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Statistical Mechanics of Elastic Moduli

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We consider continuous systems of particles in the framework of classical statistical mechanics and derive a general expression for the static elastic moduli tensor in terms of correlation functions. We find sufficient conditions for the vanishing of the shear modulus. Relationships between these conditions and others insuring translational or rotational invariance are discussed.

KEY WORDS: Classical fluids; correlation functions; Euclidean invariance; shear modulus.

1. INTRODUCTION

In this paper we start a rigorous microscopic study of elastic moduli in the framework of classical statistical mechanics. We consider particle systems with Lennard-Jones-type two-body potentials. The phase diagram of such systems is rather well understood from numerical simulations.[1] From the theoretical point of view, the situation is different: we have good approximation schemes to study the fluid phase, but we are far from understanding the solid–liquid transition.

It is a fact of everyday experience that solids are rigid and that fluids flows. It would be also desirable to deduce these macroscopic properties of matter from statistical mechanics. Again, using numerical simulations, this can be done.[15] Our aim in this paper is to attack this problem from a rigorous point of view.

Generalizing the method of dilatation of Green,[8] we first express the elastic moduli tensor $B_{\alpha\beta\gamma\delta}$ in terms of basic objects of statistical mechanics which are the correlation functions. We do the computation in the finite volume canonical ensemble (C.E.). The choice of the C.E. is justified by the

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fact that we do not want the number of particles to vary during the deformation of the system. The expression we find involves integrals over the volume Λ of two-, three-, and four-point correlation functions. We then have to face the problem of evaluating these quantities in the thermodynamical limit. This problem is hard for two reasons: first, even in the fluid phase there is no direct way of proving the existence of the thermodynamic limit of the finite volume correlation functions in the C.E.; second the convergence is expected to be slow.

However, let us remark that finite volume systems of charged particles interacting via the Coulomb force are expected to converge rapidly to their thermodynamic limit. This is indeed the case for the one-component plasma. At $\Gamma = \beta e^2 = 2$ (where the system can be solved explicitly), Piller and Rentsch have been able to compute the thermodynamic limit of $B_{\alpha\beta\gamma\delta}(\Lambda)$ at $\Gamma = 2$ where they found absence of shear ($\mu = 0$) and at $\Gamma = \infty$ where they found $\mu = e^2\rho/8$.

There is another puzzling fact: the compressibility modulus is defined by $-V\,\partial P/\partial V$. Using the expression of the virial pressure, $V\,\partial P/\partial V$ will contain two-, three-, and four-point correlation functions (as mentioned above). How does it come that in the thermodynamic limit the compressibility (which is the inverse of the compressibility modulus) can be written in terms of the two-point function only (in fact, $kT\rho^2\chi_T = \int dx[n_2(0, x) - \rho^2]$ where χ_T is the compressibility, ρ the density, and n_2 the two-points functions)?

The way we solve the problem of the thermodynamic limit at least for the fluid phase is by working in the grand canonical ensemble (G.C.E.). However, in order to compute the elastic moduli tensor in this ensemble, we propose that the mean number of particles is kept fixed during the deformation. The finite volume expression for $B_{\alpha\beta\gamma\delta}$ still envolves four-point functions but is different from the one found in the (C.E.) (this is not surprising since both ensembles are only equivalent in the thermodynamic limit). We can now use standard methods (see, e.g., Ref. 14) to take the thermodynamic limit of $B_{\alpha\beta\gamma\delta}(\Lambda)$ and express it in terms of infinite volume correlation functions. We now want to discuss in a precise way the results we have obtained.

We consider particle systems with twice continuously differentiable two-body potential. For these systems we make two types of assumptions:

(a1) The two-body potential $V(r)$ is absolutely integrable and the correlation functions have an integrable clustering (i.e., $V(r) \sim r^{-(\nu+\varepsilon)}$, $n_2(0, r) - \rho^2 \sim r^{-(\nu+\varepsilon)}$ as $r \to \infty$ where ν is the dimension and $\varepsilon > 0$, and similar assumptions for three- and four-point correlation functions).

(a2) The two-body potential $V(r)$ is of first moment integrable and the correlation functions have a clustering of first moment integrable [i.e., $V(r) \sim r^{-(\nu+1+\varepsilon)}$, $n_2(0, r) - \rho^2 \sim r^{-(\nu+1+\varepsilon)}$ as $r \to \infty$].

We prove that assumption (a1) implies that one can give a meaningful definition of the elastic moduli tensor $B_{\alpha\beta\gamma\delta}$ in the thermodynamic limit. Let us remark that assumption (a1) implies that the correlation functions are translation invariant and that the state is pure[9] (i.e., is an equilibrium state which cannot be written as a convex combination of different equilibrium states). This immediately excludes crystals. However, (a1) does not prevent orientational order, that is, there may exist liquid crystal phases for which assumption (a1) is true and for which our formula would yield a well-defined expression for $B_{\alpha\beta\gamma\delta}$ (however, we did not investigate such a situation). If we assume the validity of the stronger assumption (a2), then it comes[9] that the correlation functions of the system have to be Euclidean invariant, that is, the spatial translations and rotations are not broken symmetries. This fact immediately implies that $B_{\alpha\beta\gamma\delta}$ has only two independent components: the bulk and the shear modulus. One of the main results of our paper is to show that $B_{\alpha\beta\gamma\delta}$ is equal to $\chi_T^{-1}\delta_{\alpha\beta}\delta_{\gamma\delta}$ (where χ_T is the isothermal compressibility for which we recover the expression in terms of the two-point function). This in particular shows the absence of shear for such systems.

Hypothesis (a2) is verified for fluids because for such systems, at least away from the critical point, it is expected[7] (and can be proved in some cases[3]) that the clustering of the correlation functions has the same decay as the potential.

If amorphous materials can be described in the framework of equilibrium classical statistical mechanics of particles systems (with pairwise spherical symmetry potentials) and if their static shear modulus is nonzero, our result implies that their correlation functions have to have a slow clustering.

Finally, it must be specified that the subsequent formalism being the one of equilibrium, elastic moduli defined here must be understood as zero frequency moduli. Such an interpretation is confirmed by the study of the linear response theory. This will be the subject of a forthcoming publication.

Let us stress the fact that the paper is self-contained and does not require any knowledge of elasticity theory. It is organized as follows: Section 1 contains a thermodynamic derivation of Hooke's law. Section 2 gives a microscopic expression of the elastic moduli tensor. Section 3 deals with the problem of the thermodynamic limit and also contains the statement and the proof of our main result.

2. THERMODYNAMIC DEFINITION OF THE ELASTIC MODULI

In order to be self-contained and fix the definitions and notations, we review in this section some elements of the classical theory of elasticity. We introduce the stress tensor and Hooke's law.

We consider a material system in the domain $\Lambda \subset \mathbb{R}^\nu$, with volume $|\Lambda|$. We introduce a homogeneous isothermal deformation

$$D: \mathbb{R}^\nu \to \mathbb{R}^\nu$$

$$x \mapsto x'$$

$$x'^\alpha = (\delta_{\alpha\beta} + u_{\alpha\beta})\, x^\beta \tag{2.1}$$

$u_{\alpha\beta}$ is the displacement gradient tensor, which we assume to be independent of x. As usual, components of tensors will have the greek indices α, β, γ, δ, which run from 1 to ν, the dimension of the space. We also use the Einstein convention, summing over repeated indices. In the following, we assume $|u_{\alpha\beta}| \ll 1$. The expansion of the Helmholtz free energy of the deformed system is

$$F(\Lambda') = F(\Lambda) + |\Lambda|\, \tau_{\alpha\beta}(\Lambda)\, u_{\alpha\beta} + \tfrac{1}{2}|\Lambda|\, A_{\alpha\beta\gamma\delta}(\Lambda)\, u_{\alpha\beta} u_{\gamma\delta} + O(u^3) \tag{2.2}$$

where

$$\tau_{\alpha\beta}(\Lambda) := \frac{1}{|\Lambda|} \frac{\partial F(\Lambda')}{\partial u_{\alpha\beta}}\bigg|_{u=0} \tag{2.3}$$

is the stress tensor in the reference state, and

$$A_{\alpha\beta\gamma\delta}(\Lambda) := \frac{1}{|\Lambda|} \frac{\partial^2 F(\Lambda')}{\partial u_{\alpha\beta}\, \partial u_{\gamma\delta}}\bigg|_{u=0} \tag{2.4}$$

In order to express *Hooke's law*, which defines the stress–strain elastic moduli, we consider a second deformation of the system, D': $\Lambda' \to \Lambda''$.[16] Writing (2.1) in a matrix form

$$D(x) = x' = (E + U)x \tag{2.5}$$

where $E = (\delta_{\alpha\beta})$, $U = (u_{\alpha\beta})$, we define

$$D''(x) = D' \circ D(x) = (E + U')\, x' = (E + U'')x \tag{2.6}$$

(2.5) and (2.6) imply

$$(E + U')(E + U) = (E + U'') \tag{2.7}$$

or

$$u''_{\alpha\beta} = u_{\alpha\beta} + u'_{\alpha\beta} + u'_{\alpha\rho} u_{\rho\beta} \tag{2.8}$$

We have, from (2.3), and using (2.8),

$$\begin{aligned}
\tau_{\alpha\beta}(\Lambda') &= \frac{1}{|\Lambda'|} \frac{\partial F(\Lambda'')}{\partial u'_{\alpha\beta}}\bigg|_{u'=0} = \frac{1}{|\Lambda'|} \frac{\partial F(\Lambda'')}{\partial u''_{\gamma\delta}} \frac{\partial u''_{\gamma\delta}}{\partial u'_{\alpha\beta}}\bigg|_{u'=0} \\
&= \frac{1}{|\Lambda'|} \delta_{\alpha\gamma}(\delta_{\beta\delta} + u_{\beta\delta}) \frac{\partial F(\Lambda'')}{\partial u''_{\gamma\delta}}\bigg|_{u'=0} \\
&= \frac{1}{|\Lambda'|} (\delta_{\beta\delta} + u_{\beta\delta}) \frac{\partial F(\Lambda')}{\partial u_{\alpha\delta}}
\end{aligned} \tag{2.9}$$

