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On the Equation of State of Classical One-Component Systems with Long-Range Forces

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Several definitions of the "pressure" are introduced for one-component systems and shown to be nonequivalent in the presence of a rigid neutralizing background. Relations between these pressures are derived for finite and infinite systems; these relations depend on the asymptotic behavior of the force at infinity, with the Coulomb force at the borderline between different properties. It is argued that only one of those definitions is physically acceptable and its properties are discussed in relation to the asymptotic behavior of the force. It is seen in particular that a knowledge of the state of the infinite system is not sufficient to determine its thermodynamic properties. The results are illustrated by some typical examples.

KEY WORDS: Long-range forces; equilibrium states; BBGKY equation; equation of state; one-component plasma; shape dependence.

1. INTRODUCTION

The Wigner model of matter,$^{(1)}$ which consists of an assembly of point charges imbedded in a homogeneous neutralizing background, is a well-known example of a classical or quantum system with long-range forces.

Here, we consider the classical version of this model as a caricature of a more realistic two-component system with one *active* and one *passive* component. This means that we shall focus our attention on the properties of the particles only, while keeping the background fixed.

The current interest from a theoretical as well as experimental point of view in ν-dimensional systems with ν and $(\nu + 1)$-dimensional Coulomb interactions[2] suggests that consideration be given to arbitrary long-range

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[2] For example, for two-dimensional systems with three-dimensional Coulomb interaction see refs. 2–4.

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forces and to the properties of the equation of state of the active component as a function of the asymptotic behavior of the force at infinity. We shall still call such a system a "one-component plasma," although the force is not necessarily the Coulomb force.

As a matter of comparison, Yukawa forces are also dealt with in what follows in order to exhibit the noncommutativity of the infinite-volume and infinite-screening-length limits for a certain class of observables.

The systems considered here are subject to *free* boundary conditions and it has to be emphasized that none of the results reported below would have been obtained with *periodic* boundary conditions.

In this paper, we study the equation of state for such a one-component plasma; the first problem is to adopt a physically meaningful definition of the pressure. Indeed, using standard derivations for fluids (without a rigid background) one could introduce a priori several definitions for the pressure, which we shall refer to as the kinetic, virial, thermal, and mechanical pressures. It is the thermal pressure (erroneously called virial pressure in the literature) which is usually considered in the study of one-component systems and which leads to well-known pathologies in the case of Coulomb systems.[5-7] Although these definitions of the pressure are equivalent for fluids, we shall see that they are no longer equivalent in the presence of a rigid background *and* free boundary conditions. The following properties which we shall derive indicate that the kinetic pressure, and not the thermal or mechanical pressure, is the physically meaningful definition.

1. It is the pressure due to the active component and does not take into account the external force necessary to keep the background rigid.
2. It is identical with the virial pressure.
3. It is nonnegative and is expected to tend to zero as the temperature tends to zero; on the other hand, the thermal pressure becomes negative at low temperature in the case of Coulomb systems.
4. For a system consisting of a finite number N of particles imbedded in a very large background, it is expected that the physical pressure will tend to zero as the size of the background becomes infinite (with N fixed). This is indeed the case for the kinetic pressure, while the thermal and mechanical pressures diverge.
5. For non-Coulomb interactions, there exist states which are not locally neutral and the definition of the pressure should also make sense in those situations. Again this is the case only for the kinetic pressure.

After a short description of the model in Section 2, we introduce in Section 3 the different definitions of the pressure. The relations among these definitions are discussed in Section 4 for the case of finite systems; in particular, we show in this section that the kinetic pressure coincides with the virial pressure; furthermore, for integrable potential, the mechanical and thermal pressures coincide (but differ from the kinetic pressure); on the other hand, for Coulomb systems with spherical domains, the mechanical pressure coincides with the kinetic pressure (and differs from the thermal pressure); finally, we also give in this section a first motivation for adopting the kinetic pressure for the equation of state.

