

# The stress tensor of a molecular system: an exercise in Statistical Mechanics

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## Abstract

We prove that conservation of the stress tensor is a consequence of the invariance of the partition function under canonical diffeomorphisms. From this observation a simple and general derivation of the formula which gives the local expression of the stress tensor of a molecular system in terms of its microscopic degrees of freedom readily follows. The derivation is valid in the *canonical* as well as the *micro-canonical ensemble*. It works both in the classical and in the quantum mechanical setting and for arbitrary boundary conditions. In particular, if periodic boundary conditions are assigned to the system, the usual minimal-image prescription is naturally born out for mathematical consistency. An interesting outcome of our general analysis is that only in the case of a short-range interaction potential a truly local formula for the stress tensor can exist.

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# 1 Introduction

We show in this paper that the microscopic expression of the stress tensor of a molecular system can be derived from the general methods of Statistical Mechanics, by studying the response of the system under local (volume preserving) deformations, after coupling it to an external force. The stress tensor is identified by looking at the equilibrium condition that results from the invariance of the partition function (appropriate to the *ensemble* in consideration) under the canonical extension of the point-transformations (canonical diffeomorphisms) generating local deformations.

The problem of constructing the stress tensor from general principles has been considered in the past by a number of authors. A far from exhaustive list of papers dealing with the classical and quantum cases can be found in [1, 2, 3, 4] and [5, 6], respectively, as well as in the many references quoted therein.

In this work we rely on intrinsic invariance properties of the partition function exploiting a procedure very similar to that leading to the Nöther theorem in classical Mechanics or rather to Ward-Takahashi identities in Quantum Field Theory [7].

An important result of this general approach is that the expression of the stress tensor depends on whether the interaction potential among the elementary constituents of the system is short-range or not. While the expression we find reassuringly coincides with the standard formula currently used in actual simulations in the first case (see eq. (3.20)), this is not so if the system is endowed with a non short-range interaction potential. In such a situation the previous formula should be replaced by the expression (5.5).

The strategy we have developed can be directly extended to a quantum mechanical setting, by making reference the local unitary operator that implements the canonical diffeomorphism of the classical theory. The stress tensor, which, as it should, is an hermitian operator, acquires a somewhat complicated form because of the non-commutativity of canonically conjugate  $q$  and  $p$  variables.

It is important to emphasize that our method works with whichever boundary conditions are imposed to the system, thanks to the local nature of diffeomorphism transformations. In particular, we remark that the standard minimal-image prescription [8] automatically emerges if the system obeys periodic boundary conditions (PBC's).

We also prove that both in the classical and the quantum case the formulae we find for the stress tensor have the same expression in the *canonical* and *micro-canonical ensemble*, as expected on the basis of general theorems [9].

We wish to conclude with the following important observation. It can be show that the expressions one gets for the stress tensor in classical and quantum

mechanics are both consistent with the equations that in Statistical Mechanics lead to the virial formula for the pressure [10]. For the sake of conciseness we give here the formal proof of this statement, only in the non trivial quantum mechanical case (see Appendix B).

The plan of the paper is as follows. In Section 2 we recall the thermodynamic and the statistico-mechanical definitions of stress tensor. In Sections 3 and 4 we give a derivation of the microscopic expression of the stress tensor for a classical system with short-range potential in the *canonical* and *micro-canonical ensemble*, respectively, exploiting the invariance of the corresponding partition function under canonical diffeomorphisms. In Section 5 we derive the formula of the stress tensor for a system with non short-range interactions and discuss the *micro*  $\leftrightarrow$  *macro* transition, inherent in any statistico-mechanical approach to Thermodynamics. In Section 6 we extend our arguments to the quantum case. Conclusions can be found in Section 7. In Appendix A we discuss a technical problem related to the notion of *ensemble* average in the *micro-canonical ensemble*. The content of Appendix B was described before.

## 2 Definition of stress tensor

Following the classical books of ref. [10], we recall that the definition of the stress tensor  $\tau^{ab}(\vec{r})$  at the point  $\vec{r}$  is given by the thermodynamic formulae

$$\tau^{ab}(\vec{r}) = \left. \frac{\delta \mathcal{A}}{\delta \eta^{ab}(\vec{r})} \right|_T, \quad \text{or} \quad \tau^{ab}(\vec{r}) = -T \left. \frac{\delta \mathcal{S}}{\delta \eta^{ab}(\vec{r})} \right|_{\mathcal{E}}, \quad (2.1)$$

depending on whether one works at fixed temperature,  $T$ , or energy,  $\mathcal{E}$ . In eqs. (2.1) the symbol  $\delta/\delta\eta^{ab}(\vec{r})$  means functional derivative at the point  $\vec{r}$ , being  $\eta^{ab}(\vec{r})$  the deformation tensor at that point<sup>1</sup>. The quantities  $\mathcal{A}$  and  $\mathcal{S}$  are the total Helmholtz free energy and entropy of the system, respectively<sup>2</sup>.

The symmetric tensor  $\eta^{ab}$  describes the response of the system to a displacement of its particle coordinates of the form  $\vec{r} \rightarrow \vec{r}' = \vec{r}'(\vec{r})$ , as it controls the change of the relative square distance,  $dl^2$ , of pairs of points through the equation [10]

$$dl^2 \rightarrow dl'^2 = dl^2 + 2\eta^{ab}dx^a dx^b. \quad (2.2)$$

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<sup>1</sup>With reference to the spatial indexes  $a, b, c, \dots = 1, 2, \dots, D$ , the Einstein summation convention over repeated indexes will be adopted in the following.

<sup>2</sup>For the purpose of this paper we have written the thermodynamic formulae yielding the expression of the stress tensor in a slightly more general fashion than in ref. [10].

Introducing the definition  $\vec{u} = \vec{r} - \vec{r}'$ , one gets

$$\eta^{ab} = \frac{1}{2} \left( \frac{\partial u^a}{\partial x^b} + \frac{\partial u^b}{\partial x^a} + \frac{\partial u^c}{\partial x^a} \frac{\partial u^c}{\partial x^b} \right). \quad (2.3)$$

The formulae (2.1) have an immediate translation in the language of Statistical Mechanics, if one simply remembers that the logarithm of the partition function is (proportional to) the Helmholtz free energy in the *canonical ensemble* and to the entropy in the *micro-canonical ensemble*. In the thermodynamic limit the same result for the stress tensor should be obtained by the use of either one or the other of the two equations ( $\beta = 1/k_B T$ )

$$\tau^{ab}(\vec{r}) = -\frac{1}{\beta} \frac{\delta \log \mathcal{Z}_c}{\delta \eta^{ab}(\vec{r})}, \quad (2.4)$$

$$\tau^{ab}(\vec{r}) = -\frac{1}{\beta} \frac{\delta \log \mathcal{Z}_{mc}}{\delta \eta^{ab}(\vec{r})}, \quad (2.5)$$

where  $\mathcal{Z}_c$  and  $\mathcal{Z}_{mc}$  are the partition functions in the *canonical* and *micro-canonical ensemble*. The above equations, although formally correct, are not of practical use for the purpose of computing  $\tau^{ab}$ , because one does not know in general how to enforce the constraint  $T = \text{const}$  in eq. (2.4) or  $E = \text{const}$  in eq. (2.5), while taking the (functional) derivative with respect to the deformation tensor (recall the formulae in eq. (2.1)).

In the next sections we propose and discuss a general strategy to overcome this difficulty. The construction of  $\tau^{ab}(\vec{r})$  is carried out by subjecting the system to an external force,  $\vec{F}_{\text{ext}}$  and exploiting the invariance of the partition function of this “augmented” system under canonical point-transformation (canonical diffeomorphisms). One ends up in this way with a conservation equation of the type

$$\frac{\partial \tau^{ab}(\vec{r})}{\partial x^b} + F_{\text{ext}}^a(\vec{r}) = 0, \quad (2.6)$$

from which the expression of the stress tensor can be read off (up to the usual ambiguity which amounts to adding to it a symmetric, divergenceless tensor<sup>3</sup>).