(2.9) is the exact expression for the stress tensor in the deformed state. (2.9) was first obtained by Murnaghan,[11] starting from equilibrium equations for the strained medium. We now expand (2.9) with respect to $u_{\gamma\delta}$, using (2.2). We also use

$$\begin{aligned}
\frac{1}{|\Lambda'|} &= \frac{1}{|\Lambda| \det(E+U)} \\
&= \frac{1}{|\Lambda|}\left[1 - \delta_{\alpha\beta} u_{\alpha\beta} + \frac{1}{2}(\delta_{\alpha\beta}\delta_{\gamma\delta} + \delta_{\beta\gamma}\delta_{\alpha\delta}) u_{\alpha\beta} u_{\gamma\delta} + O(u^3)\right]
\end{aligned} \tag{2.10}$$

Taking account of the symmetry

$$A_{\alpha\beta\gamma\delta}(\Lambda) = A_{\gamma\delta\alpha\beta}(\Lambda) \tag{2.11}$$

we obtain

$$\begin{aligned}
\tau_{\alpha\beta}(\Lambda') = \tau_{\alpha\beta}(\Lambda) + [&A_{\alpha\beta\gamma\delta}(\Lambda) + \delta_{\beta\gamma}\tau_{\alpha\delta}(\Lambda) \\
&- \delta_{\gamma\delta}\tau_{\alpha\beta}(\Lambda)]\, u_{\gamma\delta} + O(u^2)
\end{aligned} \tag{2.12}$$

(2.12) is Hooke's law; it defines the tensor $B_{\alpha\beta\gamma\delta}(\Lambda)$:

$$B_{\alpha\beta\gamma\delta}(\Lambda) = A_{\alpha\beta\gamma\delta}(\Lambda) + \delta_{\beta\gamma}\tau_{\alpha\delta}(\Lambda) - \delta_{\gamma\delta}\tau_{\alpha\beta}(\Lambda) \tag{2.13}$$

Remark 2.1. For an isotropic system

$$\tau_{\alpha\beta}(\Lambda) = -\delta_{\alpha\beta} P(\Lambda) \tag{2.14}$$

$$B_{\alpha\beta\gamma\delta}(\Lambda) =: \lambda_B(\Lambda)\,\delta_{\alpha\beta}\delta_{\gamma\delta} + \mu_B(\Lambda)(\delta_{\alpha\gamma}\delta_{\beta\delta} + \delta_{\alpha\delta}\delta_{\beta\gamma}) \tag{2.15}$$

where $P(\Lambda)$ is the pressure of the system. $\lambda_B(\Lambda)$, the bulk modulus, and $\mu_B(\Lambda)$, the shear modulus are the Lamé coefficients. The subscript B recalls the origin of their definition, e.g., from the tensor $B_{\alpha\beta\gamma\delta}(\Lambda)$. They are related to the isothermal compressibility:

$$\chi_T(\Lambda) := -\frac{1}{|\Lambda|}\frac{\partial\,|\Lambda|}{\partial P(\Lambda)} \tag{2.16}$$

by

$$\frac{1}{\chi_T(\Lambda)} = \lambda_B(\Lambda) + \frac{2}{\nu}\,\mu_B(\Lambda) \tag{2.17}$$

where ν is the dimension of the system. For a fluid, it is expected that $\mu_B(\Lambda) = 0$, or equivalently

$$B_{\alpha\beta\gamma\delta}(\Lambda) = \frac{1}{\chi_T(\Lambda)}\,\delta_{\alpha\beta}\,\delta_{\gamma\delta} \tag{2.18}$$

One of the main points of this work is to show (2.18) from first principles.

Remark 2.2. In the literature, one defines the tensor

$$C_{\alpha\beta\gamma\delta}(\Lambda) := \left.\frac{\partial^2 F(\Lambda')}{\partial\eta_{\alpha\beta}\,\partial\eta_{\gamma\delta}}\right|_{\eta=0} \tag{2.19}$$

where

$$\eta_{\alpha\beta} := \tfrac{1}{2}(u_{\alpha\beta} + u_{\beta\alpha} + u_{\gamma\alpha}u_{\gamma\beta}) \tag{2.20}$$

$\eta_{\alpha\beta}$ is called the Lagrangian strain parameters tensor. Its use is motivated by the fact that free energy can depend only on the distance between original and deformated points, and $x'^{\alpha}x'^{\alpha} = x^{\alpha}(\delta_{\alpha\beta} + 2\eta_{\alpha\beta})\,x^{\beta}$. It is important to realize that $B_{\alpha\beta\gamma\delta}(\Lambda)$ is equal to $C_{\alpha\beta\gamma\delta}(\Lambda)$ only at zero pressure.[2,5,11,16] In fact, one has the relation

$$B_{\alpha\beta\gamma\delta}(\Lambda) = C_{\alpha\beta\gamma\delta}(\Lambda) + \delta_{\alpha\gamma}\,\tau_{\beta\delta}(\Lambda) + \delta_{\beta\gamma}\,\tau_{\alpha\delta}(\Lambda) - \delta_{\gamma\delta}\,\tau_{\alpha\beta}(\Lambda) \tag{2.21}$$

$B_{\alpha\beta\gamma\delta}(\Lambda)$, as opposed to $C_{\alpha\beta\gamma\delta}(\Lambda)$, does not possesses the Voigt symmetry $[C_{\alpha\beta\gamma\delta}(\Lambda) = C_{\beta\alpha\gamma\delta}(\Lambda) = C_{\gamma\delta\alpha\beta}(\Lambda)]$, unless $\tau_{\alpha\beta}(\Lambda) = -\delta_{\alpha\beta}P(\Lambda)$. In the isotropic case, the use of $C_{\alpha\beta\gamma\delta}(\Lambda)$ to define Lamé coefficients $\lambda_c(\Lambda)$, $\mu_c(\Lambda)$, analogously to (2.15), would lead to

$$\lambda_c(\Lambda) = \lambda_B(\Lambda) - P(\Lambda), \qquad \mu_c(\Lambda) = \mu_B(\Lambda) + P(\Lambda) \tag{2.22}$$

3. CANONICAL AND GRAND CANONICAL EXPRESSION FOR THE ELASTIC MODULI

The aim of this section is to find a statistical mechanics expression for $B_{\alpha\beta\gamma\delta}(\Lambda)$, the elastic moduli tensor at finite volume in the canonical and grand canonical ensemble. We shall use a strategy similar to the one used by Green to obtain the expression for the virial pressure.[8]

3.1. Canonical Ensemble Formulation of Statistical Mechanics

We first recall some features about canonical ensemble. The Helmholtz free energy is

$$F(N, \Lambda, T) = -kT \ln Q(N, \Lambda, T) \tag{3.1}$$

where

$$Q(N, \Lambda, T) = \frac{1}{N!\, h^{\nu N}} \int_{\mathbb{R}^{\nu N}} d\mathbf{p} \int_{\Lambda^N} d\mathbf{x} \exp[-\beta H^N(\mathbf{p}, \mathbf{x})] \tag{3.2}$$

is the canonical partition function ($\mathbf{p} = \{p_i, i = 1,..., N\}$; $\mathbf{x} = \{x_i, i = 1,..., N\}$; $d\mathbf{p} = \prod_{\alpha=1}^{\nu} \prod_{i=1}^{N} dp_i^\alpha$; $d\mathbf{x} = \prod_{\alpha=1}^{\nu} \prod_{i=1}^{N} dx_i^\alpha$). The Hamiltonian of the system is

$$H^N(\mathbf{p}, \mathbf{x}) = \sum_{i=1}^{N} \frac{p_i^\alpha p_i^\alpha}{2m} + \frac{1}{2} \sum_{i \neq j}^{N} V(|x_i - x_j|) \tag{3.3}$$

the properties of $V(|x_i - x_j|)$ will be specified later. The mean value of the dynamical variable $A^N(\mathbf{p}, \mathbf{x})$ is defined by

$$\langle A \rangle(N, \Lambda, T) = \frac{1}{Q(N, \Lambda, T)\, N!\, h^{\nu N}} \int_{\mathbb{R}^{\nu N}} d\mathbf{p} \int_{\Lambda^N} d\mathbf{x} \times A^N(\mathbf{p}, \mathbf{x}) \exp[-\beta H^N(\mathbf{p}, \mathbf{x})] \tag{3.4}$$

3.2. The Dilatation Method: Computation of the Stress Tensor and of the Elastic Moduli Tensor

After a deformation $D: \Lambda \to \Lambda'$, the canonical partition function becomes $Q(N, \Lambda', T)$. Doing the change of variables $x_i' = (E + U)\, x_i$ and $p_i' = (E + U^{\mathrm{tr}})^{-1} p_i$ of Jacobian 1, it can be rewritten as

$$Q(N, \Lambda', T) = \frac{1}{N!\, h^{\nu N}} \int_{\mathbb{R}^{\nu N}} d\mathbf{p} \int_{\Lambda^N} d\mathbf{x} \exp[-\beta H^N(\mathbf{p}', \mathbf{x}')] \tag{3.5}$$

with

$$H^N(\mathbf{p}', \mathbf{x}') = \sum_{i=1}^{N} \frac{1}{2m} (E + U)_{\pi\alpha}^{-1}\, p_i^\pi (E + U)_{\rho\alpha}^{-1}\, p_i^\rho + \frac{1}{2} \sum_{i \neq j}^{N} V[|(E + U)(x_i - x_j)|] \tag{3.6}$$

