International Journal of Thermophysics, Vol. 8, No.3, 1987

The Definition of the Pressure Tensor in the Statistical Mechanics of Nonuniform Classical Fluids

L. Mistura[1]

Received May 21, 1986

By means of a generalization of the similarity transformation introduced by Bogoliubov and Green to calculate pressure, we derive a unique expression of the pressure tensor for a system of interacting point particles in equilibrium according to the canonical ensemble. Our result confirms the expression originally reported by Irving and Kirkwood.

KEY WORDS: canonical ensemble; nonuniform systems; pressure tensor; statistical mechanics.

1. INTRODUCTION

The pressure tensor, defined as the negative of the equilibrium average of the microscopic stress tensor, is a basic thermodynamic quantity in the statistical mechanical theory of inhomogeneous fluids and, in particular, in the theory of the thermodynamics and structure of interfaces [1–3].

For a classical dynamical system of interacting point particles, the microscopic stress tensor σ_{ij} is composed of two parts, the kinetic part $\sigma_{ij}^{(k)}$, associated with the momentum transport, and the configurational part $\sigma_{ij}^{(\Phi)}$ that arises from the intermolecular forces. The calculation of the first part presents no problem, but for the second part it has not been possible so far to arrive at a unique expression [1, 2]. Quite the contrary, the most widespread opinion at the present time is that the stress tensor cannot be uniquely defined, although the problem is not yet considered as definitively settled [4]. Recently the whole matter has been reanalyzed by Schofield and Henderson [5], with the conclusion that there are infinitely many

---

[1] Dipartimento di Energetica, Università di Roma "La Sapienza," Via A. Scarpa 14, 00161 Roma, Italy.

ways of defining $\sigma_{ij}^{(\Phi)}$, related to the infinitely many paths in space joining two interacting particles. Neverthless, the choice, originally made by Irving and Kirkwood [6], corresponding to a straight path, is the most natural, and the one generally made, in either equilibrium [3] or nonequilibrium situations [7].

It does not seem to the present author, however, that the claimed indetermination, which would have the structure of a gauge arbitrariness, corresponds to the physical situation. In principle at least, one can determine the components of the stress, in every point of a nonuniform fluid by measuring the response of the system to an appropriate local deformation. The arbitrariness in the current definition arises from the ambiguity implicit a priori in the notion "force acting across a surface element $d\mathrm{S}$." As a matter of fact, although the formalism of classical statistical mechanics is based on the concept of direct action at distance between molecules, a given molecule cannot distinguish from which other molecule comes the force acting on it, but can see only the resultant field created by all the other molecules in the fluid, either "outside" or "inside" the tangent plane through the surface element $d\mathrm{S}$. It is only a posteriori, after the calculation of the stress tensor has been made according to an alternative definition, that the equation [6]

$$\sigma_{ij}^{(\Phi)}(\mathbf{r})\, d\mathrm{S}_j = \text{“the force acting across } d\mathrm{S}\text{”} \tag{1}$$

can be used, not to calculate $\sigma_{ij}^{(\Phi)}$, but as a definition of the rhs.

The theoretical relevance of the problem outlined above can hardly be overestimated, because an eventual arbitrariness in the definition of the stress tensor carries through to the pressure tensor and this, in turn, to the definition of the surface of tension and other interesting local quantities such as the scalar pressure, defined as one-third of the trace of the pressure tensor.

In a recent paper [8], we have proposed a new definition of the local pressure tensor as the functional derivative of the free energy with respect to the local strain tensor. The new definition is free from any ambiguity and provides directly a symmetric tensor [9]. We explicitly calculated the pressure tensor in the case that the free energy is known as a functional of the one-particle density and, in the framework of the square gradient approximation, confirmed the expression originally reported by Lovett [10].

