Journal of Statistical Physics, Vol. 45, Nos. 1/2, 1986

The Wall Theorem for Elastic Moduli

F. Bavaud[1]

Received March 3, 1986

New expressions for the elastic moduli of a classical system are derived. They involve only the two-point correlation function and the derivative of the one-point correlation function, both only on the boundary of the system. These expressions, valid for any interaction derivable from a potential, are proved from a mechanical point of view by generalizing the virial theorem of Clausius, and from a statistical point of view by a direct method that constitutes an alternative to Green's dilatation method.

KEY WORDS: Wall theorem; virial theorem; correlation functions; pressure; stress tensor; elastic moduli; compressibility; Lamé coefficients.

1. INTRODUCTION

Pressure is defined either as the mean force exerted by the colliding particles on a boundary element of a system, or as the derivative of the free energy with respect to a deformation; it is then one of the few physical quantities that can be directly defined either from a mechanical or a statistical point of view. The mechanical approach leads, via the virial theorem of Clausius(5) applied to a constrained system,(10) to the wall theorem, $P = \rho_{\text{wall}} kT$. On the other hand, in the statistical framework, the virial expression for the pressure(8) is obtained by the dilation method of Green(7); this method can be extended to the elastic modulus tensor and therefore allows us to write "virial" expressions for, e.g., the inverse compressibility and the Lamé coefficients(1,17,18) (we prefer to speak of "bulk" expressions, since the evaluation of such quantities necessitates knowledge of correlation functions up to the order $2n$ on the whole domain occupied by the system interacting through n-body forces).

[1] Ecole Polytechnique Fédérale de Lausanne, Institut de Physique Théorique, CH-1015 Lausanne, Switzerland.

In this paper we derive "wall" expressions for elastic moduli: they involve only the two-point correlation function and the derivative of the one-point correlation function, both only on the boundary of the system. Moreover, the forces do not appear in these expressions, which are valid for any domain and without assuming restrictions as two-body forces or Euclidean invariant potential.

In Section 2 we introduce the general assumptions and derive these wall expressions from a mechanical point of view; we obtain the same expressions by statistical considerations in Section 3: the dilation method is there replaced by the direct expansion of the configurational characteristic function of the deformed system. Particular cases, such as two-body forces, spherical domains, and Coulomb and hard-sphere systems, are also discussed.

2. THE MECHANICAL WALL THEOREM

2.1. Description of the System

Let $\mathscr{H}(\mathbf{x}, \mathbf{p})$, the Hamiltonian of the N-particle system, be of the form

$$\mathscr{H}(\mathbf{x}, \mathbf{p}) = H(\mathbf{x}, \mathbf{p}) + h_\Lambda(\mathbf{x}) \tag{2.1}$$

where $h_\Lambda(\mathbf{x})$ is the wall potential keeping the system confined to the bounded region $\Lambda \subset \mathbb{R}^\nu$, and

$$H(\mathbf{x}, \mathbf{p}) = \sum_{i=1}^{N} \frac{p_i^\alpha p_i^\alpha}{2m} + V(\mathbf{x}) \tag{2.2}$$

where $V(\mathbf{x})$ contains all the remaining interactions, assumed to be Λ independent:

$$V(\mathbf{x}) = \sum_{i=1}^{N} v(x_i) + \sum_{i<j}^{N} v(x_i, x_j) + \sum_{i<j<k}^{N} v(x_i, x_j, x_k) + \cdots \tag{2.3}$$

Defining $F_i^\alpha := -\partial V(\mathbf{x})/\partial x_i^\alpha$ and $f_i^\alpha := -\partial h_\Lambda(\mathbf{x})/\partial x_i^\alpha$, we obtain the classical equations of motion

$$\dot{x}_i^\alpha = p_i^\alpha/m, \qquad \dot{p}_i^\alpha = F_i^\alpha + f_i^\alpha \tag{2.4}$$

The thermodynamic definitions of the (isothermal) stress tensor and of the elastic modulus tensor are, respectively,[1,12]

$$\tau_{\alpha\beta} := \frac{1}{|\Lambda|} \frac{\partial F}{\partial u_{\alpha\beta}}\bigg|_{u=0} \tag{2.5}$$

$$B_{\alpha\beta\gamma\delta} := \frac{1}{|\Lambda|}\left(\frac{\partial^2 F}{\partial u_{\alpha\beta}\, \partial u_{\gamma\delta}}\bigg|_{u=0} + \delta_{\beta\gamma} \frac{\partial F}{\partial u_{\alpha\delta}}\bigg|_{u=0} - \delta_{\gamma\delta} \frac{\partial F}{\partial u_{\alpha\beta}}\bigg|_{u=0}\right) \tag{2.6}$$