The dependence on the displacements gradients is now contained in the Hamiltonian, and it is now easy to compute derivatives with respect to $u_{\alpha\beta}$. Using (3.2), we get

$$\frac{\partial F(N, \Lambda', T)}{\partial u_{\alpha\beta}} = -\beta Q^{-1}(N, \Lambda', T) \int_{\mathbb{R}^{\nu N}} d\mathbf{p} \int_{\Lambda^N} d\mathbf{x} \times \frac{\partial H^N(\mathbf{p}', \mathbf{x}')}{\partial u_{\alpha\beta}} \exp[-\beta H^N(\mathbf{p}', \mathbf{x}')]$$

$$= -\beta \left\langle \frac{\partial H'}{\partial u_{\alpha\beta}} \right\rangle' \tag{3.7}$$

(3.7) and (2.3) imply

$$\tau^C_{\alpha\beta}(\Lambda) = \frac{1}{|\Lambda|} \langle T_{\alpha\beta} \rangle (N, \Lambda, T) \tag{3.8}$$

the index C standing for canonical ensemble, where

$$T^N_{\alpha\beta}(\mathbf{p}, \mathbf{x}) := \left. \frac{\partial H^N(\mathbf{p}', \mathbf{x}')}{\partial u_{\alpha\beta}} \right|_{u=0} = -\sum_{i=1}^{N} \frac{p_i^\alpha p_i^\beta}{m} + \frac{1}{2} \sum_{i \neq j}^{N} \frac{\partial V(x_i - x_j)}{\partial x_i^\alpha} (x_i^\beta - x_j^\beta) = T^N_{\beta\alpha}(\mathbf{p}, \mathbf{x}) \tag{3.9}$$

Differentiating (3.7) once more, we find analogously

$$\left. \frac{\partial^2 F(N, \Lambda', T)}{\partial u_{\alpha\beta}\, \partial u_{\gamma\delta}} \right|_{u=0} = |\Lambda|\, A^C_{\alpha\beta\gamma\delta}(\Lambda) \tag{3.10}$$

$$= \langle W_{\alpha\beta\gamma\delta} \rangle (N, \Lambda, T) - \beta \langle T_{\alpha\beta}; T_{\gamma\delta} \rangle (N, \Lambda, T)$$

where

$$W^N_{\alpha\beta\gamma\delta}(\mathbf{p}, \mathbf{x}) := \left. \frac{\partial^2 H^N(\mathbf{p}', \mathbf{x}')}{\partial u_{\alpha\beta}\, \partial u_{\gamma\delta}} \right|_{u=0}$$

$$= \sum_{i=1}^{N} \frac{1}{m} (\delta_{\alpha\delta}\, p_i^\beta p_i^\gamma + \delta_{\beta\gamma}\, p_i^\alpha p_i^\delta + \delta_{\beta\delta}\, p_i^\alpha p_i^\gamma)$$

$$+ \frac{1}{2} \sum_{i \neq j}^{N} \frac{\partial^2 V(|x_i - x_j|)}{\partial x_i^\alpha\, \partial x_i^\gamma} (x_i^\beta - x_j^\beta)(x_i^\delta - x_j^\delta)$$

$$= W^N_{\gamma\delta\alpha\beta}(\mathbf{p}, \mathbf{x}) \tag{3.11}$$

We used

$$\langle B; C \rangle := \langle BC \rangle - \langle B \rangle \langle C \rangle \tag{3.12}$$

(2.13), (3.8), (3.11) imply the following canonical expression for the finite volume elastic moduli tensor:

$$B^C_{\alpha\beta\gamma\delta}(\Lambda) = \frac{1}{|\Lambda|} (\langle W_{\alpha\beta\gamma\delta} \rangle - \beta \langle T_{\alpha\beta}; T_{\gamma\delta} \rangle + \delta_{\beta\gamma} \langle T_{\alpha\delta} \rangle - \delta_{\gamma\delta} \langle T_{\alpha\beta} \rangle)(N, \Lambda, T) \tag{3.13}$$

Remarks. (1) In what precedes, we followed the thermodynamic method of Section 1, consisting essentially in correcting the second derivatives of the free energy $A_{\alpha\beta\gamma\delta}(\Lambda)$ with appropriate stresses [see (2.13)]. In order to find this correction, we needed a second deformation of the system. But at the microscopical level, there is an alternative procedure which consists in starting from the statistical expression of $\tau^C_{\alpha\beta}(\Lambda')$, where expansion in $u_{\gamma\delta}$ gives immediately the elastic moduli tensor $B^C_{\alpha\beta\gamma\delta}(\Lambda)$. This expression is

$$\begin{aligned} \tau^C_{\alpha\beta}(\Lambda') &= \frac{1}{|\Lambda'|} \langle T'_{\alpha\beta} \rangle'(N, \Lambda', T) \\ &= \frac{1}{|\Lambda| \det(E+U)\, Q(N, \Lambda', T)} \int_{\mathbb{R}^{\nu N}} d\mathbf{p} \int_{\Lambda^N} d\mathbf{x} \\ &\quad \times T^N_{\alpha\beta}(\mathbf{p}', \mathbf{x}') \exp[-\beta H^N(\mathbf{p}', \mathbf{x}')] \end{aligned} \tag{3.14}$$

where

$$\begin{aligned} T^N_{\alpha\beta}(\mathbf{p}', \mathbf{x}') = &- \sum_{i=1}^{N} \frac{1}{m} (E+U)^{-1}_{\pi\alpha}\, p^\pi_i (E+U)^{-1}_{\rho\beta}\, p^\rho_i \\ &+ \frac{1}{2} \sum_{i \neq j}^{N} \frac{\partial V[|(E+U)(x_i - x_j)|]}{\partial (E+U)_{\alpha\pi}\, x^\pi_i} (E+U)_{\beta\rho}(x^\rho_i - x^\rho_j) \end{aligned} \tag{3.15}$$

We see that, although $H^N(\mathbf{p}', \mathbf{x}')$ as given by (3.6) can be expanded with respect to the Lagrangian parameters $\eta_{\alpha\beta}$ [this fact allows the expansion of $F(N, \Lambda', T)$ in $\eta_{\alpha\beta}$], it is not the case for $T^N_{\alpha\beta}(\mathbf{p}', \mathbf{x}')$. We arrive at the conclusion that $\eta_{\alpha\beta}$ do not constitute in general convenient expansion parameters, in order to derive expressions (at the thermodynamic or statistical level) for $B_{\alpha\beta\gamma\delta}(\Lambda)$. This fact is closely related to the general absence of Voigt symmetry for $B_{\alpha\beta\gamma\delta}(\Lambda)$.

(2) As required by the standard statistical prescription, the (stress–strain isothermal) elastic moduli tensor is given by the thermodynamic limit:

$$B^C_{\alpha\beta\gamma\delta} := \lim_{\substack{|\Lambda| \to \infty \\ N \to \infty \\ N/|\Lambda| = cst}} B^C_{\alpha\beta\gamma\delta}(\Lambda) \tag{3.16}$$

Let us stress the fact that shape independence of the free energy per unit volume in the thermodynamic limit does not imply the vanishing of the shear modulus. Indeed, defining $f_A := F(A)/|A|$, it comes from (2.2), (2.10), (2.13):

$$B_{1212} = \lim_{|A| \to \infty} \left. \frac{\partial f_{A'}}{\partial u_{12}\, \partial u_{12}} \right|_{u_{12}=0} \tag{3.17}$$

But the general result (see, e.g., Ref. 14, Theorem 3.4.4),

$$\lim_{|A| \to \infty} f_{A'} = \lim_{|A| \to \infty} f_A \qquad \text{(independent of } u_{12}\text{)}$$

does not imply $B_{1212} = 0$, because the permutation of the limit and the derivative is not legitimate!

(3) When $T \to 0$, the means over kinetic contributions vanish; it is expected also that $\beta\langle T_{\alpha\beta}; T_{\gamma\delta}\rangle \to 0$. Thus, the classical results about solid state elasticity are found again (see Ref. 4; the pressure corrections are discussed in Refs. 2 and 5).

(4) The expression (3.13) (up to pressure corrections) was evaluated by numerical simulation,[15] for a system interacting by a Lennard-Jones potential, at low temperature. It appears that the shear term $B^C_{1212}(A)$ (for which pressure corrections fall) is different from 0.