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<sup>3</sup>Some time after the publication of the seminal paper of ref. [1] it was realized that the definition of stress tensor suffer from an apparently intrinsic ambiguity which amounts to the possibility of adding a symmetric, divergenceless tensor. The authors of ref. [11] suggested a way to parametrize this ambiguity and a prescription to fix it. The proposal was checked in a number of applications and found inconsistent with the general principles of Thermodynamics when applied to the calculation of properties at the interface of an heterogeneous two component system with planar and/or spherical geometry [12]. Later another interesting proposal to resolve the stress tensor definition ambiguity was put

### 3 The stress tensor in the *canonical ensemble*

Let us consider a system consisting of  $N$  particles (atoms) of mass  $m$ , contained in a box of volume  $V$  (of which for the moment we do not specify the nature of the boundary conditions), described by the (classical) Hamiltonian

$$\mathcal{H}[\{q\}, \{p\}] = \sum_{i=1}^N \frac{(\vec{p}_i)^2}{2m} + \mathcal{U}[\{q\}], \quad (3.1)$$

$$\mathcal{U}[\{q\}] = \frac{1}{2} \sum_{i=1}^N \sum_{j \neq i}^N \mathcal{U}_{ij}(q_{ij}), \quad q_{ij} = \sqrt{(\vec{q}_{ij})^2}, \quad \vec{q}_{ij} = \vec{q}_i - \vec{q}_j, \quad (3.2)$$

with  $\{q\}, \{p\}$  canonically conjugated variables and  $\mathcal{U}$  modeled as a pairwise interaction potential.

We will call  $\mathcal{U}$  a “short-range” potential, if  $\mathcal{U}_{ij}(q_{ij})$  goes smoothly to zero for  $q_{ij} > \xi$ , where  $\xi$  is a typical microscopic length (for instance, a length of the order of a few times the Van der Waals atomic radius).

As we explained before, in order to derive the correct microscopic formula for the stress tensor in its generality, we need to study the response of the system described by the classical Hamiltonian (3.1) to an external force [10]. To this end we add to the unperturbed Hamiltonian the external potential,  $\mathcal{U}_{\text{ext}}[\{q\}]$ . The *canonical* partition function of this augmented system is

$$\mathcal{Z}_c^{\text{aug}} = \int \prod (d^D p) \int_V \prod (d^D q) \exp \left( -\beta \mathcal{H}_{\text{ext}}[\{q\}, \{p\}] \right), \quad (3.3)$$

$$\mathcal{H}_{\text{ext}}[\{q\}, \{p\}] = \mathcal{H}[\{q\}, \{p\}] + \mathcal{U}_{\text{ext}}[\{q\}], \quad (3.4)$$

where  $\prod^N (d^D p) \prod^N (d^D q)$  is a short-hand for the  $D$ -dimensional integration measure over the system phase-space. While in (3.3) momentum integration is unrestricted, the integration over particle coordinates is limited to a box of volume  $V$ . We start by discussing the case of a box with impenetrable and reflecting walls.

We want to show that the obvious invariance of  $\mathcal{Z}_c^{\text{aug}}$  under the change of integration variables induced by the canonical diffeomorphism (see sect. 3.2) associated

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forward in ref. [13]. It consists in requiring that the stress tensor satisfy the so-called “Saint-Venan compatibility condition”. The latter is a (non-local) condition involving the curl of the stress tensor, which is thus capable of fixing the form of  $\tau_{ab}(\vec{r})$  uniquely. The procedure was challenged in [14] and subsequently rebutted in [15], but no consensus was reached. In conclusion, it is fair to say that the question of whether and how the apparent ambiguity in the definition of the stress tensor could be resolved is still a matter of debate in the literature (see also our observation below eq. (3.20))

with the infinitesimal point-transformation

$$\vec{q}_i \rightarrow \vec{q}_i' = \vec{q}_i + \vec{\epsilon}(\vec{q}_i) \quad (3.5)$$

leads in the language of Statistical Mechanics to an equilibrium condition of the form (2.6). A necessary condition the transformation (3.5) must fulfill is that it must not deform the box in which the system is enclosed. We will then require the vector function  $\vec{\epsilon}(\vec{q})$  to satisfy appropriate boundary conditions, chosen to match the boundary conditions obeyed by the system. Thus, if the system is contained in a box with impenetrable (and perfectly reflecting) walls, we will require  $\vec{\epsilon}(\vec{q})$  to vanish at the surface enclosing the box. If, instead, we are dealing with PBC's, the displacement (3.5) will have to be described by a function with exactly the same periodicity conditions as those imposed on the system (see sect. 3.4).

Point-displacements not complying with boundary conditions inevitably lead to difficulties, as often noticed in the literature. Examples of problematic choices are coordinate shifts like  $q_i^a \rightarrow q_i'^a = q_i^a + \sigma^{ab} q_i^b$ , with  $\sigma^{ab}$  a constant tensor [5].

### 3.1 Point-transformations

In order to clarify the relation between the local conservation law (2.6) and the invariance of the partition function under canonical diffeomorphisms, we start discussing the case in which the interaction is short-range. We defer consideration of the case where this condition is not fulfilled to sect. 5.

Under the displacement (3.5) coordinate differences are modified according to

$$q_i^a - q_j^a \rightarrow q_i'^a - q_j'^a = q_i^a + \epsilon^a(\vec{q}_i) - q_j^a - \epsilon^a(\vec{q}_j). \quad (3.6)$$

The key observation is that only pairs of particles with relative distance smaller than the interaction cut-off,  $\xi$ , appear in  $\mathcal{U}$ , when the potential is short-range, and thus need be considered. This means that the quantity  $q_{ij}$  is small for all pairs contributing to the sum in (3.2), and we can expand the last term in the r.h.s. of eq. (3.6) in powers of the difference  $\vec{q}_i - \vec{q}_j$ . What is to be meant by ‘‘small’’ in this context is explained below (see sects. 3.3 and 5). Expanding around the point  $\vec{q}_i$ , we get from (3.6) <sup>4</sup>

$$q_i'^a - q_j'^a = q_i^a + \epsilon^a(\vec{q}_i) - q_j^a - \epsilon^a(\vec{q}_i) + \epsilon^{ab}(\vec{q}_i) q_{ij}^b = [\delta^{ab} + \epsilon^{ab}(\vec{q}_i)] q_{ij}^b + \dots, \quad (3.7)$$

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<sup>4</sup>Had we chosen the mid-point  $\vec{q}_{ij}^{mp} = (\vec{q}_i + \vec{q}_j)/2$  as the expansion point, we would have gotten  $q_{ij}'^a = [\delta^{ab} + \epsilon^{ab}(\vec{q}_{ij}^{mp})] q_{ij}^b + \dots$ . Eq. (3.7) and the latter are, however, identical to the order we work, because  $\epsilon^{ab}(\vec{q}_{ij}^{mp}) = \epsilon^{ab}(\vec{q}_i) + O[q_{ij}]$ . The same conclusion holds expanding around any other point in the vicinity of  $\vec{q}_i$  and  $\vec{q}_j$ .

where ... represent terms of higher order in the differences  $q_{ij}^a = q_i^a - q_j^a$  and

$$\epsilon^{ab}(\vec{q}_i) = \frac{\partial \epsilon^a(\vec{q})}{\partial q^b} \Big|_{\vec{q}=\vec{q}_i}. \quad (3.8)$$

If we now work out the relation between  $(\vec{q}_{ij}')^2$  and  $(\vec{q}_{ij})^2$ , we find an expression which exactly parallels eq. (2.2), namely

$$(\vec{q}_{ij}')^2 = (\vec{q}_{ij})^2 + 2\delta\eta^{ab}(\vec{q}_i) q_{ij}^a q_{ij}^b + \dots, \quad (3.9)$$

$$\delta\eta^{ab}(\vec{q}_i) = \frac{1}{2} \left( \epsilon^{ab}(\vec{q}_i) + \epsilon^{ba}(\vec{q}_i) + \epsilon^{ac}(\vec{q}_i) \epsilon^{cb}(\vec{q}_i) \right), \quad (3.10)$$

with the symmetric tensor  $\delta\eta^{ab}(\vec{q}_i)$  representing the (infinitesimal) deformation tensor of the system at the point  $\vec{q}_i$ .

### 3.2 Canonical transformations and partition function invariance

As is well known from elementary Mechanics [17] in order to make the point-transformation (3.5) canonical, we must accompany it with the momentum transformation

$$p_i^a = \frac{\partial q_i'^a(\vec{q}_i)}{\partial q_i^b} p_i'^b = [\delta^{ab} + \epsilon^{ab}(\vec{q}_i)] p_i'^b. \quad (3.11)$$

The pair of eqs. (3.5) and (3.11) is what we have been referring to as a ‘‘canonical diffeomorphism’’ in this paper.