Here F is the Helmholtz free energy and $u_{\alpha\beta}$ is the displacement gradient tensor describing the deformation:

$$x'^{\alpha} = (\delta_{\alpha\beta} + u_{\alpha\beta})\, x^{\beta} =: D_{\alpha\beta} x^{\beta} \tag{2.7}$$

The evaluation of (2.5) and (2.6) in the canonical ensemble leads to[1]

$$\tau_{\alpha\beta} = \frac{1}{|\Lambda|} \langle T_{\alpha\beta} \rangle \tag{2.8}$$

$$B_{\alpha\beta\gamma\delta} = \frac{1}{|\Lambda|} (\langle W_{\alpha\beta\gamma\delta} \rangle - \beta \langle T_{\alpha\beta} T_{\gamma\delta} \rangle + \beta \langle T_{\alpha\beta} \rangle \langle T_{\gamma\delta} \rangle$$
$$+ \delta_{\beta\gamma} \langle T_{\alpha\delta} \rangle - \delta_{\gamma\delta} \langle T_{\alpha\beta} \rangle) \tag{2.9}$$

with

$$T_{\alpha\beta} := -\sum_{i=1}^{N} \frac{p_i^{\alpha} p_i^{\beta}}{m} - \sum_{i=1}^{N} F_i^{\alpha} x_i^{\beta} \tag{2.10}$$

$$W_{\alpha\beta\gamma\delta} := \sum_{i=1}^{N} \frac{1}{m} (\delta_{\alpha\delta} p_i^{\gamma} p_i^{\beta} + \delta_{\beta\delta} p_i^{\alpha} p_i^{\gamma} + \delta_{\beta\gamma} p_i^{\alpha} p_i^{\delta}) - \sum_{i,j}^{N} x_i^{\beta} x_j^{\delta} \frac{\partial F_i^{\alpha}}{\partial x_j^{\gamma}} \tag{2.11}$$

In (2.8) and (2.9), the brackets indicate the canonical average, with

$$\exp[-\beta H(\mathbf{x}, \mathbf{p})]\, \chi_{\Lambda}(\mathbf{x}) \tag{2.12}$$

as the (unnormalized) probability density, where

$$\chi_{\Lambda}(\mathbf{x}) = \prod_{i=1}^{N} \chi_{\Lambda}(x_i)$$
$$\chi_{\Lambda}(x_i) = \begin{cases} 1 & x_i \in \Lambda \\ 0 & x_i \notin \Lambda \end{cases} \tag{2.13}$$

Now, in order to obtain a mechanical formulation for $\tau_{\alpha\beta}$ and $B_{\alpha\beta\gamma\delta}$, the ensemble average is replaced by the time average along a phase space trajectory. The explicit form of $h_{\Lambda}(\mathbf{x})$ can be determined by considering $h_{\Lambda}(\mathbf{x})$ as an external potential: then (2.12) must be equivalent to $\exp[-\beta \mathscr{H}(\mathbf{x}, \mathbf{p})]$, which leads to

$$h_{\Lambda}(\mathbf{x}) = -kT \sum_{i=1}^{N} \ln \chi_{\Lambda}(x_i) \tag{2.14}$$

Instead of (2.14), the most obvious choice would be to impose elastic collisions with the wall. But it is easy to see that h_{Λ} would then be proportional to the square of the velocity [which gives some insight about the origin of the factor kT appearing in (2.14)]; on the other hand, the statistical ensemble corresponding to this situation is the microcanonical one, and nothing ensures that (2.9) remains true in that ensemble (see, e.g., Refs. 1 and 17, where new terms appear when the canonical description is replaced by the grand canonical one).

Equation (2.14) is formal in the sense that it contains the logarithm of a distribution; however, all derivations can be made rigorous if $\chi_\Lambda(x_i)$ is considered as the limit of a continuous function (see, e.g., Ref. 10). In what follows, we shall take

$$f_i^\alpha = kT \frac{\partial \chi_\Lambda(x_i)}{\partial x_i^\alpha} \tag{2.15}$$

as the force exerted by the wall on the particle i.