3.3. Grand Canonical Formulation of Statistical Mechanics

We now recall some features about grand canonical ensemble, in order to derive $B^G_{\alpha\beta\gamma\delta}(A)$, the elastic moduli tensor evaluated in this ensemble. The grand partition function is

$$\Xi(z, A, T) = \sum_{N=0}^{\infty} z^N Q(N, A, T) \tag{3.18}$$

where $z = \exp(\beta\mu)$ is the fugacity and μ the chemical potential. The mean value of the dynamical variable $A^N(\mathbf{p}, \mathbf{x})$ is defined by

$$\langle A\rangle(z, A, T) := \frac{1}{\Xi(z, A, T)} \sum_{N=0}^{\infty} \frac{z^N}{N!\, h^{\nu N}} \int_{\mathbb{R}^{\nu N}} d\mathbf{p} \int_{A^N} d\mathbf{x} \times A^N(\mathbf{p}, \mathbf{x}) \exp[-\beta H^N(\mathbf{p}, \mathbf{x})] \tag{3.19}$$

The mean number of particles is

$$\langle N\rangle(z, A, T) = z \frac{\partial}{\partial z} \ln \Xi(z, A, T) \tag{3.20}$$

We will use also

$$z\frac{\partial}{\partial z}\langle A\rangle(z, \Lambda, T) = \langle A; N\rangle(z, \Lambda, T) \tag{3.21}$$

The Helmholtz free energy of the system, when expressed in terms of the grand canonical variables, is

$$\begin{aligned} F(z, \Lambda, T) &= \mu\langle N\rangle - kT\ln \Xi(z, \Lambda, T) \\ &= kT[\langle N\rangle \ln z - \ln \Xi(z, \Lambda, T)] \end{aligned} \tag{3.22}$$

3.4. Computation of the Stress Tensor and of the Elastic Moduli Tensor in Grand Canonical Ensemble

The free energy of the deformed system is obtained from (3.18), (3.20), (3.22), with $Q(N, \Lambda, T)$ replaced by $Q(N, \Lambda', T)$ as given by (3.5). The successive derivatives of the free energy with respect to the displacement gradients have to be performed with *fixed mean number of particles.*

We use

$$\begin{aligned} \left.\frac{\partial F(z, \Lambda', T)}{\partial u_{\alpha\beta}}\right|_{\langle N\rangle} = \left.\frac{\partial F(z, \Lambda', T)}{\partial u_{\alpha\beta}}\right|_{z} - \left.\frac{\partial F(z, \Lambda', T)}{\partial z}\right|_{\Lambda'} \\ \times \left.\frac{\partial z}{\partial\langle N\rangle}\right|_{\Lambda'} \left.\frac{\partial\langle N\rangle(z, \Lambda', T)}{\partial u_{\alpha\beta}}\right|_{z} \end{aligned} \tag{3.23}$$

It comes

$$\left.\frac{\partial F(z, \Lambda', T)}{\partial u_{\alpha\beta}}\right|_{z} = -z\ln z\frac{\partial}{\partial z}\left\langle\frac{\partial H'}{\partial u_{\alpha\beta}}\right\rangle' + \left\langle\frac{\partial H'}{\partial u_{\alpha\beta}}\right\rangle' \tag{3.24}$$

$$\left.\frac{\partial F(z, \Lambda', T)}{\partial z}\right|_{\Lambda'} = kT\left.\frac{\partial\langle N\rangle}{\partial z}\right|_{\Lambda'}\ln z \tag{3.25}$$

$$\left.\frac{\partial\langle N\rangle(z, \Lambda', T)}{\partial u_{\alpha\beta}}\right|_{Z} = -\beta z\frac{\partial}{\partial z}\left\langle\frac{\partial H'}{\partial u_{\alpha\beta}}\right\rangle' \tag{3.26}$$

Therefore

$$\left.\frac{\partial F(z, \Lambda', T)}{\partial u_{\alpha\beta}}\right|_{\langle N\rangle} = \left\langle\frac{\partial H'}{\partial u_{\alpha\beta}}\right\rangle' \tag{3.27}$$

and

$$\left.\frac{\partial F(z, \Lambda', T)}{\partial u_{\alpha\beta}}\right|_{\langle N\rangle; u=0} = |\Lambda|\ \tau^{G}_{\alpha\beta}(\Lambda) = \langle T_{\alpha\beta}\rangle(z, \Lambda, T) \tag{3.28}$$

where $T_{\alpha\beta}$ is given again by (3.9), but evaluated now by the grand canonical mean (3.19) instead of the canonical one (3.4). Differentiating (3.27) once more, we find, proceeding analogously,

$$\left.\frac{\partial^2 F(z, \Lambda', T)}{\partial u_{\alpha\beta}\, \partial u_{\gamma\delta}}\right|_{\langle N\rangle; u=0}$$
$$= |\Lambda|\, A^G_{\alpha\beta\gamma\delta}(\Lambda)$$
$$= \left(\langle W_{\alpha\beta\gamma\delta}\rangle - \beta\langle T_{\alpha\beta}; T_{\gamma\delta}\rangle + \beta \frac{\langle T_{\alpha\beta}; N\rangle \langle T_{\gamma\delta}; N\rangle}{\langle N; N\rangle}\right)(z, \Lambda, T) \quad (3.29)$$

where $W_{\alpha\beta\gamma\delta}$ is given by (3.11), evaluated by the grand canonical mean.

(2.13), (3.28), and (3.29) imply the following grand-canonical expression for the finite volume elastic moduli tensor:

$$B^G_{\alpha\beta\gamma\delta}(\Lambda) = B^{GI}_{\alpha\beta\gamma\delta}(\Lambda) + B^{GII}_{\alpha\beta\gamma\delta}(\Lambda) \quad (3.30)$$

where

$$B^{GI}_{\alpha\beta\gamma\delta}(\Lambda) = \frac{1}{|\Lambda|}\left(\langle W_{\alpha\beta\gamma\delta}\rangle - \beta\langle T_{\alpha\beta}; T_{\gamma\delta}\rangle + \delta_{\beta\gamma}\langle T_{\alpha\delta}\rangle - \delta_{\gamma\delta}\langle T_{\alpha\beta}\rangle\right)(z, \Lambda, T) \quad (3.31)$$

and

$$B^{GII}_{\alpha\beta\gamma\delta}(\Lambda) = \frac{\beta}{|\Lambda|} \frac{\langle T_{\alpha\beta}; N\rangle \langle T_{\gamma\delta}; N\rangle}{\langle N; N\rangle}(z, \Lambda, T) \quad (3.32)$$

The term $\langle N; N\rangle$ appearing in (3.32) is related in the literature to the compressibility by

$$\chi_T(\Lambda) = \beta\, |\Lambda|\, \frac{\langle N; N\rangle}{\langle N\rangle^2}(\Lambda, z, T) \quad (3.33)$$

One of our results will precisely consist in showing the consistency between (3.33) and the definition of the compressibility obtained from $B^G_{\alpha\beta\gamma\delta}(\Lambda)$, at least for the fluid case.

Remarks. (1) It is straightforward to verify that

$$\tau^G_{\alpha\beta}(z, \Lambda, T) = \frac{1}{|\Lambda|} \left.\frac{\partial F(z, \Lambda', T)}{\partial u_{\alpha\beta}}\right|_{\langle N\rangle; u=0} = -\frac{kT}{|\Lambda|} \left.\frac{\partial \ln \Xi(z, \Lambda', T)}{\partial u_{\alpha\beta}}\right|_{u=0} \quad (3.34)$$

where the last expression is to be computed *without* the restriction $\langle N\rangle = cst$. (3.34) constitutes the generalization of the well-known prescription:

$$P^G(z, \Lambda, T) = kT \frac{\partial}{\partial V} \ln \Xi(z, \Lambda, T) \quad (3.35)$$

(2) Let us recall that, by definition, $B^{G}_{\alpha\beta\gamma\delta}(\Lambda) = B^{GI}_{\alpha\beta\gamma\delta}(\Lambda) + B^{GII}_{\alpha\beta\gamma\delta}(\Lambda)$ describes the linear part of the dependence of $\tau^{G}_{\alpha\beta}(\Lambda')$ versus $u_{\gamma\delta}$. By checking the derivation of (3.30), it appears that $B^{GII}_{\alpha\beta\gamma\delta}(\Lambda)$ represents exactly the correction due to restriction $\langle N\rangle = cst$. On the other hand, it will appear that, for the fluid case, $\lim_{|\Lambda|\to\infty} B^{GI}_{\alpha\beta\gamma\delta}(\Lambda) = 0$. The physical interpretation of this last fact is: it does not cost any force to deform a fluid when we allow the number of particles to vary (we compress a fluid in a holed container!).

(3) It can appear at first view, by comparing (3.13) and (3.31) that the only difference between canonical and grand canonical expression is constituted by the term $B^{GII}_{\alpha\beta\gamma\delta}(\Lambda)$; however, the analogy between $B^{C}_{\alpha\beta\gamma\delta}(\Lambda)$ and $B^{GI}_{\alpha\beta\gamma\delta}(\Lambda)$ is only superficial: for example, the correlation of $T^{K}_{\alpha\beta}$ and $T^{V}_{\alpha\beta}$, defined, respectively, as the kinetic and potential part of $T^{N}_{\alpha\beta}(\mathbf{p}, \mathbf{x})$, gives

$$\begin{aligned} &\langle T^{K}_{\alpha\beta}; T^{V}_{\gamma\delta}\rangle_C = 0 \\ &\langle T^{K}_{\alpha\beta}; T^{V}_{\gamma\delta}\rangle_G = -\delta_{\alpha\beta} kT \langle N; T^{V}_{\gamma\delta}\rangle_G \end{aligned} \tag{3.36}$$

(4) For the ideal gas, the equivalence of the canonical and grand canonical expression for the elastic moduli tensor holds already in a finite volume:

$$B^{C}_{\alpha\beta\gamma\delta}(\Lambda) = B^{G}_{\alpha\beta\gamma\delta}(\Lambda) = \delta_{\alpha\beta}\delta_{\gamma\delta}\rho kT \tag{3.37}$$

the density being defined by

$$\rho := \frac{N}{|\Lambda|} \qquad \text{in the canonical ensemble}$$

$$\rho := \frac{\langle N\rangle}{|\Lambda|} \qquad \text{in the grand canonical ensemble}$$

(5) Following the standard procedure, we introduce correlation functions in either ensemble:

$$n_s^{C/G,\Lambda}(x_1,..., x_s) := \left\langle \sum_{i_1 \neq \cdots \neq i_s}^{N} \delta(x_1 - x_{i_1}) \cdots \delta(x_s - x_{i_s}) \right\rangle_{C/G} \tag{3.38}$$

$B^{C/G}_{\alpha\beta\gamma\delta}(\Lambda)$ will be expressed by terms having the form

$$I^{C/G}(\Lambda) := \frac{1}{|\Lambda|} \int_\Lambda dx_1 \cdots dx_s \, n_s^{C/G,\Lambda}(x_1,..., x_s)\, h(x_1,..., x_s) \tag{3.39}$$