In Section 5, we study the pressure in the thermodynamic limit; it is shown that the kinetic and mechanical pressures are not entirely defined by the state of the infinite system, i.e., a knowledge of the state of the infinite system is not sufficient to describe its thermodynamic properties. It is seen that these pressures consists of two contributions: a *bulk contribution*, which is defined by the state of the infinite system,[3] and a *surface contribution*, which is defined by the state of a semiinfinite system. The analysis of the bulk contribution to the kinetic pressure shows a very different behavior (factor $\frac{1}{2}$) between the Coulomb force and forces which decrease faster at infinity; moreover, it is shown that for Coulomb systems with cubic symmetry, this contribution is proportional to the "moment of inertia" of the charge distribution of the unit cell. The analysis of the bulk contribution to the mechanical pressure shows again a different behavior between the Coulomb force and those with a faster decrease at infinity: it coincides with the thermal pressure if the force decreases faster than Coulomb, but coincides with the kinetic pressure for Coulomb systems without a quadrupole moment. The discussion of the surface contribution is restricted to Coulomb systems with spherical symmetry and it is shown to be related to a surface "dipole moment."

A general investigation of the surface contribution is not given, but we discuss in Section 6 some of its properties for typical examples [ν-dimensional Coulomb, $(\nu+1)$-dimensional Coulomb and Yukawa interactions].

Finally, we summarize our results in the last section and give a series of conjectures.

2. DEFINITION OF THE SYSTEM

We consider a classical "one-component plasma" (OCP), i.e., a system of identical particles in $\mathbb{R}^\nu$, with positive unit charge, imbedded in the uniform background of fixed negative charges with charge density $-\rho_b$ ($\rho_b \geqslant 0$).

The particle–particle and particle–bath interactions are described by means of a two-body potential $\phi(\mathbf{x}_1 - \mathbf{x}_2)$ such that the force

$$\mathbf{F}(\mathbf{x}) = -\nabla\phi(\mathbf{x}) = -\mathbf{F}(-\mathbf{x})$$

is C^1 and bounded for $|\mathbf{x}| > R$, locally integrable, and continuous away from the origin.

[3] At least if the force decreases faster than Coulomb at infinity and for those states of Coulomb systems that do not have any quadrupole moment.

In particular the following interactions are of special interest:

Coulomb force: $\mathbf{F}(\mathbf{x}) = e^2(\mathbf{x}/|\mathbf{x}|^\nu)$

pseudo-Coulomb: $\mathbf{F}(\mathbf{x}) = e^2(\mathbf{x}/|\mathbf{x}|^{\nu+1})$ (away from the origin)

Yukawa: $\nu = 1, \quad \phi(x) = \mu^{-1}[\exp(-\mu|x|) - 1]$

$\nu = 2, \quad \phi(\mathbf{x}) = K_0(\mu|\mathbf{x}|) + \ln(\tfrac{1}{2}\gamma\mu)$

$\nu = 3, \quad \phi(\mathbf{x}) = |\mathbf{x}|^{-1}\exp(-\mu|\mathbf{x}|)$

The *equilibrium states* of the *finite* system contained in the domain $\Lambda \subset \mathbb{R}^\nu$ are described by correlation functions which are solutions of the BBGKY hierarchy:

$$kT\,\nabla_1 \rho_\Lambda^{(n)}(x_1,\dots,x_n) = \left[\mathbf{E}_{\rho_\Lambda}(x_1) + \sum_{j=2}^{n} \mathbf{F}(x_1 - x_j)\right] \times \rho_\Lambda^{(n)}(x_1,\dots,x_n) + \int_\Lambda dy\,\mathbf{F}(x_1 - y) \times [\rho_\Lambda^{(n+1)}(x_1,\dots,x_n,y) - \rho_\Lambda^{(1)}(y)\rho_\Lambda^{(n)}(x_1,\dots,x_n)] \tag{1}$$

$$\mathbf{E}_{\rho_\Lambda}(x) = \mathbf{E} + \int_\Lambda dy\,[\mathbf{F}(x-y) - \mathbf{F}(-y)]c_\Lambda(y)$$

where $c_\Lambda(y) = \rho_\Lambda^{(1)}(y) - \rho_b$ represents the "*charge density*" at y and $\mathbf{E} = \mathbf{E}_{\rho_\Lambda}(x = 0)$ represents the "*effective electric field*" at the origin.

