writing

$$q_i^a - q_j^a \rightarrow q_i^a + \epsilon^a(\vec{q}_i) - q_j^a - \epsilon^a(\vec{q}_j) = \nabla^b \epsilon^a(\vec{q}_i) (q_i^b - q_j^b) + \dots, \quad (19)$$

$$q_{ij} \rightarrow q_{ij} + \frac{1}{2} [\nabla^a \epsilon^b(\vec{q}_i) + \nabla^b \epsilon^a(\vec{q}_i)] \frac{q_{ij}^a q_{ij}^b}{q_{ij}} \dots = q_{ij} + \eta^{ab}(\vec{q}_i) \frac{q_{ij}^a q_{ij}^b}{q_{ij}} \dots, \quad (20)$$

where dots represent terms of higher order in the differences q_{ij}^a , that we neglect. When eq. (20) is introduced in $\mathcal{U}[\{q\}]$, the second term immediately emerges by expanding in the small quantity η^{ab} .

We stress that, as expected, in (16) the body deformation is completely described by the tensor η^{ab} , while the displacement ϵ^a is directly coupled only to the external force.

Inserting the Hamiltonian (16) in the formulae for the partition function and free energy, one obtains the sought for functional dependence on η^{ab} and ϵ^a . To first order in η^{ab} and ϵ^a one thus gets for the free energy variation

$$d\mathcal{A}(\eta, \epsilon) = \frac{1}{\mathcal{Z}_c^0} \int \prod (d^D p) \int_V \prod (d^D q) e^{-\beta \mathcal{H}_{\text{ext}}^0[\{q\}, \{p\}]}.$$

$$\cdot \left[- \sum_{i=1}^N \eta^{ab}(q_i) \frac{p_i^a p_i^b}{m} - \frac{1}{2} \sum_{j \neq i=1}^N \eta^{ab}(q_i) q_{ij}^a \mathcal{F}_{ij}^b[\{q\}] - \sum_{i=1}^N \epsilon^a(q_i) \mathcal{F}_{i,\text{ext}}^a[\{q\}] \right]. \quad (21)$$

For an easy comparison to the equations of sect. 2 it is convenient to introduce in each term of the sum over the index i , the identity $\int_V d^3r \delta(\vec{r} - \vec{q}_i) = 1$. Having done this, eq. (21) can be cast in the form

$$\begin{aligned} d\mathcal{A}(\eta, \epsilon) &= \\ &= \int_V d^3r \eta^{ab}(\vec{r}) \left\langle - \sum_{i=1}^N \delta(\vec{r} - \vec{q}_i) \frac{p_i^a p_i^b}{m} - \frac{1}{2} \sum_{j \neq i=1}^N \delta(\vec{r} - \vec{q}_i) q_{ij}^a \mathcal{F}_{ij}^b[\{q\}] \right\rangle + \\ &- \int_V d^3r \epsilon^a(\vec{r}) \left\langle \sum_{i=1}^N \delta(\vec{r} - \vec{q}_i) \mathcal{F}_{i,\text{ext}}^a[\{q\}] \right\rangle, \end{aligned} \quad (22)$$

where $\langle \dots \rangle$ means *ensemble* average. Comparing with eq. (6), the expression of $\tau^{ab}(\vec{r})$ in terms of the elementary dof's of the system is readily identified as the tensor that multiplies the deformation tensor in the formula for the work done by the system under a local deformation. One finds in this way

$$\tau^{ab}(\vec{r}) = - \left\langle \sum_{i=1}^N \delta(\vec{r} - \vec{q}_i) \left(\frac{p_i^a p_i^b}{m} + \frac{1}{2} \sum_{j (\neq i)=1}^N q_{ij}^a \mathcal{F}_{ij}^b[\{q\}] \right) \right\rangle. \quad (23)$$

This formula is in agreement with [1] and, once integrated over volume, with the expression that can be found in the classical papers of ref. [5].

In closing we observe that the approach we have developed allows to answer the old question of whether a stress tensor obeying eq. (4) is unique or not [6]. The question arises, as from a purely geometrical point of view, one could imagine to add to whichever expression of τ^{ab} an arbitrary divergenceless, symmetric rank-two tensor, still fulfilling eq. (4). However if, as we advocate in this paper, τ^{ab} is identified as the tensor which multiplies the deformation tensor, η^{ab} , in the formula which expresses the work done by the system under an infinitesimal local deformation (eq. (6)), such a freedom does not exist anymore.

4 Conclusions

In this note we have given a consistent derivation of the microscopic expression of the stress tensor of a body, that complies with the principles of Thermodynamics and takes properly into account the geometrical constraints existing between the particle displacement vector and the body deformation tensor. In agreement with what is known to happen in the case of a continuum system, we find that the

possibility of defining a (local) stress tensor rests on the assumption that the interaction potential between the body elementary constituents (for the rest fully arbitrary) is “short-range”. The discussion we give is totally general and holds in any *ensemble* and whichever the boundary conditions imposed to the system might be. Remarkably the whole procedure goes through also in a quantum-mechanical setting [1].

A consequence of the line of reasoning we have presented above is that apparently there is no room for any ambiguity in the expression of the stress tensor we derive, if τ^{ab} is identified with the tensor which multiplies the deformation tensor in the formula for the work done by the system under an infinitesimal local deformation.

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