The essential point is that, although the ensemble equivalence implies

$$\lim_{|\Lambda| \to \infty} n_s^{C,\Lambda}(x_1,..., x_s) = \lim_{|\Lambda| \to \infty} n_s^{G,\Lambda}(x_1,..., x_s) =: n_s(x_1,..., x_s) \quad (3.40)$$

it is generally illegitimate to take the limit of the *canonical* correlation functions under the integral; indeed, in this case, the thermodynamic limit is approached too slowly (as $|\Lambda|^{-1}$). For the ideal gas, for instance,

$$n_2^{C,\Lambda}(x_1, x_2) = \frac{N(N-1)}{|\Lambda|^2} = n_2(x_1, x_2) - \frac{\rho}{|\Lambda|}$$

$$n_2^{G,\Lambda}(x_1, x_2) = \frac{\langle N(N-1)\rangle}{|\Lambda|^2} = \frac{\langle N\rangle^2}{|\Lambda|^2} = \rho^2 = n_2(x_1, x_2)$$

An other well-known example is provided by the compressibility, as it appears in (3.32):

$$\lim_{|\Lambda| \to \infty} \frac{1}{|\Lambda|} \int_\Lambda dx\, dy [n_2^{C,\Lambda}(x, y) - n_1^{C,\Lambda}(x)\, n_1^{C,\Lambda}(y)]$$

$$= \lim_{|\Lambda| \to \infty} \frac{1}{|\Lambda|} \int_\Lambda dx [(N-1)\, n_1^{C,\Lambda}(x) - N n_1^{C,\Lambda}(x)]$$

$$= \lim_{|\Lambda| \to \infty} -\frac{1}{|\Lambda|} \int_\Lambda dx\, n_1^{C,\Lambda}(x) = -\rho$$

But

$$\lim_{|\Lambda| \to \infty} \frac{1}{|\Lambda|} \int_\Lambda dx\, dy \lim_{|\Lambda| \to \infty} [n_2^{C,\Lambda}(x, y) - n_1^{C,\Lambda}(x)\, n_1^{C,\Lambda}(y)]$$

$$= \lim_{|\Lambda| \to \infty} \frac{1}{|\Lambda|} \int_\Lambda dx\, dy [n_2(x, y) - n_1(x)\, n_1(y)]$$

$$= \lim_{|\Lambda| \to \infty} \frac{1}{|\Lambda|} (\langle N; N\rangle - \langle N\rangle) = \rho(\chi_T \rho k T - 1)$$

Therefore, for $\chi_T \neq 0$, the permutation of the limit and the integration give different results in the canonical case!

(6) An exception is constitued by the one-component plasma (O.C.P.). Its compressibility is zero and its thermodynamic limit converges faster than in not charged particles systems. For the two-dimensional O.C.P., the canonical procedure has been applied, (with deforming the bath with constant charge), at a certain temperature ($\Gamma = 2$) corresponding

to a fluid phase, where the correlation functions are exactly known. It was found $B_{1212}=0$.[12] At $T=0$, we have $\mu=e^2\rho/8$, which is the same result as the one obtained by Alastuey and Jancovici by another method.[10]

4. THE MAIN RESULT

In this section and the following, we shall use only the grand canonical ensemble (the index G then disappears). We shall rigorously show that, under hypotheses which are characteristic of a fluid phase, the (infinite volume) expression for the (grand canonical) elastic moduli tensor $B_{\alpha\beta\gamma\delta}$ leads to (i) an expression for the isothermal compressibility which is the same as the well-known one, given by (3.33), (ii) a vanishing shear modulus ($\mu=B_{1212}=0$).

In order to fulfil this program, we give in Section 4.1 the expression of $B_{\alpha\beta\gamma\delta}(\Lambda)$ in terms of correlation functions; we take the thermodynamic limit in Section 4.3, using the hypotheses introduced in Section 4.2. Section 4.4 is devoted to the analysis of the stress tensor and Section 4.5, deals with the reduction of $B_{\alpha\beta\gamma\delta}$ by using the BBGKY hierarchy, in order to obtain the above results.

4.1. Expression in Terms of Correlation Functions

The finite volume (grand canonical) correlation functions were introduced in (3.37). In order to have compact expressions, we introduce the following notations:

$$f_{\alpha\beta}(x,y):=\frac{\partial V(|x-y|)}{\partial x_\alpha}(x^\beta-y^\beta)=f_{\beta\alpha}(x,y)=f_{\alpha\beta}(y,x) \tag{4.1}$$

$$g_{\alpha\beta\gamma\delta}(x,y):=\frac{\partial^2 V(|x-y|)}{\partial x_\alpha\,\partial x_\gamma}(x^\beta-y^\beta)(x^\delta-y^\delta)=g_{\alpha\beta\gamma\delta}(y,x) \tag{4.2}$$

($g_{\alpha\beta\gamma\delta}$ is symmetric under permutation of all indices)

$$\begin{aligned}[(n_4^\Lambda-n_2^\Lambda n_2^\Lambda)\,f_{\alpha\beta}f_{\gamma\delta}]_\Lambda:=\frac{1}{|\Lambda|}\int_\Lambda &dx\,dy\,dz\,dw\\ &\times[n_4^\Lambda(x,y,z,w)-n_2^\Lambda(x,y)\,n_2^\Lambda(z,w)]\\ &\times f_{\alpha\beta}(x,y)\,f_{\gamma\delta}(z,w)\end{aligned} \tag{4.3}$$

$$[n_3^\Lambda f_{\alpha\beta}f_{\gamma\delta}]_\Lambda:=\frac{1}{|\Lambda|}\int_\Lambda dx\,dy\,dz\,n_3^\Lambda(x,y,z)\,f_{\alpha\beta}(x,y)\,f_{\gamma\delta}(x,z) \tag{4.4}$$

$$[(n_3^A - n_2^A n_1^A) f_{\alpha\beta}]_A := \frac{1}{|A|} \int_A dx\, dy\, dz [n_3^A(x, y, z) - n_2^A(x, y)\, n_1^A(z)]\, f_{\alpha\beta}(x, y) \tag{4.5}$$

$$[n_2^A g_{\alpha\beta\gamma\delta}]_A := \frac{1}{|A|} \int_A dx\, dy\, n_2^A(x, y)\, g_{\alpha\beta\gamma\delta}(x, y) \tag{4.6}$$

$$[n_2^A f_{\alpha\beta}]_A := \frac{1}{|A|} \int_A dx\, dy\, n_2^A(x, y)\, f_{\alpha\beta}(x, y) \tag{4.7}$$

$$[n_2^A f_{\alpha\beta} f_{\gamma\delta}]_A := \frac{1}{|A|} \int_A dx\, dy\, n_2^A(x, y)\, f_{\alpha\beta}(x, y)\, f_{\gamma\delta}(x, y) \tag{4.8}$$

$$[n_2^A - n_1^A n_1^A]_A := \frac{1}{|A|} \int_A dx\, dy [n_2^A(x, y) - n_1^A(x)\, n_1^A(y)] \tag{4.9}$$

$$[n_1^A]_A := \frac{1}{|A|} \int_A dx\, n_1^A(x) = \frac{\langle N \rangle_A}{|A|} = \rho \tag{4.10}$$

With this condensed writing, we obtain, using $\langle \sum_{i=1}^N p_i^\alpha p_i^\beta / m \rangle = \delta_{\alpha\beta} \langle N \rangle_A kT$,

$$\frac{1}{|A|} \langle T_{\alpha\beta} \rangle_A = \tau_{\alpha\beta}(A) = -\delta_{\alpha\beta} kT [n_1^A]_A + \frac{1}{2} [n_2^A f_{\alpha\beta}]_A \tag{4.11}$$

$$\frac{1}{|A|} \langle W_{\alpha\beta\gamma\delta} \rangle_A = (\delta_{\alpha\gamma} \delta_{\beta\delta} + 2\delta_{\alpha\delta} \delta_{\beta\gamma})\, kT [n_1^A]_A + \frac{1}{2} [n_2^A g_{\alpha\beta\gamma\delta}]_A \tag{4.12}$$

$$\begin{aligned} \frac{1}{|A|} \langle T_{\alpha\beta}; T_{\gamma\delta} \rangle_A = {} & \frac{1}{4} [(n_4^A - n_2^A n_2^A)\, f_{\alpha\beta} f_{\gamma\delta}]_A + [n_3^A f_{\alpha\beta} f_{\gamma\delta}]_A \\ & + \frac{1}{2} [n_2^A f_{\alpha\beta} f_{\gamma\delta}]_A - \frac{\delta_{\alpha\beta}}{2} kT [(n_3^A - n_2^A n_1^A)\, f_{\gamma\delta}]_A \\ & - \frac{\delta_{\gamma\delta}}{2} kT [(n_3^A - n_2^A n_1^A)\, f_{\alpha\beta}] - \delta_{\alpha\beta} kT [n_2^A f_{\gamma\delta}]_A \\ & - \delta_{\gamma\delta} kT [n_2^A f_{\alpha\beta}]_A + \delta_{\alpha\beta} \delta_{\gamma\delta} (kT)^2 [(n_2^A - n_1^A n_1^A)]_A \\ & + (\delta_{\alpha\beta} \delta_{\gamma\delta} + \delta_{\alpha\gamma} \delta_{\beta\delta} + \delta_{\alpha\delta} \delta_{\beta\gamma})(kT)^2 [n_1^A]_A \end{aligned} \tag{4.13}$$