2.2. Derivation of the Wall Expressions

f_i^α is a distribution whose support is the wall $\partial\Lambda$. On the other hand, straighforward evaluation of (2.8) and (2.9) requires the knowledge of F_i^α on the whole domain. The program consists now in replacing F_i^α by f_i^α, i.e., in transforming bulk expressions into wall expressions. The famous virial theorem of Clausius[5] fulfills exactly this task; let us repeat the argument: we define

$$N_{\alpha\beta} := \sum_{i=1}^{N} p_i^\alpha x_i^\beta \tag{2.16}$$

$$C_{\alpha\beta} := \sum_{i=1}^{N} f_i^\alpha x_i^\beta \tag{2.17}$$

Relations (2.4) and (2.10) lead to

$$\dot{N}_{\alpha\beta} = -T_{\alpha\beta} + C_{\alpha\beta} \tag{2.18}$$

Since $N_{\alpha\beta}$ is a bounded observable, the time average of its derivative is zero; consequently,

$$\langle T_{\alpha\beta} \rangle_t = \langle C_{\alpha\beta} \rangle_t \tag{2.19}$$

where the brackets now represent time averages. On the other hand, we get from (2.15)

$$\begin{aligned}\langle C_{\alpha\beta}\rangle_t &= kT\left\langle \sum_{i=1}^{N} \frac{\partial\chi_A(x_i)}{\partial x_i^\alpha}\, x_i^\beta \right\rangle_t \\ &= kT\int dx\, \frac{\partial\chi_A(x)}{\partial x^\alpha}\, x^\beta n_1(x) \\ &= -kT\int_{\partial A} d\sigma_x^\alpha\, x^\beta n_1(x) \end{aligned} \tag{2.20}$$

Here $n_1(x) := \langle \sum_{i=1}^{N} \delta(x - x_i)\rangle_t$ is the one-point correlation function and $d\sigma_x^\alpha$ represents the α component of the outward-oriented surface element of ∂A. An integration by parts and Stokes' theorem lead to the last expression of (2.20), which is the wall formulation for the stress tensor. When $n_1(x)$ is constant on ∂A, we get

$$\tau_{\alpha\beta}(A) = -\delta_{\alpha\beta} P(A) \tag{2.21}$$

$$P(A) = kT n_1(\partial A) \tag{2.22}$$

Equation (2.22) is the well-known wall theorem for the pressure, and constitutes the straightforward generalization to nonideal systems of the kinetic equation of state for the ideal gas. Equation (2.22) was derived by Lebowitz,[10] using the virial theorem, by Fisher,[6] who compared the virial expansion of the pressure and of the wall density, and by Siegert and Meeron,[17] in the particular case of a spherical domain with arguments similar to those of Section 3.

It remains to transform the bulk expression (2.9) of $B_{\alpha\beta\gamma\delta}(A)$ into a wall expression. This is done by the two identities

$$\langle W_{\alpha\beta\gamma\delta}\rangle_t = \beta\langle T_{\alpha\beta} T_{\gamma\delta}\rangle_t - \beta\langle T_{\alpha\beta} C_{\gamma\delta}\rangle_t - \delta_{\beta\gamma}\langle C_{\alpha\delta}\rangle_t \tag{2.23}$$

$$\langle T_{\alpha\beta} C_{\gamma\delta}\rangle_t = \langle C_{\alpha\beta} C_{\gamma\delta}\rangle_t + \delta_{\alpha\delta} kT\langle C_{\gamma\beta}\rangle_t + kT\left\langle \sum_{i=1}^{N} x_i^\beta x_i^\delta \frac{\partial f_i^\alpha}{\partial x_i^\gamma}\right\rangle \tag{2.24}$$

To get (2.23), we start from

$$0 = \left\langle \frac{d}{dt}(T_{\alpha\beta} N_{\gamma\delta})\right\rangle_t = \langle \dot{T}_{\alpha\beta} N_{\gamma\delta}\rangle_t - \langle T_{\alpha\beta} T_{\gamma\delta}\rangle_t + \langle T_{\alpha\beta} C_{\gamma\delta}\rangle_t \tag{2.25}$$

Replacing the relevant observables by their explicit expressions (2.10), (2.11), (2.16), and (2.17) and using (2.19), we get (2.23) under the hypothesis that kinetic and configurational degrees of freedom are uncorrelated, in the sense that

$$\langle A(\mathbf{x})\, p_\alpha p_\beta\rangle_t = \delta_{\alpha\beta} kT\langle A(\mathbf{x})\rangle_t \tag{2.26}$$