The free energy as a functional of the density is obtained most directly in a grand canonical ensemble [11]. In the present paper we wish to report on a new unambiguous calculation of the pressure tensor in a canonical ensemble. Our method will then appear quite explicitly as a generalization of a device introduced independently by Bogoliubov [12] and Green [13] to calculate the scalar pressure in a homogeneous fluid and later adapted by Buff [14], McLellan [15], and Harasima [16] to derive a statistical mechanics expression for the surface tension. While these authors introduced new reduced variables by means of a global similarity transformation, we introduce new particle coordinates by means of a general point transformation. The method is fully described in the next section. Our calculation confirms the Irving and Kirkwood definition [6].

2. EVALUATION OF THE PRESSURE TENSOR IN A CANONICAL ENSEMBLE

The direct calculation of the pressure tensor, according to the familiar definition of classical elasticity, namely,

$$p_{\alpha\beta} = -\left(\frac{\delta F}{\delta u_{\alpha\beta}}\right)_T \tag{2}$$

where $u_{\alpha\beta}$ is the strain tensor and F is the Helmholtz free energy, is not possible because one does not know the explicit dependence of F on the strain. However, if one regards the deformation as a coordinate transformation, one can write Eq. (2) in the alternative, equivalent forms [8]

$$\frac{1}{2}\sqrt{g}\,p^{\alpha\beta} = -\left(\frac{\delta F}{\delta g_{\alpha\beta}}\right)_T \tag{3a}$$

$$\frac{1}{2}\sqrt{g}\,p_{\alpha\beta} = \left(\frac{\delta F}{\delta g^{\alpha\beta}}\right)_T \tag{3b}$$

where g is the determinant of the matrix $\|g_{\alpha\beta}\|$, $g_{\alpha\beta}$ are the components of the metric tensor, and with the subscript and superscript indices we, respectively, denote covariant and contravariant components. The problem is then to find out the explicit dependence of F on the $g_{\alpha\beta}$.

To this purpose let us consider a classical system of N identical point particles of mass m, in the presence of an external field φ_e, which acts independently on each particle. In classical statistical mechanics it is customary to identify the configuration of the system by means of the position vectors $\mathbf{r}_i$, whose components r_i^α $(\alpha = 1, 2, 3)$ are taken in the direction of three rectangular axes. The conjugate momenta are then $\mathbf{p}_i = m\dot{\mathbf{r}}_i$ and the hamiltonian H will consist of three parts: the kinetic energy $K = \sum_{i1}^{n} p_i^2/2m$, the energy of interaction among the particles

$\Phi(\mathbf{r}_1,\ldots,\mathbf{r}_n)$, and the energy of interaction of all the particles with the external field $\sum_{i\,1}^{n}\varphi_e(\mathbf{r}_i)$, so that

$$H(\mathbf{r}_1\cdots\mathbf{r}_n;\,\mathbf{p}_1\cdots\mathbf{p}_n)=\sum_{1}^{n}{}_i\frac{p_i^2}{2m}+\Phi(\mathbf{r}_1\cdots\mathbf{r}_n)+\sum_{1}^{n}{}_i\,\varphi_e(\mathbf{r}_i) \tag{4}$$

The Helmholtz free energy $F(T, V, N)$ for such a system is then given by

$$F(T, V, N) = -kT\ln Z(T, V, N) \tag{5}$$

where $Z(T, V, N)$ is the canonical partition function

$$Z(T, V, N)=\frac{1}{h^n n!}\int\exp\left(-\frac{H}{kT}\right)\prod_{1}^{n}{}_i\,d\mathbf{r}_i\,d\mathbf{p}_i \tag{6}$$

It follows from Liouville theorem that the partition function given by Eq. (6) and, consequently, the free energy given by Eq. (5) are invariant with respect to a canonical transformation and therefore, in particular, with respect to a point transformation, namely, an unrestricted coordinate transformation.