To get (4.13), we used (3.21) and

$$\begin{aligned}
z\frac{\partial}{\partial z}\, & n_s^{\Lambda}(x_1,\ldots,x_s)\\
&= s n_s^{\Lambda}(x_1,\ldots,x_s) + \int_{\Lambda} dx_{s+1}\\
&\quad\times [n_{s+1}^{\Lambda}(x_1,\ldots,x_s,x_{s+1}) - n_s^{\Lambda}(x_1,\ldots,x_s)\, n_1^{\Lambda}(x_{s+1})]
\end{aligned} \tag{4.14}$$

We also have

$$\begin{aligned}
\frac{1}{|\Lambda|}\langle T_{\alpha\beta}; N\rangle_{\Lambda} &= \frac{1}{2}[(n_3^{\Lambda} - n_2^{\Lambda} n_1^{\Lambda})\, f_{\alpha\beta}]_{\Lambda} + [n_2^{\Lambda} f_{\alpha\beta}]_{\Lambda}\\
&\quad - \delta_{\alpha\beta} kT([n_2^{\Lambda} - n_1^{\Lambda} n_1^{\Lambda}]_{\Lambda} + [n_1^{\Lambda}]_{\Lambda})
\end{aligned} \tag{4.15}$$

$$\frac{1}{|\Lambda|}\langle N; N\rangle_{\Lambda} = [n_2^{\Lambda} - n_1^{\Lambda} n_1^{\Lambda}]_{\Lambda} + [n_1^{\Lambda}]_{\Lambda} \tag{4.16}$$

Using (3.31), (4.11), (4.12), (4.13), we put $B^{\mathrm{I}}_{\alpha\beta\gamma\delta}(\Lambda)$ on the form

$$B^{\mathrm{I}}_{\alpha\beta\gamma\delta}(\Lambda) = B^{\mathrm{Ia}}_{\alpha\beta\gamma\delta}(\Lambda) + B^{\mathrm{Ib}}_{\alpha\beta\gamma\delta}(\Lambda) \tag{4.17}$$

where

$$\begin{aligned}
B^{\mathrm{Ia}}_{\alpha\beta\gamma\delta}(\Lambda) = & -\frac{\beta}{4}[(n_4^{\Lambda} - n_2^{\Lambda} n_2^{\Lambda})\, f_{\alpha\beta} f_{\gamma\delta}]_{\Lambda} - \beta[n_3^{\Lambda} f_{\alpha\beta} f_{\gamma\delta}]_{\Lambda}\\
& - \frac{\beta}{2}[n_2^{\Lambda} f_{\alpha\beta} f_{\gamma\delta}]_{\Lambda} + \frac{\delta_{\gamma\delta}}{2}[(n_3^{\Lambda} - n_2^{\Lambda} n_1^{\Lambda})\, f_{\alpha\beta}]_{\Lambda}\\
& + \frac{1}{2}[n_2^{\Lambda} g_{\alpha\beta\gamma\delta}]_{\Lambda} + \frac{\delta_{\beta\gamma}}{2}[n_2^{\Lambda} f_{\alpha\delta}]_{\Lambda} + \frac{\delta_{\gamma\delta}}{2}[n_2^{\Lambda} f_{\alpha\beta}]_{\Lambda}
\end{aligned} \tag{4.18}$$

and

$$\begin{aligned}
B^{\mathrm{Ib}}_{\alpha\beta\gamma\delta}(\Lambda) &= \frac{\delta_{\alpha\beta}}{2}[(n_3^{\Lambda} - n_2^{\Lambda} n_1^{\Lambda})\, f_{\gamma\delta}]_{\Lambda} + \delta_{\alpha\beta}[n_2^{\Lambda} f_{\gamma\delta}]_{\Lambda}\\
&\quad - \delta_{\alpha\beta}\delta_{\gamma\delta} kT[n_2^{\Lambda} - n_1^{\Lambda} n_1^{\Lambda}]_{\Lambda}
\end{aligned} \tag{4.19}$$

Proceeding analogously, we get

$$\begin{aligned}
B^{\mathrm{II}}_{\alpha\beta\gamma\delta}(\Lambda) = \beta\{& [n_2^{\Lambda} - n_1^{\Lambda} n_1^{\Lambda}]_{\Lambda} + [n_1^{\Lambda}]_{\Lambda}\}^{-1}\\
& \times \{\tfrac{1}{2}[(n_3^{\Lambda} - n_2^{\Lambda} n_1^{\Lambda})\, f_{\alpha\beta}]_{\Lambda} + [n_2^{\Lambda} f_{\alpha\beta}]_{\Lambda}\\
& - \delta_{\alpha\beta} kT([n_2^{\Lambda} - n_1^{\Lambda} n_1^{\Lambda}]_{\Lambda} + [n_1^{\Lambda}]_{\Lambda})\}\\
& \times \{\tfrac{1}{2}[(n_3^{\Lambda} - n_2^{\Lambda} n_1^{\Lambda})\, f_{\gamma\delta}]_{\Lambda} + [n_2^{\Lambda} f_{\gamma\delta}]_{\Lambda}\\
& - \delta_{\gamma\delta} kT([n_2^{\Lambda} - n_1^{\Lambda} n_1^{\Lambda}]_{\Lambda} + [n_1^{\Lambda}]_{\Lambda})\}
\end{aligned} \tag{4.20}$$

4.2. The Hypotheses

We now present and discuss the hypotheses which will be used. We define $n_s(x_1,..., x_s) := \lim_{|\Lambda| \to \infty} n_s^\Lambda(x_1,..., x_s)$.

(v) The particles interact by means of a Euclidean invariant pair potential $V(x)$, twice continuously differentiable such that $|x| [\partial V(x)/\partial |x|] \in L_1(\mathbb{R}^\nu; dx)$; moreover, there exists $B \geqslant 0$ such that $\sum_{1 \leqslant i < j \leqslant n} V(x_i - x_j) \geqslant -nB$ for all $n \geqslant 0$ and $x_1,..., x_n \in \mathbb{R}^\nu$.

(V) The same as (v); moreover, $[\partial V(x)/\partial |x|]$ and $[\partial V(x)/\partial |x|] |x|^2 \in L_1(\mathbb{R}^\nu; dx)$.

(n^Λ) For any subset X and Y of Λ with $X = \{x_1,..., x_s\}$, $Y = \{y_1,..., y_{s'}\}$, $1 \leqslant s + s' \leqslant 4$ the correlation functions obey the clustering bound:

$$|n_{s+s'}^\Lambda(X, Y) - n_s^\Lambda(X)\, n_{s'}^\Lambda(Y)| \leqslant \sum_{x_i \in X} \sum_{y_j \in Y} k^\Lambda(x_i, y_j)$$

where $\int dy\, |k^\Lambda(x, y)| \leqslant C$ uniformly in Λ and x.

(n) The same as (n^Λ), but for the thermodynamic limit:

$$|n_{s+s'}(X, Y) - n_s(X)\, n_{s'}(Y)| \leqslant \sum_{x_i \in X} \sum_{y_j \in Y} k(x_i - y_j)$$

where $k(x) \in L_1(\mathbb{R}^\nu; dx)$.

(N) The same as (n); moreover, $k(x)\, |x| \in L_1(\mathbb{R}^\nu; dx)$.

(c) $|n_s^\Lambda(X) - n_s(X)| \leqslant C/\text{dist}(X, \partial\Lambda)^b$, with $b > \nu$, where $\text{dist}(X, Y) := \min_{x_i \in X} \min_{y_j \in Y} \text{dist}(x_i, y_j)$.

4.3. Discussion of the Hypotheses

1. Hypothesis (v) is a stability condition (it prevents the collapse of the system). Lennard-Jones potentials fulfil these assumptions, except for the short-range integrability which is introduced here to avoid technicalities. If we want to allow more singular repulsive forces, we have to assume that the correlation functions vanish sufficiently rapidly when two of their arguments coincide, which is reasonable. For instance, in the low fugacity regime, one can prove

$$n_s(X) = \exp\left[-\beta \frac{1}{2} \sum_{i \neq j}^{s} V(x_i - x_j) \right] \sigma(X)$$

where $\sigma(x_1,..., x_s)$ is bounded and continuous (see Ref. 14, p. 106).

2. It can be shown[3] that, at low fugacity, the asymptotic behavior of the truncated correlation functions is the same as that of the potential. Then, in this regime, (v) implies (n) and (V) implies (N).

3. In the region of convergence of the low fugacity expansion, a strong decrease of the potential at infinity $[V(x) \sim |x|^{-\gamma}$ with $\gamma > 2\nu]$ implies (n^{Λ}) and (c). The proof of (n^{Λ}) follows from a theorem by Duneau and Souillard.[6] For the proof of (c), see Ref. 14, Theorem 4.2.3, which gives the bound $b > \gamma - \nu$.

As discussed in Remark 5 of Section 3.4, hypothesis (c) is generally violated in canonical ensemble.

4. It is a well-known fact that (v) and (n) imply that the system is in a pure state, invariant under translations and rotations, i.e., Euclidean invariant (see, e.g., Ref. 9). In other words, (v) and (n) imply that the system is *fluid* in some sense, and exclude the case of liquid crystals.