Recalling that under a canonical transformation the phase-space measure is invariant (*i.e.*  $\prod^N(d^D p) \prod^N(d^D q) = \prod^N(d^D p') \prod^N(d^D q')$ ), we can conveniently express the partition function (3.3) as an integral over the old variables  $\{q\}, \{p\}$  through the formulae

$$\mathcal{Z}_c^{\text{aug}} = \int \prod^N(d^D p) \int_V \prod^N(d^D q) \exp \left( -\beta \mathcal{H}_{\text{ext}}[\{q'\}, \{p'\}] \right), \quad (3.12)$$

$$\mathcal{H}_{\text{ext}}[\{q'\}, \{p'\}] = \sum_{i=1}^N \left( \frac{(\vec{p}_i')^2}{2m} + \frac{1}{2} \sum_{j(\neq i)=1}^N \mathcal{U}_{ij}(q'_{ij}) \right) + \mathcal{U}_{\text{ext}}[\{q'\}], \quad (3.13)$$

where the primed variables,  $\vec{q}_i'$ ,  $q'_{ij}$  and  $\vec{p}_i'$  are given by eqs. (3.5), (3.9) and (3.11), respectively. Explicitly, using the definitions (3.10) and (3.8) and limiting the expansions to  $O(\vec{\epsilon})$  terms, one finds

$$q'_{ij} = q_{ij} + \delta\eta^{ab}(\vec{q}_i) \frac{q_{ij}^a q_{ij}^b}{q_{ij}} + \dots = q_{ij} + \frac{1}{2} \left( \epsilon^{ab}(\vec{q}_i) + \epsilon^{ba}(\vec{q}_i) \right) \frac{q_{ij}^a q_{ij}^b}{q_{ij}} + \dots, \quad (3.14)$$

$$(\vec{p}_i')^2 = (\vec{p}_i)^2 - 2\delta\eta^{ab}(\vec{q}_i) p_i^a p_i^b + \dots = (\vec{p}_i)^2 - \left( \epsilon^{ab}(\vec{q}_i) + \epsilon^{ba}(\vec{q}_i) \right) p_i^a p_i^b + \dots$$

The canonical invariance of  $\mathcal{Z}_c^{\text{aug}}$  is now expressed by the condition that the r.h.s. of eq. (3.12) is independent of the vector function  $\vec{\epsilon}(\vec{r})$ . A convenient way to spell out the consequences of this invariance is to make reference to the condition <sup>5</sup>

$$\left. \frac{\delta \log \mathcal{Z}_c^{\text{aug}}}{\delta \epsilon^a(\vec{r})} \right|_{\vec{\epsilon}(\vec{r})=0} = 0. \quad (3.15)$$

With the aid of the formulae (see eqs. (3.14))

$$\left. \frac{\delta q'_{ij}}{\delta \epsilon^a(\vec{r})} \right|_{\vec{\epsilon}(\vec{r})=0} = -\frac{q_{ij}^a q_{ij}^b}{q_{ij}} \frac{\partial \delta(\vec{r} - \vec{q}_i)}{\partial x^b}, \quad (3.16)$$

$$\left. \frac{\delta (\vec{p}_i')^2}{\delta \epsilon^a(\vec{r})} \right|_{\vec{\epsilon}(\vec{r})=0} = 2p_i^a p_i^b \frac{\partial \delta(\vec{r} - \vec{q}_i)}{\partial x^b}, \quad (3.17)$$

where higher order terms in  $q_{ij}$  have been neglected, an explicit calculation gives

$$\begin{aligned} 0 &= -\frac{1}{\beta} \left. \frac{\delta \log \mathcal{Z}_c^{\text{aug}}}{\delta \epsilon^a(\vec{r})} \right|_{\vec{\epsilon}(\vec{r})=0} = \frac{1}{\mathcal{Z}_c^{\text{aug}}} \int \prod (d^D p) \int_V \prod (d^D q) e^{-\beta \mathcal{H}_{\text{ext}}[\{q\}, \{p\}]} \\ &\left[ \frac{\partial}{\partial x^b} \sum_{i=1}^N \delta(\vec{r} - \vec{q}_i) \left( \frac{p_i^a p_i^b}{m} - \frac{1}{2} \sum_{j(\neq i)=1}^N \frac{\partial \mathcal{U}_{ij}(q_{ij})}{\partial q_{ij}} \frac{q_{ij}^a q_{ij}^b}{q_{ij}} \right) + \sum_{i=1}^N \delta(\vec{r} - \vec{q}_i) \frac{\partial \mathcal{U}_{\text{ext}}[\{q\}]}{\partial q_i^a} \right] = \\ &= \frac{\partial}{\partial x^b} \left\langle \sum_{i=1}^N \delta(\vec{r} - \vec{q}_i) \left( \frac{p_i^a p_i^b}{m} + \frac{1}{2} \sum_{j(\neq i)=1}^N q_{ij}^a \mathcal{F}_{ij}^b(\vec{q}_{ij}) \right) \right\rangle_c^{\text{aug}} + \\ &- \left\langle \sum_{i=1}^N \delta(\vec{r} - \vec{q}_i) \mathcal{F}_{i,\text{ext}}^a[\{\vec{q}\}] \right\rangle_c^{\text{aug}}. \end{aligned} \quad (3.18)$$

In the above formulae  $\delta(\vec{r} - \vec{q}_i)$  is the  $D$ -dimensional Dirac  $\delta$ -distribution centered at  $\vec{r} = \vec{q}_i$  and the symbol  $\langle \dots \rangle_c^{\text{aug}}$  means *canonical* average in the presence of the external potential,  $\mathcal{U}_{\text{ext}}$ . In the last equality we have introduced the definitions

$$\mathcal{F}_{ij}^a(\vec{q}_{ij}) = -\frac{\partial \mathcal{U}_{ij}(q_{ij})}{\partial q_i^a} = -\frac{\partial \mathcal{U}_{ij}(q_{ij})}{\partial q_{ij}} \cdot \frac{q_{ij}^a}{q_{ij}}, \quad \mathcal{F}_{i,\text{ext}}^a[\{\vec{q}\}] = -\frac{\partial \mathcal{U}_{\text{ext}}[\{q\}]}{\partial q_i^a}, \quad (3.19)$$

which represent the force on the particle  $i$  exerted by particle  $j$  and the external force acting on particle  $i$ , respectively.

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<sup>5</sup>This procedure is very much reminiscent of the way in which Ward-Takahashi identities are derived in Quantum Field Theory [7].

### 3.3 Stress tensor

Comparing eq. (3.18) with the mechanical equilibrium condition (2.6), we can read off the (correctly normalized) expression of the stress tensor. Setting  $\mathcal{U}_{\text{ext}} = 0$ , we finally obtain for  $\tau^{ab}$  the microscopic formula

$$\tau^{ab}(\vec{r}) = -\left\langle \sum_{i=1}^N \delta(\vec{r} - \vec{q}_i) \left( \frac{p_i^a p_i^b}{m} + \frac{1}{2} \sum_{j(\neq i)=1}^N q_{ij}^a \mathcal{F}_{ij}^b(\vec{q}_{ij}) \right) \right\rangle_c. \quad (3.20)$$

From the first of eqs. (3.19) we see that, as expected,  $\tau^{ab}$  is a symmetric tensor. Furthermore, as shown in Appendix B, eq. (3.20) leads to the virial expression of the pressure [10]. In view of this observation we may conclude that the leftover ambiguity in the definition of the stress tensor which corresponds to the possibility of adding to it a symmetric, divergenceless tensor (recall the note below eq. (2.6)) is actually reduced to tensors which on top of that are also traceless.

We end this section by showing that eq. (3.20) leads to the formula currently used in actual simulations where *ensemble* averages are replaced by sums over configurations.