In the same way

$$0=\left\langle \frac{d}{dt}(N_{\alpha\beta}C_{\gamma\delta})\right\rangle_t = -\langle T_{\alpha\beta}C_{\gamma\delta}\rangle_t + \langle C_{\alpha\beta}C_{\gamma\delta}\rangle_t + \langle N_{\alpha\beta}\dot{C}_{\gamma\delta}\rangle_t \quad (2.27)$$

leads to (2.24). Equations (2.9), (2.23), and (2.24) allow us to write

$$B_{\alpha\beta\gamma\delta}(\Lambda)=\frac{1}{|\Lambda|}\left[-\beta\langle C_{\alpha\beta}C_{\gamma\delta}\rangle+\beta\langle C_{\alpha\beta}\rangle\langle C_{\gamma\delta}\rangle-\left\langle \sum_{i=1}^{N} x_i^\beta x_i^\delta \frac{\partial f_i^\alpha}{\partial x_i^\gamma}\right\rangle \right.$$
$$\left. -\delta_{\alpha\delta}\langle C_{\gamma\beta}\rangle-\delta_{\gamma\delta}\langle C_{\alpha\beta}\rangle\right] \quad (2.28)$$

Equation (2.28) constitutes the wall formulation for the elastic modulus tensor. Proceeding as in (2.20), we get its expression in terms of correlation functions:

$$B_{\alpha\beta\gamma\delta}(\Lambda)=\frac{kT}{|\Lambda|}\left[-\int_{\partial\Lambda} d\sigma_x^\alpha \int_{\partial\Lambda} d\sigma_y^\gamma\, n_2^T(x,y)\, x^\beta x^\delta \right.$$
$$-\int_{\partial\Lambda} d\sigma_x^\alpha\, x^\beta x^\delta \frac{\partial n_1(x)}{\partial x^\gamma}$$
$$\left. +\delta_{\alpha\delta}\int_{\partial\Lambda} d\sigma_x^\gamma x^\beta n_1(x)-\delta_{\beta\gamma}\int_{\partial\Lambda} d\sigma_x^\alpha\, x^\delta n_1(x)\right] \quad (2.29)$$

Here

$$n_2^T(x,y) := n_2(x,y)-n_1(x)\,n_1(y) \quad (2.30)$$

$$n_2(x,y) := \left\langle \sum_{i\neq j}^{N} \delta(x-x_i)\,\delta(y-x_j)\right\rangle \quad (2.31)$$

Equation (2.29) contains many interesting features: its evaluation necessitates only the two-point correlation function and the derivative of the one-point correlation function, both only on the boundary $\partial\Lambda$ of the domain. Moreover, the potential $V(\mathbf{x})$ does not appear in this expression, which is valid without assuming restrictions such as two-body forces or Euclidean invariance. This wall theorem for elastic moduli can greatly simplify numerical work in a computer simulation: the traditional bulk version given by (2.9) (see, e.g., Refs. 1, 17, and 18) requires knowledge of the correlation functions up to order $2n$ on the whole domain Λ for a system interacting with n-body forces.

3. THE STATISTICAL WALL THEOREM

In this section, we derive the wall expressions for $\tau_{\alpha\beta}$ and $B_{\alpha\beta\gamma\delta}$ by purely statistical arguments. The only difference between these two procedures lies in the fact that in formulas (2.20) and (2.29) time-averaged correlation functions must be replaced by ensemble-averaged ones.

The canonical partition function is

$$Q(N, \Lambda, \beta)=\frac{1}{N!\, h^{\nu N}}\int d\mathbf{p}\, d\mathbf{x}\, \chi_\Lambda(\mathbf{x}) \exp[-\beta H(\mathbf{x}, \mathbf{p})] \tag{3.1}$$

A well-known trick[1,7] consists in absorbing in $H(\mathbf{x}, \mathbf{p})$ the deformation $\Lambda \to \Lambda'$ by the change of variables $x' = Dx$ and $p' = D^{-1\mathrm{tr}} p$ of Jacobian 1, where D is defined in (2.7). This procedure leads to bulk expressions for $\tau_{\alpha\beta}$ and $B_{\alpha\beta\gamma\delta}$.