4.3. The Thermodynamic Limit

In this section, we consider the thermodynamic limit of $B_{\alpha\beta\gamma\delta}(\Lambda)$, which is composed of terms of the form

$$\begin{aligned} I(\Lambda) := |\Lambda|^{-1} \int_{\Lambda} dx_1 \cdots dx_{s'} \\ \times [n^{\Lambda}_{s+s'}(x_1,..., x_{s+s'}) - n^{\Lambda}_{s}(x_1,..., x_s)\, n^{\Lambda}_{s'}(x_{s+1},..., x_{s+s'})] \\ \times h(x_1,..., x_s)\, h(x_{s+1},..., x_{s+s'}) \end{aligned} \tag{4.21}$$

Because of the fast convergence of $n^{\Lambda}_{s+s'}$ to its limit $n_{s+s'}$ [see hypothesis (c)], and using (n^{Λ}) and (v), we shall be able to prove by standard argument

$$\begin{aligned} \lim_{|\Lambda| \to \infty} I(\Lambda) = \lim_{|\Lambda| \to \infty} |\Lambda|^{-1} \int_{\Lambda} dx_1 \cdots dx_{s'} \\ \times [n_{s+s'}(x_1,..., x_{s+s'}) - n_s(x_1,..., x_s)\, n_{s'}(x_{s+1},..., x_{s+s'})] \\ \times h(x_1,..., x_s)\, h(x_{s+1},..., x_{s+s'}) \end{aligned} \tag{4.22}$$

(i.e., it is legitimate to take the limit under the integral). The translation invariance of the infinite volume correlation function and the clustering property (n) will enable us to write

$$\begin{aligned} \lim_{|\Lambda| \to \infty} I(\Lambda) = \int dx_2 \cdots dx_{s'}\, [n_{s+s'}(0, x_2,..., x_{s+s'}) \\ - n_s(0, x_2,..., x_s)\, n_{s'}(x_{s+1},..., x_{s'+s})] \\ \times h(0, x_2,..., x_s)\, h'(x_{s+1},..., x_{s+s'}) \end{aligned} \tag{4.23}$$

The details are done in Section A1 of the Appendix.

4.4. The Stress Tensor

Using the same procedure as the one given in Section A1, it is easy to show with hypothesis (v) only that $\tau_{\alpha\beta}(\Lambda)$, as it appears in (4.11), has a well-defined limit which can be taken under the integral. On the other hand, hypothesis (n) implies the translation invariance of $n_2(x, y)$ and we get the following:

Proposition 4.4.1. Under hypothesis (v), (n):

$$\lim_{|\Lambda| \to \infty} \tau_{\alpha\beta}(\Lambda) = -\delta_{\alpha\beta}\left[\rho kT - \frac{1}{\nu}\int dx\, n_2(x, 0)\frac{\partial V(x)}{\partial x^\alpha}x^\beta\right] = -\delta_{\alpha\beta}P$$

where P appears by its virial expression.[8]

4.5. Reduction of $B_{\alpha\beta\gamma\delta}$

We shall prove that $B^{\mathrm{I}}_{\alpha\beta\gamma\delta} = 0$ (in fact, $B^{\mathrm{Ia}}_{\alpha\beta\gamma\delta}$ and $B^{\mathrm{Ib}}_{\alpha\beta\gamma\delta}$ vanish separately). The idea of the proof is the following: we use the BBGKY hierarchy to express the four-point correlation functions in terms of the three-point function and a boundary term which will vanish because of the clustering hypothesis. We use the same strategy to eliminate the three-point function in favor of the two-point function. The BBGKY equation reads

$$\frac{\partial n_s(x_1,..., x_s)}{\partial x_1^\alpha} = -\beta n_s(x_1,..., x_s)\sum_{j=2}^{s}\frac{\partial V(x_1 - x_j)}{\partial x_1^\alpha}$$
$$-\beta\int dx_{s+1}\, n_{s+1}(x_1,..., x_{s+1})\frac{\partial V(x_1 - x_{s+1})}{\partial x_1^\alpha} \tag{4.24}$$

Proposition 4.5.1:

$$(V), (N) \Rightarrow B^{\mathrm{Ia}}_{\alpha\beta\gamma\delta} = 0$$

Proposition 4.5.2:

$$(V), (N) \Rightarrow B^{\mathrm{Ib}}_{\alpha\beta\gamma\delta} = 0$$

Proposition 4.5.3:

$$(V), (N) \Rightarrow B^{\mathrm{II}}_{\alpha\beta\gamma\delta} = \frac{1}{\chi_T}\delta_{\alpha\beta}\delta_{\gamma\delta}$$

[Recall (see Section 4.3) that $B^{\mathrm{Ia}}_{\alpha\beta\gamma\delta}$, $B^{\mathrm{Ib}}_{\alpha\beta\gamma\delta}$, and $B^{\mathrm{II}}_{\alpha\beta\gamma\delta}$ are given by the limits "under the integral" of the expressions (4.18), (4.19), and (4.20), respectively; χ_T is *defined* as the limit of the expression appearing in (3.33).]

Proof of Proposition 4.5.1. We start from the term involving n_4:

$$-\frac{\beta}{4}\,[(n_4-n_2n_2)\,f_{\alpha\beta}\,f_{\gamma\delta}]$$

$$= -\frac{\beta}{4}\int dx\,dy\,dz[n_4(x, y, z, 0)-n_2(x, y)\,n_2(z, 0)] \times\frac{\partial V(x-y)}{\partial x^\alpha}\,(x^\beta-y^\beta)\,\frac{\partial V(z)}{\partial z^\gamma}\,z^\delta \tag{4.25}$$

$$= -\frac{\beta}{2}\int dx\,dy\,dz[n_4(x, y, z, 0)-n_2(x, y)\,n_2(z, 0)] \times\frac{\partial V(x-y)}{\partial x^\alpha}\,x^\beta\,\frac{\partial V(z)}{\partial z^\gamma}\,z^\delta \tag{4.26}$$

$$=\frac{1}{2}\int dx\,dz\,x^\beta\,\frac{\partial V(z)}{\partial z^\gamma}\,z^\delta\,\frac{\partial}{\partial x^\alpha}\,[n_3(x, z, 0)-n_1(x)\,n_2(z, 0)] +\frac{\beta}{2}\int dx\,dz\,n_3(x, z, 0)\left[\frac{\partial V(x-z)}{\partial x^\alpha}+\frac{\partial V(x)}{\partial x^\alpha}\right]x^\beta\,\frac{\partial V(z)}{\partial z^\gamma}\,z^\delta \tag{4.27}$$

Although (v) and (n) constitute a sufficient condition for the boundeness of (4.25), we must suppose (V) and (N) to show the boundeness of (4.26) (see Section A2 in the Appendix). The passage from (4.26) to (4.27) is done by writing the BBGKY equations for $\partial n_3(x, z, 0)/\partial x^\alpha$ and $\partial n_1(x)/\partial x^\alpha$. An integration by parts and (A3) in the Appendix (which shows the vanishing of the boundary term) allow us to write

$$\frac{1}{2}\int dx\,dz\,x^\beta\,\frac{\partial V(x)}{\partial z^\gamma}\,z^\delta\,\frac{\partial}{\partial x^\alpha}\,[n_3(x, z, 0)-n_1(x)\,n_2(z, 0)]$$

$$= -\frac{\delta_{\alpha\beta}}{2}\int dx\,dz[n_3(x, z, 0)-n_1(x)\,n_2(z, 0)]\,\frac{\partial V(z)}{\partial z^\gamma}\,z^\delta$$

$$= -\frac{\delta_{\alpha\beta}}{2}\,[(n_3-n_2n_1)\,f_{\gamma\delta}] \tag{4.28}$$

We consider also the term

$$\frac{1}{2}\,[n_2\,g_{\alpha\beta\gamma\delta}]$$

$$=\frac{1}{2}\int dx\,n_2(0, x)\,\frac{\partial V(x)}{\partial x^\alpha\,\partial x^\gamma}\,x^\beta x^\delta \tag{4.29}$$

$$= -\frac{1}{2}\int dx\, \frac{\partial n_2(0,x)}{\partial x^\alpha}\frac{\partial V(x)}{\partial x^\gamma}\, x^\beta x^\delta - \frac{\delta_{\alpha\beta}}{2}\int dx\, n_2(x,0)\frac{\partial V(x)}{\partial x^\gamma}\, x^\delta$$

$$- \frac{\delta_{\alpha\delta}}{2}\int dx\, n_2(x,0)\frac{\partial V(x)}{\partial x^\gamma}\, x^\delta \tag{4.30}$$

$$= \frac{\beta}{2}[n_2 f_{\alpha\beta} f_{\gamma\delta}] + \frac{\beta}{2}\int dx\, dz\, n_3(x,z,0)\frac{\partial V(x-z)}{\partial x^\alpha}\frac{\partial V(x)}{\partial x^\gamma}\, x^\beta x^\delta$$

$$- \frac{\delta_{\alpha\beta}}{2}[n_2 f_{\gamma\delta}] - \frac{\delta_{\alpha\delta}}{2}[n_2 f_{\alpha\beta}] \tag{4.31}$$

Again, (4.29) with an integration by parts of vanishing boundary term [see (A3)] allow us to write (4.30), which, together with the BBGKY equations implies (4.31).

Using the change of variables $x' = x + z$, $z' = -z$, we transform the term appearing in (4.27) in

$$\frac{\beta}{2}\int dx\, dz\, n_3(x,z,0)\frac{\partial V(x)}{\partial x^\alpha}\, x^\beta \frac{\partial V(z)}{\partial z^\gamma}\, z^\delta$$

$$= \frac{\beta}{2}\int dx\, dz\, n_3(x,z,0)\frac{\partial V(x-z)}{\partial x^\alpha}(x^\beta - z^\beta)\frac{\partial V(z)}{\partial z^\gamma}\, z^\delta \tag{4.32}$$

Finally, rassembling the expressions appearing in (4.27), (4.28), (4.31), (4.32) it becomes

$$-\frac{\beta}{4}[(n_4 - n_2 n_2) f_{\alpha\beta} f_{\gamma\delta}] - \beta[n_3 f_{\alpha\beta} f_{\gamma\delta}] + \frac{1}{2}[n_2\, g_{\alpha\beta\gamma\delta}]$$

$$= -\frac{\delta_{\alpha\beta}}{2}[(n_3 - n_2 n_1) f_{\gamma\delta}] - \frac{\delta_{\alpha\beta}}{2}[n_2 f_{\gamma\delta}]$$

$$-\frac{\delta_{\alpha\delta}}{2}[n_2 f_{\gamma\beta}] + \frac{\beta}{2}[n_2 f_{\alpha\beta} f_{\gamma\delta}] \tag{4.33}$$

(4.33) and (4.18) imply Proposition 4.5.1.