The fundamental issue in this discussion is under which conditions it is possible to assume that the difference  $q_{ij} = |\vec{q}_i - \vec{q}_j|$  is small so as to be entitled to use eqs. (3.16) and (3.17). The answer can only be given by looking at the *micro*  $\rightarrow$  *macro* transition step inherent in the construction of Thermodynamics from Statistical Mechanics. The way to properly carry out this step is to construct the (continuum-like) definition of the stress tensor at the point  $\vec{r}$  by taking the average of its microscopic expression over a volume,  $v_{\vec{r}}$ , centered around  $\vec{r}$ , with linear dimensions much smaller than the macroscopic scale set by the resolution power of the measuring apparatus,  $R_{rp}$ , but very large compared to the microscopic scale set by the interaction radius,  $\xi$ . The condition  $v_{\vec{r}} \gg \xi$  is necessary precisely to “quench” the statistical fluctuations associated with the granularity of the microscopic scale and can be fulfilled at the same time as  $v_{\vec{r}}^{1/D} \ll R_{rp}$ , provided the hierarchy of scales  $\xi \ll v_{\vec{r}}^{1/D} \ll R_{rp}$  holds, *i.e.* provided the interaction potential is short-range on the scale of  $R_{rp}$ . If this is the case, when we perform the volume average over  $v_{\vec{r}}$ , the only terms contributing to the double sum in eq. (3.20) are those which involve pairs of particle  $i, j$  whose relative distance,  $q_{ij}$ , is indeed “small” compared to the linear dimensions of  $v_{\vec{r}}$ . Obviously one must also have a not too low number density in order not to have too few average particles belonging to  $v_{\vec{r}}$ . Only if all these conditions are met, then by replacing the *ensemble* average,  $\langle \dots \rangle_c$ , with the sum over configurations,  $\frac{1}{N_{\text{conf}}} \sum_{\ell=1}^{N_{\text{conf}}} [\dots]_{(\ell)}$ , one obtains from eq. (3.20) (after averaging over  $v_{\vec{r}}$ ) the correct smoothly varying local expression of  $\tau^{ab}$  that could be used in actual simulations. Notice that the

formula routinely used and most frequently reported in books is the one obtained after averaging over the full volume occupied by the system.

### 3.4 The case of periodic boundary conditions

It is interesting to explicitly see how formulae (3.18) and (3.20) get modified if PBC's are assigned to the system. We recall that mathematically PBC's are implemented by taking  $\mathcal{U}$  as a periodic function of its arguments. For instance, for a hyper-cubic periodic box of side  $L$  one has

$$\mathcal{U}_{ij}(q_{ij}) = \sum_{\vec{n}} \mathcal{U}_{ij}(q_{ij}^{(\vec{n})}), \quad q_{ij}^{(\vec{n})} = |\vec{q}_i - \vec{q}_j - \vec{n}L|, \quad (3.21)$$

where  $\vec{n} \equiv (n^1, n^2, \dots, n^D)$ ,  $n^a \in \mathbf{Z}$ ,  $a = 1, 2, \dots, D$ , and it is understood that the term with  $\vec{n} = (0, 0, \dots, 0)$  is absent in the sum over  $\vec{n}$  when  $i = j$ .

As we pointed out before (see the remarks below eq. (3.5) in sect. 3), in this situation the infinitesimal parameter  $\vec{\epsilon}(\vec{q})$  will have to match the periodicity properties of the potential. In fact, since

$$I) \vec{q}_i \rightarrow \vec{q}_i + \vec{\epsilon}(\vec{q}_i) \quad \text{implies} \quad II) \vec{q}_i + \vec{n}L \rightarrow \vec{q}_i + \vec{n}L + \vec{\epsilon}(\vec{q}_i + \vec{n}L), \quad (3.22)$$

by adding the vector  $\vec{n}L$  to the two sides of the relation  $I)$ , we find for consistency from  $II)$  that also  $\vec{\epsilon}(\vec{q})$  must be a periodic function of  $\vec{q}$ , satisfying

$$\vec{\epsilon}(\vec{q}) = \vec{\epsilon}(\vec{q} + \vec{n}L). \quad (3.23)$$

A relation similar to eq. (3.7) holds even in the case of PBC's. More precisely eqs. (3.6) and (3.7) are replaced by the formulae

$$\begin{aligned} q_i^a - (q_j^a + n^a L) &\rightarrow \\ \rightarrow q_i'^a - (q_j'^a + n^a L) &= q_i^a + \epsilon^a(\vec{q}_i) - [q_j^a + n^a L + \epsilon^a(\vec{q}_j + \vec{n}L)], \end{aligned} \quad (3.24)$$

$$\begin{aligned} q_i'^a - (q_j'^a + n^a L) &= q_i^a - (q_j^a + n^a L) + \epsilon^{ab}(\vec{q}_i)[q_i^b - (q_j^b + n^b L)] + \dots = \\ &= [\delta^{ab} + \epsilon^{ab}(\vec{q}_i)] [q_i^b - (q_j^b + n^b L)] + \dots, \end{aligned} \quad (3.25)$$

respectively. Again we remark that the expansion in eq. (3.25) works just because we are assuming that the interaction potential is short-range, in other words that only pairs of particles with  $|\vec{q}_i - \vec{q}_j - \vec{n}L| < \xi$  contribute to  $\mathcal{U}$ .

The whole argument developed in sects. 3.2 and 3.3 goes through as before, provided everywhere  $\vec{q}_{ij}$  is replaced by  $\vec{q}_{ij}^{(\vec{n})}$ . The final expression of  $\tau^{ab}(\vec{r})$  is

$$\tau^{ab}(\vec{r}) = - \left\langle \sum_{i=1}^N \delta(\vec{r} - \vec{q}_i) \left( \frac{p_i^a p_i^b}{m} + \frac{1}{2} \sum_{j=1}^N \sum_{\vec{n}} q_{ij}^{(\vec{n})a} \mathcal{F}_{ij}^b(\vec{q}_{ij}^{(\vec{n})}) \right) \right\rangle_c, \quad (3.26)$$

where the point  $\vec{r}$  belongs to the “central” box on which we concentrate our attention and the double dash in the sum over  $j$  means that the term with  $j = i$  is absent if  $\vec{n} = (0, 0, \dots, 0)$ . Clearly, if the interaction potential is cut-off at distances smaller than half the linear dimension of the box (as it is always done in order to avoid interactions with mirror self-images), the sum over  $\vec{n}$  is effectively reduced to  $n^a = 0, \pm 1$ ,  $a = 1, 2, \dots, D$ . One can then drop the sum over  $\vec{n}$  altogether and employ the minimal-image prescription [8] in computing the virial term in eq. (3.26), which is what is currently done in numerical applications.

## 4 The stress tensor in the *micro-canonical ensemble*

Extending the arguments given in the previous section to the *micro-canonical ensemble* is not difficult. For definiteness let us explicitly illustrate the case of impenetrable walls. The case of PBC’s can be dealt with along similar lines.

The expression of the *micro-canonical* partition function is

$$\mathcal{Z}_{mc} = \int \prod (d^D p) \int_V \prod (d^D q) \delta[\mathcal{E} - \mathcal{H}[\{q\}, \{p\}]], \quad (4.1)$$

from which the basic relations of Thermodynamics for temperature and pressure are obtained

$$\frac{1}{k_B T} = \left. \frac{\partial \log \mathcal{Z}_{mc}}{\partial \mathcal{E}} \right|_V, \quad \frac{\pi}{k_B T} = \left. \frac{\partial \log \mathcal{Z}_{mc}}{\partial V} \right|_{\mathcal{E}}. \quad (4.2)$$

The *ensemble* average of a generic thermodynamic quantity  $f[\{q\}, \{p\}]$  is computed according to the formula

$$\langle f \rangle_{mc} = \frac{1}{\mathcal{Z}_{mc}} \int \prod (d^D p) \int_V \prod (d^D q) \delta[\mathcal{E} - \mathcal{H}[\{q\}, \{p\}]] f[\{q\}, \{p\}]. \quad (4.3)$$

For future use we note that eq. (4.2) takes the explicit form

$$\beta = \frac{1}{k_B T} = \frac{1}{\mathcal{Z}_{mc}} \int \prod (d^D p) \int_V \prod (d^D q) \delta'[\mathcal{E} - \mathcal{H}[\{q\}, \{p\}]], \quad (4.4)$$

where  $\delta'(x) = d\delta(x)/dx$  is the derivative of the Dirac  $\delta$ -distribution.