The alternative we shall develop here is to work directly with $\chi_{\Lambda'}(\mathbf{x})$: when its derivatives appear under an integral, integration by parts allows us to apply Stokes' theorem, leaving a boundary contribution only. We use

$$\chi_{\Lambda'}(x_i) = \chi_{D\Lambda}(x_i) = \chi_\Lambda(D^{-1} x_i) \tag{3.2}$$

and

$$\partial D^{-1}_{\alpha\beta} / \partial u_{\gamma\delta} = -D^{-1}_{\alpha\gamma} D^{-1}_{\delta\beta} \tag{3.3}$$

Equations (3.2) and (3.3) imply

$$\left.\frac{\partial \chi_{\Lambda'}(x_i)}{\partial u_{\alpha\beta}}\right|_{u=0} = -\frac{\partial \chi_\Lambda(x_i)}{\partial x_i^\alpha}\, x_i^\beta \tag{3.4}$$

$$\left.\frac{\partial^2 \chi_{\Lambda'}(x_i)}{\partial u_{\alpha\beta}\, \partial u_{\gamma\delta}}\right|_{u=0} = \frac{\partial^2 \chi_\Lambda(x_i)}{\partial x_i^\alpha\, \partial x_i^\gamma}\, x_i^\beta x_i^\delta + \delta_{\alpha\delta} \frac{\partial \chi_\Lambda(x_i)}{\partial x_i^\gamma} + \delta_{\beta\gamma} \frac{\partial \chi_\Lambda(x_i)}{\partial x_i^\alpha}\, x_i^\delta \tag{3.5}$$

The derivatives of the free energy

$$F(N, \Lambda', T) = -kT \ln Q(N, \Lambda', T) \tag{3.6}$$

with respect to the displacement gradients are now computed by the method described above. $\tau_{\alpha\beta}$ and $B_{\alpha\beta\gamma\delta}$ are obtained by (2.5) and (2.6); the final results are, as claimed before,

$$\tau_{\alpha\beta}(\Lambda) = -\frac{kT}{|\Lambda|}\int_{\partial\Lambda} d\sigma_x^\alpha\, x^\beta n_1(x) \tag{3.7}$$

$$B_{\alpha\beta\gamma\delta}(\Lambda)=\frac{kT}{|\Lambda|}\left[-\int_{\partial\Lambda} d\sigma_x^\alpha \int_{\partial\Lambda} d\sigma_y^\gamma\, x^\beta x^\delta n_2^T(x, y)\right.$$
$$-\int_{\partial\Lambda} d\sigma_x^\alpha\, x^\beta x^\delta \frac{\partial n_1(x)}{\partial x^\gamma}$$
$$\left.+\delta_{\alpha\delta}\int_{\partial\Lambda} d\sigma_x^\gamma\, x^\beta n_1(x)-\delta_{\beta\gamma}\int_{\partial\Lambda} d\sigma_x^\alpha\, x^\delta n_1(x)\right] \tag{3.8}$$

where the correlation functions are now to be considered as ensemble averages.

It is easy to obtain bulk expressions for $\tau_{\alpha\beta}$ and $B_{\alpha\beta\gamma\delta}$ from (3.7) and (3.8) by using the BBGKY hierarchy: taking, e.g., the stress tensor in the case of two-body forces, we get

$$\tau_{\alpha\beta}(\Lambda)=-\frac{kT}{|\Lambda|}\int_\Lambda dx\left[\delta_{\alpha\beta}n_1(x)+x^\beta\frac{\partial n_1(x)}{\partial x^\alpha}\right]$$
$$=-\delta_{\alpha\beta}\rho kT+\frac{1}{|\Lambda|}\int_\Lambda dx\, dy\, x^\beta n_2^T(x, y)\frac{\partial v(x, y)}{\partial x^\alpha} \tag{3.9}$$

We recognize in (3.9) the well-known virial expression for the pressure. The bulk expression for $B_{\alpha\beta\gamma\delta}(\Lambda)$ is obtained in a similar way.