In order to exploit this invariance property of the free energy we consider a special point transformation. Instead of identifying the position of a particle, in the single particle configuration space, by means of three rectangular coordinates r_i^α, we adopt three general curvilinear coordinates x_i^β so that

$$r_i^\alpha = r_i^\alpha(x_i^\beta), \qquad \dot{r}_i^\alpha=\frac{\partial r_i^\alpha}{\partial x_i^\beta}\,\dot{x}_i^\beta = a_\beta^\alpha(x_i)\,\dot{x}_i^\beta \tag{7}$$

The reduced variables introduced in Refs. 12–16 are of this type, but with $a_\beta^\alpha = l_\alpha\delta_\beta^\alpha$ and $l_\alpha = \text{const}$.

We now express the Hamiltonian given by Eq. (4) in terms of the new variables.

For the kinetic energy one gets immediately from Eqs. (7)

$$K=\frac{1}{2}m\sum_{1}^{n}{}_i\,g_{\alpha\beta}(x_i)\,\dot{x}_i^\alpha\dot{x}_i^\beta \tag{8}$$

where we have introduced the covariant components $g_{\alpha\beta}(x_i)$ of the metric tensor defined by

$$g_{\alpha\beta}(x_i)=\sum_{1}^{3}{}_\gamma\,a_\alpha^\gamma a_\beta^\gamma \tag{9}$$

But in the Hamiltonian given by Eq. (4) we need the kinetic energy expressed in terms of the conjugate momenta defined by

$$y_{i\alpha}=\frac{\partial K}{\partial \dot{x}_i^\alpha}=mg_{\alpha\beta}(x_i)\dot{x}_i^\beta=m\dot{x}_{i\alpha} \tag{10}$$

so that the kinetic enery can be written as

$$K=\frac{m}{2}\overset{n}{\underset{1}{\sum}}{}_i\, g^{\alpha\beta}(x_i)\dot{x}_{i\alpha}\dot{x}_{i\beta}=\frac{1}{2m}\overset{n}{\underset{1}{\sum}}{}_i\, g^{\alpha\beta}(x_i)\,y_{i\alpha}\,y_{i\beta} \tag{11}$$

Introducing the microscopic number density $\tilde{\rho}(x)$ defined by

$$\tilde{\rho}(x)=\overset{n}{\underset{1}{\sum}}{}_i\,\delta(x-x_i) \tag{12}$$

so that $\int \tilde{\rho}(x)\,dx=N$, where $dx=\prod_\alpha dx_\alpha$, we can rewrite K as an integral over the whole volume occupied by the system

$$K=\frac{1}{2m}\int \tilde{\rho}(x)\;g^{\alpha\beta}(x)\;y_{i\alpha}\,y_{i\beta}\,dx \tag{13}$$

Similarly, we can rewrite the energy of interaction with the external field as

$$\overset{n}{\underset{1}{\sum}}{}_i\,\varphi_{\mathrm{e}}(\mathbf{r}_i)=\int \tilde{\rho}(x)\,\varphi_{\mathrm{e}}(x)\,dx \tag{14}$$

As far as $\Phi(\mathbf{r}_1\cdots\mathbf{r}_n)$ is concerned it will depend on the $g^{\alpha\beta}$ through the distances between the particles. For the sake of comparison and definiteness we assume that Φ is a sum of pair interactions

$$\Phi(\mathbf{r}_1\cdots\mathbf{r}_n)=\frac{1}{2}\overset{n}{\underset{1}{\sum}}{}_i\,\overset{n}{\underset{1}{\sum}}{}_{j\neq i}\,\varphi(r_{ij}) \tag{15}$$

where $r_{ij}=|\mathbf{r}_j-\mathbf{r}_i|$, although there is no difficulty, at least in principle, to perform the calculation in more general cases.