The construction of the stress tensor in the *micro-canonical ensemble* is straightforward, given the results we have already gotten. Like in sect. 3.2, it is enough to exploit the invariance of the augmented *micro-canonical* partition function

$$\mathcal{Z}_{mc}^{\text{aug}} = \int \prod (d^D p) \int_V \prod (d^D q) \delta[\mathcal{E} - \mathcal{H}_{\text{ext}}[\{q\}, \{p\}]], \quad (4.5)$$

under the canonical transformation defined by the eqs. (3.5) and (3.11). As before,  $\mathcal{Z}_{mc}^{\text{aug}}$  describes the Thermodynamics of the system in the presence of the external potential  $\mathcal{U}_{\text{ext}}$ . By the same steps that brought us to eq. (3.18) we now obtain

$$0 = -\frac{1}{\beta} \frac{\delta \log \mathcal{Z}_{mc}^{\text{aug}}}{\delta \epsilon^a(\vec{r})} \Big|_{\vec{\epsilon}(\vec{r})=0} = \frac{1}{\beta \mathcal{Z}_{mc}^{\text{aug}}} \int \prod (d^D p) \int_V \prod (d^D q) \delta'[\mathcal{E} - \mathcal{H}[\{q\}, \{p\}]] \cdot \left[ \frac{\partial}{\partial x^b} \sum_{i=1}^N \delta(\vec{r} - \vec{q}_i) \left( \frac{p_i^a p_i^b}{m} + \frac{1}{2} \sum_{j(\neq i)=1}^N q_{ij}^a \mathcal{F}_{ij}^b(\vec{q}_{ij}) \right) + \sum_{i=1}^N \delta(\vec{r} - \vec{q}_i) \frac{\partial \mathcal{U}_{\text{ext}}[\{q\}]}{\partial q_i^a} \right]. \quad (4.6)$$

The only delicate point about this equation is that it is not immediately of the form of a “bona fide” *micro-canonical ensemble* average, like eq. (4.3). The integrand in eq. (4.6) contains, in fact, the derivative of a Dirac  $\delta$ -distribution,  $\delta'[\mathcal{E} - \mathcal{H}]$ , and not just  $\delta[\mathcal{E} - \mathcal{H}]$ . In Appendix A we show that in the thermodynamic limit ( $N, V \rightarrow \infty, V/N = \text{fix}$ ), in alternative to eq. (4.3), *ensemble* expectation values can be equally well expressed by a phase-space integral where the distribution  $\delta'[\mathcal{E} - \mathcal{H}]$  enters, by means of the formula (see eq. (4.4))

$$\langle f \rangle_{mc} = \frac{1}{\beta \mathcal{Z}_{mc}} \int \prod (d^D p) \int_V \prod (d^D q) \delta'[\mathcal{E} - \mathcal{H}[\{q\}, \{p\}]] f[\{q\}, \{p\}]. \quad (4.7)$$

With this result the rest of the proof goes through exactly as in sect. 3.3, because all the arguments we made after eq. (3.18) apply also here. We then conclude that a relation which exactly parallels eq. (3.20) holds, *i.e.*

$$\tau^{ab}(\vec{r}) = -\left\langle \sum_{i=1}^N \delta(\vec{r} - \vec{q}_i) \left( \frac{p_i^a p_i^b}{m} + \frac{1}{2} \sum_{j(\neq i)=1}^N q_{ij}^a \mathcal{F}_{ij}^b(\vec{q}_{ij}) \right) \right\rangle_{mc}, \quad (4.8)$$

the only difference being that now the average is obviously taken over the *micro-canonical ensemble*.

## 5 The case of a non short-range potential

In this section we want to see how the previous formulae get modified if the interaction potential between the elementary constituents of the system is not short-range.

Going back to the argument developed in sect. 3, we see that the only modification we need to make in computing the functional derivative of the *canonical* partition function <sup>6</sup> is that we have to keep the point-transformation  $\vec{q}_i \rightarrow \vec{q}_i'$  in

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<sup>6</sup>For definiteness we refer to the *canonical* case, but exactly the same argument could be made for the *micro-canonical* partition function.

the form (3.5), without truncating it to the first term as done in eq. (3.7). Thus with respect to what was done in sect. 3.2 we have to replace (3.16) with

$$\frac{\delta q'_{ij}}{\delta \epsilon^a(\vec{r})} \Big|_{\vec{\epsilon}(\vec{r})=0} = \frac{q_{ij}^a}{q_{ij}} \left[ \delta(\vec{r} - \vec{q}_i) - \delta(\vec{r} - \vec{q}_j) \right]. \quad (5.1)$$

This change affects eq. (3.18), which now becomes

$$\begin{aligned} & \frac{\partial}{\partial x^b} \left\langle \sum_{i=1}^N \delta(\vec{r} - \vec{q}_i) \frac{p_i^a p_i^b}{m} \right\rangle_c^{\text{aug}} + \\ & + \left\langle \frac{1}{2} \sum_{i=1}^N \sum_{j(\neq i)=1}^N \frac{q_{ij}^a}{q_{ij}} \frac{\partial \mathcal{U}_{ij}(q_{ij})}{\partial q_{ij}} \left[ \delta(\vec{r} - \vec{q}_i) - \delta(\vec{r} - \vec{q}_j) \right] \right\rangle_c^{\text{aug}} + \\ & - \left\langle \sum_{i=1}^N \delta(\vec{r} - \vec{q}_i) \mathcal{F}_{i,\text{ext}}^a[\{\vec{q}\}] \right\rangle_c^{\text{aug}} = 0. \end{aligned} \quad (5.2)$$

We notice that the second term in eq. (5.2) is not immediately of the form of a divergence of a two-index (symmetric) tensor. To prove that this is, however, the case, it is convenient to ‘‘Taylor-expand’’ the difference of Dirac  $\delta$ -distributions in the square parenthesis by replacing eq. (5.1) with the series

$$\frac{\delta q'_{ij}}{\delta \epsilon^a(\vec{r})} \Big|_{\vec{\epsilon}(\vec{r})=0} = -\frac{q_{ij}^a q_{ij}^b}{q_{ij}} \frac{\partial}{\partial x^b} \sum_{n=0}^{\infty} \frac{1}{(n+1)!} \left[ \vec{q}_{ij} \frac{\partial}{\partial \vec{r}} \right]^n \delta(\vec{r} - \vec{q}_i). \quad (5.3)$$

It may be useful to rewrite eq. (5.3) in the more compact form

$$\frac{\delta q'_{ij}}{\delta \epsilon^a(\vec{r})} \Big|_{\vec{\epsilon}(\vec{r})=0} = -\frac{q_{ij}^a q_{ij}^b}{q_{ij}} \frac{\partial}{\partial x^b} \int_0^1 dt \delta[\vec{r} - \vec{q}_i + t\vec{q}_{ij}], \quad (5.4)$$

which explicitly shows that, if one can set  $\vec{q}_{ij} = 0$  in the argument of the Dirac  $\delta$ -distribution, one gets back eq. (3.16) from which the kind of formulae for the stress tensor we derived in the previous sections follow. Viceversa, keeping the full form of eq. (5.4), one obtains

$$\tau^{ab}(\vec{r}) = - \left\langle \sum_{i=1}^N \left( \delta(\vec{r} - \vec{q}_i) \frac{p_i^a p_i^b}{m} + \frac{1}{2} \sum_{j(\neq i)=1}^N q_{ij}^a \mathcal{F}_{ij}^b(q_{ij}) \int_0^1 dt \delta[\vec{r} - \vec{q}_i + t\vec{q}_{ij}] \right) \right\rangle_c. \quad (5.5)$$

This formula is in full agreement with the expression given in ref. [1]. Our procedure is thus seen to provide a further justification for the choice of the straight line integration path between pairs of particles in the force term contribution to eq. (5.5).

The emergence of a *non-local* formula may appear somewhat surprising in view of the fact that coordinate differences and momenta, hence the whole Hamiltonian, are exactly invariant under a  $q$ -independent transformation (constant translation). Unlike what happens in Field Theory where global invariance is sufficient to derive the existence of a conserved *local* quantity when the transformation is made local, here we get a *non-local* conserved tensor because the interaction potential, differently from the case of Field Theory, is not point-like.

The real difficulty with eq. (5.5) is that, unlike the situation where the inequalities  $\xi \ll v_{\vec{r}}^{1/D} \ll R_{rp}$  hold, the value of the stress tensor at the point  $\vec{r}$  receives contributions also from particles located at large distances, where “large” here means larger than the apparatus resolution power. This makes impossible to define a quenching volume for statistical fluctuations (like  $v_{\vec{r}}$  in the short-range case), hence very problematic the construction of a spatially smoothly varying stress tensor in the thermodynamic limit.

We close this section with two observations. The first is that, as already remarked by the authors of ref. [18], the Fourier transform of eq. (5.5) takes a somewhat more manageable form which can be of help in numerical simulations. One gets, in fact

$$\begin{aligned} \hat{\tau}^{ab}(\vec{k}) &\equiv \int d\vec{r} \tau^{ab}(\vec{r}) e^{i\vec{k}\vec{r}} = \\ &= - \left\langle \sum_{i=1}^N \left( \frac{p_i^a p_i^b}{m} e^{i\vec{k}\vec{q}_i} + \frac{1}{2} \sum_{j(\neq i)=1}^N q_{ij}^a \mathcal{F}_{ij}^b(q_{ij}) \frac{e^{i\vec{k}\vec{q}_i} - e^{i\vec{k}\vec{q}_j}}{i\vec{k}\vec{q}_{ij}} \right) \right\rangle_c. \end{aligned} \quad (5.6)$$

Secondly we note that eq. (5.5) reduces to the local formula not only, as we remarked above, if one can drop the term  $t\vec{q}_{ij}$  in the argument of the Dirac  $\delta$ -distribution, but also if the latter is replaced by some smoother (normalized) sharply peaked function. The proof of compatibility of this procedure with the general equation of continuum Mechanics as well as interesting applications of this prescription can be found in the papers of ref. [19].