Remarks

1. When $V(\mathbf{x})$ contains two-body translation-invariant interactions only, we get

$$\int_{\partial\Lambda} d\sigma_y^\gamma\, n_2^T(x, y)=-\partial n_1(x)/\partial x^\gamma \tag{3.10}$$

[(3.10) is proved by applying the BBGKY hierarchy to both sides).
The elastic modulus tensor can then be written in the more compact form

$$B_{\alpha\beta\gamma\delta}(\Lambda)=\frac{kT}{|\Lambda|}\int_{\partial\Lambda} d\sigma_x^\alpha\int_{\partial\Lambda} d\sigma_y^\gamma\,(x^\beta x^\delta-x^\beta y^\delta)\, n_2^T(x, y)$$
$$-\delta_{\alpha\delta}\tau_{\gamma\beta}(\Lambda)+\delta_{\beta\gamma}\tau_{\alpha\delta}(\Lambda) \tag{3.11}$$

2. In a recent paper, Powles *et al.*[14] considered Λ as the ball $B(0, R)$ of radius R centered at the origin; by evaluating

$$-\frac{kT}{|B(0, r)|}\int_{\partial B(0,r)} d\sigma_x^\alpha\, x^\beta n_1(x), \qquad r\leqslant R$$

either directly, or by using the BBGKY hierarchy, they obtained the identity

$$\rho(r)\,kT=\bar{\rho}(r)\,kT+\frac{1}{\nu\,|B(0,r)|}\left\langle\sum_{i=1}^{N}x_i^\alpha F_i^\alpha\theta(r-|x_i|)\right\rangle \tag{3.12}$$

where $\rho(r)$ is the local density at distance r and $\bar{\rho}(r)$ is the mean density inside $B(0, r)$. Equation (3.12) is then interpreted as defining $P(r)$, the local pressure at distance r.

3. For hard sphere systems, the wall theorem was obtained by Leff and Coopersmith[11] by direct computation of the correlation function $n_1(x)$ in the one-dimensional case, and by Reiss *et al.*,[15] who considered the work of formation of a cavity in the system. For such systems the contact theorem holds,[8]

$$P=\rho kT+\frac{kT}{2\nu}a^\nu\,|\partial\Omega_\nu|\,n_2(0,a) \tag{3.13}$$

where $|\partial\Omega_\nu|$ is the surface of the ν-dimensional unit ball, a is the diameter of the hard spheres, and $n_2(0, a)$ is the contact value of the distribution function. Equation (3.13) follows in straightforward way from the thermodynamic limit of (3.9), and is therefore to be considered as a bulk expression. However, there is an analogy between the contact and the wall theorems in the sense that they are both direct consequences of the same singularity in the particle–particle and particle–wall interactions, respectively.

4. Systems with periodic boundary conditions possess no boundary, and the potential $V(\mathbf{x})$ is, by construction, Λ-dependent; therefore the virial theorem cannot be applied (see, e.g., Ref. 2, p. 9, for a definition of the pressure in such systems).

5. The one-component plasma is constituted by charged particles interacting by Coulomb forces inside a neutralizing homogeneous bath. There are three possible deformations of such a system (and consequently, three different pressures and elastic moduli):

(i) The bath is left underformed.

(ii) The bath is deformed, keeping its total charge fixed.

(iii) The bath is deformed, keeping its density fixed.

The three choices correspond, respectively, to the so-called virial, thermal, and mechanical pressures, as discussed in Refs. 4 and 13. The $V(\mathbf{x})$ as given by (2.2) is of course Λ-independent in the case (i) only, and therefore the density of the particles at the wall determines the "virial" pressure. Bonomi *et al.*[3] studied by computer simulation the density profile near the wall for a one-dimensional, one-component plasma. Jancovici[9] calculated exactly in two dimensions the density near the wall and its dependence on a possible total charge excess, for $kT = e^2/2$.

6. When the domain Λ is $B(0, R)$, the ν-dimensional ball of radius R centered at the origin, it is easy to check from symmetry considerations that the elastic modulus tensor, as given by (3.8), can be written as

$$B_{\alpha\beta\gamma\delta} = \lambda\delta_{\alpha\beta}\delta_{\gamma\delta} + \mu(\delta_{\alpha\beta}\delta_{\gamma\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma}) \tag{3.14}$$