In curvilinear coordinates the distance r_{ij}, between particle i and particle j, may be expressed as follows. Let $x^\alpha=x^\alpha(\lambda)$ $(\alpha=1,2,3)$ be the parametric equations of the oriented (from i to j) straight line joining the two distanct particles, and let the parameter λ be so chosen that $x^\alpha(0)=x_i^\alpha$ and $x^\alpha(1)=x_j^\alpha$. Then

$$r_{ij}=\int_0^1 d\lambda\,\sqrt{g_{\alpha\beta}(\lambda)\,\frac{dx^\alpha}{d\lambda}\,\frac{dx^\beta}{d\lambda}} \tag{16}$$

where $g_{\alpha\beta}(\lambda)$ is the value of covariant components of the metric tensor at the point $x(\lambda)$ on the straight line segment between x_i and x_j, so that

$$g_{\alpha\beta}(\lambda)=\int \delta[x-x(\lambda)]\, g_{\alpha\beta}(x)\, dx \tag{17}$$

With these preliminaries it is not difficult to calculate the pressure tensor according to Eqs. (3)–(6). We have

$$\frac{\delta F}{\delta g^{\alpha\beta}(x)}=-kT\frac{1}{Z}\frac{\delta Z}{\partial g^{\alpha\beta}(x)}=\left\langle\frac{\delta H}{\delta g^{\alpha\beta}(x)}\right\rangle \tag{18}$$

where the derivative is a functional derivative made at constant temperature. On the other hand, from Eqs. (11)–(13) we obtain

$$\frac{\delta K}{\delta g^{\alpha\beta}(x)}=\frac{1}{2m}\tilde{\rho}(x)\, y_{i\alpha}\, y_{i\beta} \tag{19}$$

while according to Eq. (14), the interaction with the external field gives no contribution. As far as the intermolecular energy is concerned, we have

$$\frac{\delta \Phi}{\delta g_{\alpha\beta}(x)}=\frac{1}{2}\sum_{1}^{n}{}_{i}\sum_{1}^{n}{}_{j\neq i}\frac{\partial\varphi}{\partial r_{ij}}\frac{\delta r_{ij}}{\delta g_{\alpha\beta}(x)} \tag{20}$$

and taking into account Eqs. (16) and (17), we have

$$\frac{\delta \Phi}{\delta g_{\alpha\beta}(x)}=\frac{1}{2}\sum_{1}^{n}{}_{i}\sum_{1}^{n}{}_{j\neq i}\frac{\partial\varphi}{\partial r_{ij}}\int_{0}^{1} d\lambda\left(\frac{dx^{\alpha}}{d\lambda}\frac{dx^{\beta}}{d\lambda}\right)\Bigg/\left[2\sqrt{g_{\alpha\beta}(\lambda)\frac{dx^{\alpha}}{d\lambda}\frac{dx^{\beta}}{d\lambda}}\right]\delta[x-x(\lambda)] \tag{21}$$

Finally, substituting Eqs. (18), (19), and (21) into Eq. (3b), we get the following expression for the pressure tensor

$$\begin{aligned}\sqrt{g}\, p_{\alpha\beta}=&\left\langle\sum_{1}^{n}{}_{i}\,\delta(x-x_i)\frac{y_{i\alpha}\, y_{i\beta}}{m}\right\rangle\\&-\left\langle\sum_{1}^{n}{}_{i}\sum_{1}^{n}{}_{j\neq i}\frac{\partial\varphi}{\partial r_{ij}}\int_{0}^{1}d\lambda\left(\frac{dx^{\alpha}}{d\lambda}\frac{dx^{\beta}}{d\lambda}\right)\Bigg/\left[2\sqrt{g_{\alpha\beta}(\lambda)\frac{dx^{\alpha}}{d\lambda}\frac{dx^{\beta}}{d\lambda}}\right]\delta[x-x(\lambda)]\right\rangle\end{aligned} \tag{22}$$

where we have taken into account that for any invariant functional S of the metric tensor, one has the identity

$$\delta S=\int\frac{\delta S}{\delta g^{\alpha\beta}(x)}\,\delta g^{\alpha\beta}(x)\, dx=-\int\frac{\delta S}{\delta g_{\alpha\beta}(x)}\,\delta g_{\alpha\beta}(x)\, dx$$