## 6 The stress tensor in quantum Statistical Mechanics

In a quantum mechanical framework the partition function which describes the Statistical Mechanics of a system with canonically conjugate variables  $\{q\}, \{p\}$  takes the form <sup>7</sup>

$$\mathcal{Z}_c^{qu} = \text{Tr} \left[ \exp \left( -\beta \mathcal{H}^{qu}[\{q\}, \{p\}] \right) \right] \quad (6.1)$$

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<sup>7</sup>For simplicity we will keep using the symbols  $\{q\}$  and  $\{p\}$  for the quantum mechanical operators describing the system coordinates and momenta.

in the *canonical ensemble*, and

$$\mathcal{Z}_{mc}^{qu} = \text{Tr} \left[ \delta \left( \mathcal{E} - \mathcal{H}^{qu}[\{q\}, \{p\}] \right) \right] \quad (6.2)$$

in the *micro-canonical* one, where  $\mathcal{H}^{qu}[\{q\}, \{p\}]$  is the quantum mechanical operator which represents the Hamiltonian of the system. Concretely in the  $q$ -representation  $\mathcal{H}^{qu}[\{q\}, \{p\}]$  is obtained from the classical expression (3.1) with the replacement  $p_i^a \rightarrow -i\hbar \partial / \partial q_i^a$  (correspondence principle).

The traces in eqs. (6.1) and (6.2) are taken over an orthonormal basis in the Hilbert space of states of the system. In this paper we only consider the case of Bose particles<sup>8</sup>. Furthermore, we will explicitly illustrate the construction of the stress tensor only in the case of the *canonical ensemble*, because, as it will be apparent from the analysis that follows, the construction in the *micro-canonical* case can be dealt with in a completely analogous way, just like we did in the classical setting, previously discussed in sects 3 and 4.

## 6.1 Point-transformations in Quantum Mechanics

In order to extend to the quantum case the construction of the stress tensor carried out in the previous sections, we need to determine the form of the unitary operator,  $U[\{\vec{\epsilon}\}]$ , that implements the (infinitesimal) point-transformation (3.5). Requiring

$$U[\{\vec{\epsilon}\}] q_i^a U^\dagger[\{\vec{\epsilon}\}] = q_i^a + \epsilon^a(\vec{q}_i) + \mathcal{O}(\epsilon^2), \quad (6.3)$$

one gets, to first order in  $\vec{\epsilon}$  (which is what is of interest to us here)

$$U[\{\vec{\epsilon}\}] = \mathbb{1} + \frac{\iota}{2\hbar} \sum_{j=1}^N \left[ \vec{p}_j \cdot \vec{\epsilon}(\vec{q}_j) + \vec{\epsilon}(\vec{q}_j) \cdot \vec{p}_j \right] + \mathcal{O}(\epsilon^2). \quad (6.4)$$

With the aid of eq. (6.3) and the formula

$$U[\{\vec{\epsilon}\}] p_i^a U^\dagger[\{\vec{\epsilon}\}] = p_i^a - \frac{\iota}{\hbar} \left[ (p_i^a \vec{\epsilon}(\vec{q}_i)) \vec{p}_i + \frac{1}{2} p_i^a \vec{p}_i \vec{\epsilon}(\vec{q}_i) \right] + \mathcal{O}(\epsilon^2), \quad (6.5)$$

one can compute the behaviour of the kinetic and potential terms of  $\mathcal{H}^{qu}[\{q\}, \{p\}]$  under the transformation induced by  $U[\{\vec{\epsilon}\}]$ . For each term contributing to the

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<sup>8</sup>A powerful formulation of Quantum Statistical Mechanics, valid both for Bose and Fermi particles, is possible if the representation of the partition function as a functional integral over (non-relativistic) creation and annihilation field variables is employed. In this formalism field variables for Bose particles are functions that take  $c$ -number values, while for Fermi particles they take value in a Grassmannian algebra. The use of this general formalism is beyond the scope of this paper.

sums over  $j$  and/or  $i$  in the Hamiltonian (from now on ignoring irrelevant  $O(\epsilon^2)$  terms), one obtains

$$U[\{\bar{\epsilon}\}]\mathcal{U}_{ij}(q_{ij})U^\dagger[\{\bar{\epsilon}\}] = \mathcal{U}_{ij}(q_{ij}) + \frac{\partial\mathcal{U}_{ij}(q_{ij})}{\partial q_{ij}}\frac{1}{q_{ij}}\vec{q}_{ij} \cdot [\bar{\epsilon}(\vec{q}_i) - \bar{\epsilon}(\vec{q}_j)], \quad (6.6)$$

$$U[\{\bar{\epsilon}\}]p_i^a p_i^a U^\dagger[\{\bar{\epsilon}\}] = p_i^a p_i^a + \frac{i}{\hbar}\left[2(p_i^a \bar{\epsilon}(\vec{q}_i))\vec{p}_i p_i^a + (p_i^a \vec{p}_i \bar{\epsilon}'(\vec{q}_i))p_i^a + (p_i^a p_i^a \bar{\epsilon}(\vec{q}_i))\vec{p}_i + \frac{1}{2}(p_i^a p_i^a \vec{p}_i \bar{\epsilon}'(\vec{q}_i))\right]. \quad (6.7)$$

## 6.2 Invariance of the quantum partition function

The invariance of the quantum partition function,  $\mathcal{Z}_c^{qu}$  (the same would hold for  $\mathcal{Z}_{mc}^{qu}$ ), under point-transformations follows from the identity

$$\text{Tr}\left[U[\{\bar{\epsilon}\}]\exp\left(-\beta\mathcal{H}^{qu}[\{q\},\{p\}]\right)U^\dagger[\{\bar{\epsilon}\}]\right] = \text{Tr}\left[\exp\left(-\beta\mathcal{H}^{qu}[\{q\},\{p\}]\right)\right]. \quad (6.8)$$

This statement remains true also if we add an external potential to  $\mathcal{H}^{qu}[\{q\},\{p\}]$  and we consider the augmented system described by the Hamiltonian

$$\mathcal{H}_{\text{ext}}^{qu}[\{q\},\{p\}] = \mathcal{H}^{qu}[\{q\},\{p\}] + \mathcal{U}_{\text{ext}}[\{q\}]. \quad (6.9)$$

Analogously to the classical case, in order to deduce the expression of the stress tensor, we proceed by exploiting the condition ensuing from the vanishing of the functional derivative of the quantum mechanical partition function of the augmented system with respect to the parameters of the unitary operator (6.4). This condition reads

$$\begin{aligned} 0 &= -\frac{1}{\beta}\text{Tr}\left[\frac{\delta\exp\left(-\beta\mathcal{H}_{\text{ext}}^{qu}[\{q\},\{p\};\{\bar{\epsilon}\}]\right)}{\delta\epsilon^a(\vec{r})}\Big|_{\bar{\epsilon}(\vec{r})=0}\right] = \\ &= \text{Tr}\left[\exp\left(-\beta\mathcal{H}_{\text{ext}}^{qu}[\{q\},\{p\}]\right)\frac{\delta\mathcal{H}_{\text{ext}}^{qu}[\{q\},\{p\};\{\bar{\epsilon}\}]}{\delta\epsilon^a(\vec{r})}\Big|_{\bar{\epsilon}(\vec{r})=0}\right], \end{aligned} \quad (6.10)$$

where

$$\mathcal{H}_{\text{ext}}^{qu}[\{q\},\{p\};\{\bar{\epsilon}\}] = U[\{\bar{\epsilon}\}]\mathcal{H}_{\text{ext}}^{qu}[\{q\},\{p\}]U^\dagger[\{\bar{\epsilon}\}]. \quad (6.11)$$

The second equality in eq. (6.10) is not completely trivial because we are dealing here with operator functions which do not necessarily commute. However, one can convince oneself that under the trace operation the reordering of operators implicit in the way the above formula has been written is perfectly legitimate.