Here the Lamé coefficients λ and μ are, respectively, the bulk and the shear modulus. They are related to the isothermal compressibility χ_T

$$\chi_T^{-1} := -|\Lambda|\, \partial P(\Lambda)/\partial(\Lambda) \tag{3.15}$$

by

$$\chi_T^{-1} = \lambda + (2/\nu)\, \mu \tag{3.16}$$

where ν is the dimension of the system. The form (3.14) implies that the system is isotropic. However, it must be realized that such an isotropy does not exclude solid phases; it means simply that the possible anisotropic pure phases have been averaged in all directions, leading to an effective isotropic elastic modulus tensor. (Recall that a pure phase is an equilibrium state which cannot be written as a convex combination of different equilibrium states; see, e.g., Ref. 16). In the following, we shall assume for simplicity that the potential is a two-body one. We shall now give the expressions for χ_T^{-1} and μ in the cases $\nu = 1, 2, 3$; we get from (3.11):

For $\nu = 3$

$$\chi_T^{-1} = \frac{2}{3} kT\pi R^3 \int_0^\pi d\gamma \sin\gamma(\cos\gamma - 1)\, n_2^T(\cos\gamma) \tag{3.17}$$

$$\mu = \frac{1}{5} kT\pi R^3 \int_0^\pi d\gamma \sin\gamma(-3\cos^2\gamma + 2\cos\gamma + 1)\, n_2^T(\cos\gamma) \tag{3.18}$$

For $\nu = 2$

$$\chi_T^{-1} = \frac{1}{2} kTR^2 \int_0^{2\pi} d\gamma(\cos\gamma - 1)\, n_2^T(\cos\gamma) \tag{3.19}$$

$$\mu = \frac{1}{4} kTR^2 \int_0^{2\pi} d\gamma(-2\cos^2\gamma + \cos\gamma + 1)\, n_2^T(\cos\gamma) \tag{3.20}$$

For $\nu = 1$

$$\chi_T^{-1} = -kTLn_2^T(L/2, -L/2) \tag{3.21}$$

In (3.17)–(3.20), have written $n_2^T(x, y) \equiv n_2^T(\cos\gamma)$, where γ is the angle between x and y. In (3.21), whose physical interpretation is obvious, we put $\Lambda = [-L/2, L/2]$.

Formulas (3.17) and (3.19), which give the inverse compressibility, are in full agreement with formula (8.11) of Ref. 17 when (3.10) is used.

For the ideal gas, where $n_2^T(x, y) = -\rho/|\Lambda|$, the above formulas lead to

$$\lambda = \chi_T^{-1} = \rho kT, \qquad \mu = 0 \tag{3.22}$$

Equations (3.18) and (3.20) constitute sum rules for fluids in the sense that $\mu = 0$ implies that $n_2^T(\cos\gamma)$ must be orthogonal to the relevant weight factor.

REFERENCES

1. F. Bavaud, P. Choquard, and J.-R. Fontaine, *J. Stat. Phys.* **42**:621 (1986).
2. B. J. Berne, *Statistical Mechanics* (Plenum Press, New York, 1977), Part B, p. 9.
3. E. Bonomi, E. Jamin, and M. R. Feix, *Phys. Lett.* **70A**:199 (1979).
4. P. Choquard, P. Favre, and C. Gruber, *J. Stat. Phys.* **23**:405 (1980).
5. R. Clausius, *Phil. Mag.* **40**:122 (1870).
6. I. Z. Fisher, *The Statistical Theory of Liquids* (Hindustan Publishing Corporation, 1964), p. 117.
7. H. S. Green, *Proc. Phys. Soc. A* **189**:103 (1947).
8. T. L. Hill, *Statistical Mechanics* (McGraw-Hill, New York, 1956), p. 190 and 216.
9. B. Jancovici, *J. Phys. Lett. (Paris)* **42**:L-223 (1981).
10. J. L. Lebowitz, *Phys. Fluids* **3**:64 (1960).
11. H. S. Leff and M. H. Coopersmith, *J. Math. Phys.* **8**:306 (1966).
12. F. D. Murnaghan, *Am. J. Math.* **49**:235 (1937).
13. M. Navet, E. Jamin, and M. R. Feix, *J. Phys. Lett.* **41**:*L*-69 (1980).
14. J. G. Powles, G. Rickayzen, and M. L. Williams, *J. Chem. Phys.* **83**:293 (1985).
15. H. Reiss, H. L. Frisch, and J. L. Lebowitz, *J. Chem. Phys.* **31**:369 (1959).
16. D. Ruelle, *Statistical Mechanics* (Benjamin, New York, 1969), p. 162.
17. A. Siegert and E. Meeron, *J. Math. Phys.* **7**:741 (1966).
18. D. R. Squire, A. C. Holt, and W. G. Hoover, *Physica* **42**:388 (1969).