Going back now to Cartesian coordinates, so that $g_{\alpha\beta}=\delta^{\alpha}_{\beta}\sqrt{g}=1$ $x^{\alpha}(\lambda)=r^{\alpha}_{i}(1-\lambda)+\lambda r^{\alpha}_{j}$ and, consequently, $(dx^{\alpha}/d\lambda)=r^{\alpha}_{j}-r^{\alpha}_{i}=r^{\alpha}_{ij}$ and $r_{ij}=\sqrt{g_{\alpha\beta}(\lambda)(dx^{\alpha}/d\lambda)(dx^{\beta}/d\lambda)}$, Eq. (22) becomes

$$p_{\alpha\beta}=\sum_{1}^{n}{}_{i}\left\langle\frac{p^{\alpha}_{i}\,p^{\beta}_{i}}{m}\,\delta(\mathbf{r}-\mathbf{r}_{i})\right\rangle-\frac{1}{2}\left\langle\sum_{1}^{n}{}_{i}\sum_{1}^{n}{}_{j\neq i}\frac{\partial\varphi}{\partial r_{ij}}\,\frac{r^{\alpha}_{ij}r^{\beta}_{ij}}{r_{ij}}\int_{0}^{1}d\lambda\,\delta[\mathbf{r}-(1-\lambda)\mathbf{r}_{i}-\lambda\mathbf{r}_{j}]\right\rangle \tag{23}$$

This expression is identical to that obtained by Irving and Kirkwood [6] starting from Eq. (1); however, in the present calculation there is no ambiguity in the choice of the path joining two molecules. Indeed the path come in only in the definition of the distance between two particles and this is uniquely defined as the length of the straight line segment joining them.

ACKNOWLEDGMENT

The author wishes to thank Prof. C. Cercignani for a number of valuable suggestions on a earlier version of the paper.

REFERENCES

1. S. Ono and S. Kondo, in *Encyclopedia of Physics*, S. Flugge, ed. (Springer, Berlin, 1960), Vol. 10, p. 134.
2. J. S. Rowlinson and B. Widom, *The Molecular Theory of Capillarity* (Oxford University Press, London, 1982), Chap. 4.
3. H. T. Davis and L. E. Scriven, *Adv. Chem. Phys. XLIX*, I. Prigogine and S. A. Rice, eds. (1982).
4. See Ref. 2, p. 113.
5. P. Schofield and J. R. Henderson, *Proc. R. Soc.* **A379**:231 (1982).
6. J. H. Irving and J. G. Kirkwood, *J. Chem. Phys.* **18**:817 (1950).
7. J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic Press, New York, 1976), p. 257.
8. L. Mistura, *J. Chem. Phys.* **83**:3633 (1985).
9. A sililar approach has been proposed by M. Boiteux and J. Kerins, *Physica* **121A**:399 (1983).
10. See footnote 15 of A. J. M. Yang, P. D. Fleming, III, and J. H. Gibbs, *J. Chem. Phys.* **64**:3732 (1976).
11. R. Evans, *Adv. Phys.* **28**:143 (1979).
12. N. N. Bogoliubov, *Problems of a Dynamical Theory in Statistical Physics* (1946) [English translation in *Studies in Statistical Mechanics I, Part A*, J. De Boer and G. E.Uhlenbeck, eds. (North-Holland, Amsterdam, 1962)].
13. H. S. Green, *Proc. R. Soc.* **A189**:103 (1947).
14. F. P. Buff, *Z. Elektrochem.* **56**:311 (1952).
15. A. G. McLellan, *Proc. R. Soc.* **A213**:274 (1952).
16. A. Harasima, *J. Phys. Soc. Jap.* **8**:343 (1953).