From now on, the calculation is pretty much analogous to the one that was carried out in sect. 3.2 in the case of a short-range potential, and in sect. 5 in the opposite case. For simplicity we report below only the formulae valid for the

case of a short-range potential, but formulae for the other case can be immediately recovered by replacing eq. (3.16) with eq. (5.1).

It is worth observing that the somewhat involved form taken by the variation of the kinetic term of the quantum Hamiltonian (see eq. (6.7)) comes about because the parameter  $\vec{\epsilon}(\vec{q}_i)$  is a coordinate dependent function which does not commute with the canonically conjugate momentum operators  $\vec{p}_i$ . In spite of this complication, the resulting functional derivative can be cast in the form of the divergence of a two index symmetric tensor. Indeed one gets for  $\tau^{ab}(\vec{r})$  (compare with eq. (3.20))

$$\begin{aligned} \tau^{ab}(\vec{r}) = & - \left\langle \sum_{i=1}^N \delta(\vec{r} - \vec{q}_i) \left( \frac{p_i^a p_i^b}{m} + \frac{1}{2} \sum_{j(\neq i)=1}^N q_{ij}^a \mathcal{F}_{ij}^b(\vec{q}_{ij}) \right) + \right. \\ & \left. + \frac{1}{2m} \sum_{i=1}^N \left[ (p_i^b \delta(\vec{r} - \vec{q}_i)) p_i^a + (p_i^a \delta(\vec{r} - \vec{q}_i)) p_i^b + \frac{1}{2} (p_i^a p_i^b \delta(\vec{r} - \vec{q}_i)) \right] \right\rangle_c^{qu}, \quad (6.12) \end{aligned}$$

where  $\langle \dots \rangle_c^{qu} = \text{Tr} \left[ \dots \exp \left( - \beta \mathcal{H}^{qu}[\{q\}, \{p\}] \right) \right]$ .

The formula (6.12) defines an hermitian operator and it is fully consistent with the correspondence principle of Quantum Mechanics. In particular, we show in Appendix B that the expression of the pressure for a (homogeneous) system that one would get employing the standard thermodynamic equation (which defines the pressure as proportional to the derivative of the Helmholtz free energy with respect to the volume) leads precisely to the quantum analog of the classical virial formula for the pressure. This is consistent with the fact that (after replacing the momenta acting on the Dirac  $\delta$ -distributions by derivatives with respect to the coordinates of the external point,  $\vec{r}$ ) the last three terms in eq. (6.12) can be cast in the form

$$\left\{ \frac{\hbar}{2m\mu} \frac{\partial}{\partial x^b} \left[ \left\langle \sum_{i=1}^N \delta(\vec{r} - \vec{q}_i) p_i^a \right\rangle_c^{qu} + \frac{1}{4} \frac{\partial}{\partial x^a} \left\langle \sum_{i=1}^N \delta(\vec{r} - \vec{q}_i) \right\rangle_c^{qu} \right] \right\} + \{a \leftrightarrow b\}, \quad (6.13)$$

which shows that they will give vanishing contributions upon integration over the volume of the box containing the system.

We wish to end this section by observing that the whole procedure we have discussed above is based on the construction the unitary operator that implements the classical notion of canonical diffeomorphisms in the quantum mechanical formalism. In this way we have been able to go one little step beyond the known results present in the literature (see, for instance, refs. [5, 6] and the many papers quoted therein), which all have the seminal works in ref. [20] as basic starting points. We have extended the standard computation of the ground state expectation value of the stress tensor operator, which is relevant at zero temperature, by establishing a formula valid at any temperature. This has required computing the expectation value of the stress tensor in all the energy eigenstates of the system.

## 7 Conclusions

In this paper we have given a simple and generally valid derivation of the microscopic expression of the stress tensor of a molecular system in the *canonical* and *micro-canonical ensemble*, using the methods of Statistical Mechanics both in the classical and the quantum case. The approach exploits the invariance of the partition function under the canonical or, respectively, unitary, infinitesimal point-transformations (canonical diffeomorphisms). The stress tensor is identified by looking at the response of the system to an external force. The strategy we are advocating can be applied to systems with any type of boundary conditions. The latter are, in fact, encoded in the boundary conditions to be assigned to the deformation parameter  $\vec{\epsilon}(\vec{r})$ . Formulae for the cases of impenetrable, perfectly reflecting, walls and of PBC's have been explicitly worked out.

We have shown that, not unexpectedly [10], a truly local form of the stress tensor only exists for systems with short-range potentials. In this case one gets an expression which can be made to coincide with the kind of formulae currently used in simulations, after averaging over appropriately chosen spatial volumes. For systems with long-range potentials, instead, it does not appear to be possible to arrive at a sensible definition of a spatially smoothly varying stress tensor.

The procedure we have presented is very elegant and simple, but where it shows all its power is in dealing with the case of a quantum system. To our best knowledge the approach we have spelled out in this paper is the only one which can be consistently employed in this situation. As we have seen the use of a point-dependent deformation parameter is mandatory if we want to comply with the specific boundary conditions imposed to the system and arrive at the construction of a local expression for the stress tensor. The extra complication that because of this arises quantum-mechanically is that the coordinate dependent quantity  $\vec{\epsilon}(\vec{q}_i)$  does not commute with the canonically conjugate momentum operators  $\vec{p}_i$ . Mathematically this is the origin of the somewhat complicated structure taken by the kinetic contribution in eq. (6.12). This structure, however, automatically emerges from the formalism and it is necessary for the stress tensor to be an hermitian quantum operator.

We end by observing that the formulae we find for  $\tau^{ab}$  in the various instances we have discussed are in full agreement with the corresponding expressions for the pressure one can independently derive from the general relations of Thermodynamics, i.e. the relations in eqs. (4.2) and (B.1) in the classical and quantum case, respectively. This agreement is explicitly checked in Appendix B in the non trivial quantum-mechanical setting.

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## Appendix A - On *micro-canonical averages*

In this Appendix we prove that in the thermodynamic limit ( $N, V \rightarrow \infty, V/N = \text{fix}$ ) the *micro-canonical ensemble* expectation value (4.3) of the extensive quantity  $f$  can be equally well expressed by a phase-space integral, where the distribution  $\delta'[\mathcal{E} - \mathcal{H}]$  (instead of  $\delta[\mathcal{E} - \mathcal{H}]$ ) enters. Indeed, with the definition

$$\langle\langle f \rangle\rangle = \frac{1}{\beta \mathcal{Z}_{mc}} \int \prod (d^D p) \int_V \prod (d^D q) \delta'[\mathcal{E} - \mathcal{H}[\{q\}, \{p\}]] f[\{q\}, \{p\}], \quad (\text{A.1})$$

we want to show that

$$\lim_{N, V \rightarrow \infty, V/N = \text{fix}} \frac{\langle\langle f \rangle\rangle - \langle f \rangle_{mc}}{\langle f \rangle_{mc}} = 0. \quad (\text{A.2})$$

To this end we first note that from eq. (4.4) the algebraic identity

$$\frac{\partial[\langle f \rangle_{mc}]}{\partial \mathcal{E}} = \beta [\langle\langle f \rangle\rangle - \langle f \rangle_{mc}] \quad (\text{A.3})$$

readily follows. The key observation at this point is that in the thermodynamic limit one can successively write

$$\begin{aligned} \beta \frac{\langle\langle f \rangle\rangle - \langle f \rangle_{mc}}{\langle f \rangle_{mc}} &= \frac{1}{\langle f \rangle_{mc}} \frac{\partial[\langle f \rangle_{mc}]}{\partial \mathcal{E}} = \frac{1}{\langle f \rangle_{mc}} \frac{\partial \beta}{\partial \mathcal{E}} \frac{\partial[\langle f \rangle_{mc}]}{\partial \beta} = \\ &= \left[ \frac{\partial[\langle \mathcal{H} \rangle_c]}{\partial \beta} \right]^{-1} \frac{1}{\langle f \rangle_c} \frac{\partial[\langle f \rangle_c]}{\partial \beta} = -\frac{1}{\langle f \rangle_c} \frac{\langle f \mathcal{H} \rangle_c - \langle f \rangle_c \langle \mathcal{H} \rangle_c}{\langle \mathcal{H}^2 \rangle_c - \langle \mathcal{H} \rangle_c^2}. \end{aligned} \quad (\text{A.4})$$

The third equality of this chain is obtained exploiting the thermodynamic equivalence of *canonical* and *micro-canonical ensembles*. According to the general assumptions of Statistical Mechanics [9], we conclude that the last term in eq. (A.4) vanishes in the thermodynamic limit, because the first factor, which is the inverse of the *ensemble* expectation value of an extensive quantity, behaves as  $1/N$ , while the second factor is a quantity of order 1. The latter is, in fact, a ratio of quadratic fluctuations which have an equal (linear) rate of growth with  $N$ .