Proof of Proposition 4.5.2., 4.5.3. With the same technique as the one used previously, we can show that (V) and (N) imply

$$\tfrac{1}{2}[(n_3 - n_2 n_1) f_{\alpha\beta}] = \delta_{\alpha\beta} kT[n_2 - n_1 n_1] - [n_2 f_{\alpha\beta}] \tag{4.34}$$

Introducing (4.34) into the limit of (4.19) leads to $B^{\mathrm{Ib}}_{\alpha\beta\gamma\delta} = 0$; we have also for $B^{\mathrm{II}}_{\alpha\beta\gamma\delta}$, given by the limit of (4.20),

$$B^{\mathrm{II}}_{\alpha\beta\gamma\delta} = \delta_{\alpha\beta}\delta_{\gamma\delta} kT\{[n_2 - n_1 n_1] - [n_1]\}^{-1}$$

$$= \delta_{\alpha\beta}\delta_{\gamma\delta}\frac{1}{\chi_T}$$

We summarize these results by

$$(V), (N) \Rightarrow B_{\alpha\beta\gamma\delta} = \delta_{\alpha\beta}\delta_{\gamma\delta}\frac{1}{\chi_T} \tag{4.35}$$

or

$$(V), (N) \Rightarrow \lambda := B_{1122} = \frac{1}{\chi_T}, \qquad \mu := B_{1212} = 0 \tag{4.36}$$

APPENDIX

A1. Proof of 4.23

We shall only show in detail that

$$\lim_{|\Lambda| \to \infty} \frac{1}{|\Lambda|}\int_\Lambda dx\, dy\, dz\, dw\, F^\Lambda(x, y, z, w)\, r(x-y)\, s(z-w)$$
$$= \int dx\, dy\, dz\, F(x, y, z, 0)\, r(x-y)\, s(z-w)$$

where $F^\Lambda(x, y, z, w) := n_4^\Lambda(x, y, z, w) - n_2^\Lambda(x, y)\, n_2^\Lambda(z, w)$ and $r(x)$, $s(x) \in L_1(\mathbb{R}; dx)$. (The proof of convergence of the others terms is similar.)

Let Λ be a cube of size length R centered at the origin. We divide Λ into a bulk cube Λ_0 of size $R - 2R^a$ centered at the origin $(0 < a < 1)$ and a boundary part $\Lambda \setminus \Lambda_0$.

(i) $\lim_{R\to\infty} |\Lambda|^{-1} \int dx\, dy\, dz\, dw\, |(F^\Lambda - F)\, r(x-y)\, s(z-w)\, \chi_{\Lambda_0}(x)\, \chi_{\Lambda_0}(y)\, \chi_{\Lambda_0}(z)\, \chi_{\Lambda_0}(w)| = 0$. Here χ_{Λ_0} denotes the characteristic function associated to the set Λ_0. Indeed, using (c)

$$\leqslant \lim_{R\to\infty} |\Lambda|^{-1}\frac{C}{R^{ab}}\int_{\Lambda_0} dx\, dy\, dz\, dw\, |r(x-y)|\, |s(z-w)|$$

$$\leqslant \lim_{R\to\infty} \frac{C' R^v}{R^{ab}} = 0 \qquad \text{for a choice } ab > v$$

(ii) $\lim_{R\to\infty} |\Lambda|^{-1} \int_\Lambda dx\, dy\, dz\, dw\, |(F^\Lambda - F)\, r(x-y)\, s(z-w)|\, [1 - \chi_{\Lambda_0}(x)] = 0$. (We took account of the fact that $[1 - \prod_{i=1}^4 \chi_{\Lambda_0}(x_i)] \leqslant \sum_{i=1}^4 [1 - \chi_{\Lambda_0}(x_i)]$, and of the symmetry of the integrand with respect to the arguments.) But, using (n^Λ) and (v),

$$\int_\Lambda dy\, dz\, dw\, |F^\Lambda r(x-y)\, s(z-w)|$$
$$\leqslant \int_\Lambda dy\, dz\, dw\, |r(x-y)|\, |s(z-w)|$$
$$\times [k^\Lambda(x, z) + k^\Lambda(x, w) + k^\Lambda(y, z) + k^\Lambda(y, w)]$$
$$\leqslant 4\, |r|_1\, |s|_1\, |k^\Lambda|_1 \leqslant C$$

uniformly in x and Λ by Young's inequality (see Ref. 7, p. 28). The evaluation of the term involving F is similar. Since x runs through the boundary part of Λ ($a<1$), part (ii) is proved.

It remains to show the boundeness of the limit. Using the fact that (v) and (n) imply

$$\int_\Lambda dy\, dz\, dw\, |Fr(x-y)\, s(z-w)| \leqslant 4\, |r|_1\, |s|_1\, |k|_1$$

uniformly in x and Λ, it follows immediately that

$$\lim_{|\Lambda|\to\infty} |\Lambda|^{-1} \int_\Lambda dx\, dy\, dz\, dw\, F(x, y, z, w)\, r(x-y)\, s(z-w) < \infty$$

The treatment of the other terms is similar.

A2. Boundeness of 4.26

We shall prove that

$$\int dx\, dy\, dz\, |F(x, y, z, 0)|\, |x|\, |r(x-y)|\, |s(z)| < \infty$$

where $F(x, y, z, 0) := n_4(x, y, z, 0) - n_2(x, y)\, n_2(z, 0)$ and $r(x)$, $s(x)$, $|x|\, r(x)$, $|x|\, s(x) \in L_1(\mathbb{R}^\nu; dx)$. Using ($N$) we have

$$\leqslant \int dx\, dy\, dz [k(x-z) + k(x) + k(y-z) + k(y)]$$
$$\times\, |x|\, |r(x-y)|\, |s(z)|$$

The bound $|x| \leqslant |x-z| + |z|$ implies

$$\int dx\, dy\, dz\, k(x-z)\, |x-z|\, |r(x-y)|\, |s(z)|$$
$$+ \int dx\, dy\, dz\, k(x-z)\, |z|\, |r(x-y)|\, |s(z)|$$
$$\leqslant |k(x)\, |x||_1\, |r(x)|_1\, |s(z)|_1$$
$$+ |k(x)|_1\, |r(x)|_1\, |s(z)\, |z||_1$$

We used again Young's inequality. The remaining terms are estimated in a similar way.

A3. Vanishing of the Boundary Terms

With conditions (V) and (N),

$$\int dx\, dz \frac{\partial}{\partial x^\alpha}\left\{[n_3(x, z, 0) - n_1(x)\, n_2(z, 0)]\, x^\beta \frac{\partial V(z)}{\partial z^\gamma} z^\delta\right\} = 0$$

$$\int dx \frac{\partial}{\partial x^\alpha}\left[n_2(0, x) \frac{\partial V(x)}{\partial x^\gamma} x^\beta x^\delta\right] = 0$$

$$\int dx \frac{\partial}{\partial x^\alpha}[n_2(0, x) - n_1(x)\, n_1(0)] = 0$$

We shall prove the first equality only. The proof of the other equalities is similar. We consider that the domain of integration of x is the ball of radius R, $B(0, R)$, where we do $R \to \infty$; using the divergence theorem, and writing $d\sigma_x^\alpha$ for the α component of the outward-oriented surface element of ∂B, we get

$$\begin{aligned}&\int_{\partial B(0,R)} d\sigma_x^\alpha \int dz[n_3(x, z, 0) - n_1(x)\, n_2(z, 0)]\, x^\beta \frac{\partial V(z)}{\partial z^\gamma} z^\delta \\ &\quad\leqslant \int_{\partial B(0,R)} d\sigma_x^\alpha \int dz[k(x-z) + k(x)]\, |x|\, |z| \left|\frac{\partial V(z)}{\partial |z|}\right|\end{aligned}$$

We estimate each term separately:

$$\begin{aligned}&\text{(i)} \quad \int_{\partial B(0,R)} d\sigma_x^\alpha\, k(x)\, |x| \int dz\, |z| \left|\frac{\partial V(z)}{\partial |z|}\right| \\ &\qquad\qquad \leqslant C \int_{\partial B(0,R)} d\sigma_x^\alpha\, k(x)\, |x| \leqslant C \frac{R^\nu}{R^{\nu+1+\varepsilon}} \to 0\end{aligned}$$

$$\text{(ii)} \quad \int_{\partial B(0,R)} d\sigma_x^\alpha \int dz\, k(x-z)\, |x| \left|\frac{\partial V(z)}{\partial |z|}\right| |z|$$

Using the bound $|x| \leqslant |x-z| + |z|$ and the Young inequality

$$\int dx \int dz\, k(x-z)\, |x-z| \left|\frac{\partial V(z)}{\partial |z|}\right| |z| < |k(x)\, |x||_1 \left|\frac{\partial V(z)}{\partial |z|} |z|\right|_1 < \infty$$

$$\int dx \int dz\, k(x-z)\, |z|^2 \left|\frac{\partial V(z)}{\partial |z|}\right| < |k(x)|_1 \left|\frac{\partial V(z)}{\partial |z|} |z|^2\right|_1 < \infty$$

we deduce that

$$\int dz\, k(x-z)(|x-z|+|z|)\left|\frac{\partial V(z)}{\partial\, |z|}\,|z|\right|$$

is absolutely integrable, and we conclude as in case (i).

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