## Appendix B - The virial formula for the pressure in Quantum Statistical Mechanics

In this Appendix we want to show that, consistently with the correspondence principle, the virial formula for the pressure [10] also holds for a quantum mechanical

system, with the obvious understanding that now  $\{q\}$ 's and  $\{p\}$ 's are not numbers, but hermitian operators acting on the Hilbert space of states and the *ensemble* average is performed by tracing with the quantum Boltzmann weight factor. As observed in sect. 6.2, this is also the result one gets from eq. (6.12) after averaging over volume and tracing over spatial indexes.

For definiteness we discuss the case of the *canonical ensemble*, though the argument we develop applies essentially unchanged if we were to work in the *micro-canonical ensemble*. The statistico-mechanical definition of pressure is

$$\pi = \frac{1}{\beta} \frac{\partial \log \mathcal{Z}_c^{qu}}{\partial V} = \frac{1}{\beta} \frac{\partial \log \text{Tr}[e^{-\beta \mathcal{H}^{qu}}]}{\partial V}, \quad (\text{B.1})$$

where in the second equality we have used eq. (6.1). It is convenient to express the trace of the operator  $e^{-\beta \mathcal{H}^{qu}}$  as the sum of its eigenvalues. In this way one gets

$$\pi = \frac{1}{\beta} \frac{\partial \log \sum_n e^{-\beta E_n}}{\partial V} = - \frac{1}{\sum_n e^{-\beta E_n}} \sum_n e^{-\beta E_n} \frac{\partial E_n}{\partial V}, \quad (\text{B.2})$$

where the  $E_n$ 's are the eigenvalues of the quantum Hamiltonian

$$\mathcal{H}^{qu}[\{q\}, \{p\}] \psi_n[\{q\}] = E_n \psi_n[\{q\}], \quad (\text{B.3})$$

$$\mathcal{H}^{qu}[\{q\}, \{p\}] = - \frac{\hbar^2}{2m} \sum_{i=1}^N \frac{\partial^2}{\partial \vec{q}_i \partial \vec{q}_i} + \mathcal{U}[\{q\}]. \quad (\text{B.4})$$

The boundary conditions assigned to the system translate into appropriate mathematical constraints that make (B.3) a well posed Sturm-Liouville problem.

The derivative of  $E_n$  with respect to  $V$  is more easily computed employing the quantum mechanical relation

$$E_n = \int_V \prod_{i=1}^N (d^D q) \psi_n^*[\{q\}] \mathcal{H}^{qu}[\{q\}, \{p\}] \psi_n[\{q\}], \quad (\text{B.5})$$

because the implicit  $V$  dependence of  $E_n$  can be made fully apparent by the rescaling  $\vec{s}_i = \vec{q}_i/L$  of the integration variables. With reference to a hyper-cubic box of volume  $V$ , where  $L = V^{1/D}$ , eq. (B.5) can, in fact, be cast in the expressive form

$$E_n = V^N \int_{B_1} \prod_{i=1}^N (d^D s) \psi_n^*[\{Ls\}] \mathcal{H}^{qu}[\{Ls\}, \{\frac{\hbar}{2mL} \frac{\partial}{\partial s}\}] \psi_n[\{Ls\}], \quad (\text{B.6})$$

where  $B_1$  is the unit  $D$ -dimensional hyper-cube. The key observation is now that in computing the derivative of  $E_n$  with respect to  $V$  only the explicit volume dependence in the Hamiltonian gives a non-vanishing contribution. The reason

is that the term that results from taking the derivative of the factor  $V^N$  is exactly canceled by the contributions coming from the volume dependence of the eigenfunctions. For the first term one simply gets  $NE_n/V$  (after reabsorbing the factor  $V^N$ , when the original integration variables are reintroduced). On the other hand, when the volume derivative acts on the eigenfunction  $\psi_n$  and its complex conjugate, one obtains

$$\begin{aligned} & \int_{B_1} \prod (d^D s) \left\{ \sum_{i=1}^N \vec{s}_i \frac{\partial \psi_n^*[\{q\}]}{\partial \vec{q}_i} \Big|_{\vec{q}=L\vec{s}} \mathcal{H}^{qu}[\{Ls\}, \{\frac{\hbar}{2m\mu L} \frac{\partial}{\partial s}\}] \psi_n[\{Ls\}] + \right. \\ & \left. + \psi_n^*[\{Ls\}] \mathcal{H}^{qu}[\{Ls\}, \{\frac{\hbar}{2m\mu L} \frac{\partial}{\partial s}\}] \sum_{i=1}^N \vec{s}_i \frac{\partial \psi_n[\{q\}]}{\partial \vec{q}_i} \Big|_{\vec{q}=L\vec{s}} \right\} \frac{V^{N+1/D}}{VD}. \end{aligned} \quad (\text{B.7})$$

Replacing the hermitian operator  $\mathcal{H}^{qu}$  acting on the eigenfunction  $\psi_n$  (first line), or on  $\psi_n^*$  (second line) by the corresponding eigenvalue,  $E_n$ , the two terms in eq. (B.7) can be combined together to give

$$\begin{aligned} & \frac{E_n}{VD} V^{N+\frac{1}{D}} \int_{B_1} \prod (d^D s) \sum_{i=1}^N \vec{s}_i \frac{\partial |\psi_n[\{q\}]|^2}{\partial \vec{q}_i} \Big|_{\vec{q}=L\vec{s}} = \\ & = \frac{E_n}{VD} \int_V \prod (d^D q) \sum_{i=1}^N \vec{q}_i \frac{\partial |\psi_n[\{q\}]|^2}{\partial \vec{q}_i}, \end{aligned} \quad (\text{B.8})$$

where in the second equality the original integration variables  $\{q\}$  have been reintroduced. Now an integration by parts immediately shows that the quantity (B.8) equals  $-NE_n/V$  and exactly cancels the previous contribution. As a result (just like in the classical case) the only terms we are left with are those coming from the Hamiltonian volume dependence visible in eq. (B.6). One thus gets

$$\frac{\partial E_n}{\partial V} = \frac{1}{VD} \int_V \prod (d^D q) \psi_n^*[\{q\}] \left[ \frac{\hbar^2}{m} \sum_{i=1}^N \frac{\partial^2}{\partial \vec{q}_i \partial \vec{q}_i} + \sum_{i=1}^N \vec{q}_i \frac{\partial \mathcal{U}[\{q\}]}{\partial \vec{q}_i} \right] \psi_n[\{q\}]. \quad (\text{B.9})$$

In the first term in the square bracket of eq. (B.9) one recognizes (minus) twice the kinetic energy operator ( $2\mathcal{K}$ ) and in the second (minus) the virial of the forces ( $\mathcal{W}$ ). Inserting the result (B.9) back into eq. (B.2), one can successively write

$$\begin{aligned} \pi &= - \frac{1}{\sum_n e^{-\beta E_n}} \sum_n e^{-\beta E_n} \frac{\partial E_n}{\partial V} = \\ &= \frac{1}{VD} \frac{1}{\sum_n e^{-\beta E_n}} \sum_n e^{-\beta E_n} \int_V \prod (d^D q) \psi_n^*[\{q\}] (2\mathcal{K} + \mathcal{W}) \psi_n[\{q\}] = \\ &= \frac{1}{VD} \frac{1}{\sum_n e^{-\beta E_n}} \sum_n \int_V \prod (d^D q) \psi_n^*[\{q\}] (2\mathcal{K} + \mathcal{W}) e^{-\beta \mathcal{H}^{qu}} \psi_n[\{q\}] = \end{aligned}$$

$$= \frac{1}{VD} \frac{1}{\text{Tr}[e^{-\beta\mathcal{H}^{qu}}]} \text{Tr}[(2\mathcal{K} + \mathcal{W})e^{-\beta\mathcal{H}^{qu}}] = \frac{1}{VD} \langle 2\mathcal{K} + \mathcal{W} \rangle_c^{qu}. \quad (\text{B.10})$$

The latter is the virial formula for the pressure. Recalling eqs (6.12) and (6.13)), we see that it coincides with the volume average of  $\sum_{a=1}^D \tau^{aa}/D$ .

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