In other words, the equilibrium states of the OCP are parametrized by Λ = domain, T = temperature, ρ = particle density, ρ_b = bath density, and $\mathbf{E}$ = electric field at the origin.

If Λ is invariant under inversion around the origin, i.e., $\Lambda = -\Lambda$, then the state is invariant under the transformation $x \to -x$ if and only if $\mathbf{E} = 0$.

The *regular equilibrium states* (RE states) of the *infinite* system are parametrized by $\{V_\lambda\}$, T, ρ, ρ_b, and $\mathbf{E}$, where $\{V_\lambda\}$ is a sequence of domains converging to $\mathbb{R}^\nu$; the RE states are defined by correlation function solutions of the BBGKY hierarchy[8]:

$$kT\,\nabla_1 \rho^{(n)}(x_1,\dots,x_n) = \left[\mathbf{E}_\rho(x_1) + \sum_{j=2}^{n} \mathbf{F}(x_1 - x_j)\right] \times \rho^{(n)}(x_1,\dots,x_n) + \int_{\mathbb{R}^\nu} dy\,\mathbf{F}(x_1 - y) \times [\rho^{(n+1)}(x_1,\dots,x_n,y) - \rho^{(1)}(y)\rho^{(n)}(x_1,\dots,x_n)]$$

$$\mathbf{E}_\rho(x) = \mathbf{E} + \lim_{\lambda\to\infty} \int_{V_\lambda} dy\,[\mathbf{F}(x-y) - \mathbf{F}(-y)]c(y),$$

$$c(y) = \rho^{(1)}(y) - \rho_b$$

which are clustering:

$$\int |\rho_T^{(n)}(x_1,\dots,x_n)|\,dx_1 < \infty, \qquad \forall n \geqslant 2$$

It is known that the RE states are always *lo ally neutral*, i.e.,

$$\lim_{\Lambda\to\mathbb{R}^\nu} \frac{1}{|\Lambda|}\int_\Lambda dx\,\rho^{(1)}(x) = \rho_b \tag{2}$$

if the force decreases as *Coulomb* or slower at infinity and if the state is invariant under some translation group. Furthermore, the state is invariant under the inversion $\mathbf{x} \to -\mathbf{x}$ only if $\mathbf{E} = 0$.[8]

We shall assume that the RE state parametrized by $\{V_\lambda\}$ arises as the thermodynamic limit of the finite system $\{\Lambda\}$, where $\{\Lambda\}$ is a subsequence of $\{V_\lambda\}$. In the following, we consider only volume sequences $\{V_\lambda\}$ such that $V_\lambda = -V_\lambda$ and $\mathbf{E} = 0$: i.e., we shall consider only states which are invariant under inversion around the origin.

3. DEFINITION OF THE "PRESSURE" (FOR FINITE SYSTEMS)

In this section, we recall several standard definitions of the pressure for OCP consisting of N particles contained in a finite domain Λ. These definitions are usually shown to be equivalent for fluids (i.e., $\rho_b = 0$), but this will not be the case for the OCP with $\rho_b > 0$.

3.1. Kinetic Pressure

In the kinetic theory the pressure $p_\Lambda^{(k)}$ is introduced as

$$-\sum_{i=1}^{N} \overline{\mathbf{x}_i \mathbf{F}_i^{\text{wall}^t}} = \int_{\partial\Lambda} p_\Lambda(\mathbf{y})\mathbf{y}\,d\boldsymbol{\sigma}(\mathbf{y}) = \nu p_\Lambda^{(k)}|\Lambda|$$

where $p_\Lambda(\mathbf{y})\,d\boldsymbol{\sigma}(\mathbf{y})$ represents the time average force exerted by the particles on the surface element $d\boldsymbol{\sigma}$ of the boundary $\partial\Lambda$ of Λ ($|\Lambda|$ is the volume of Λ). With $p_\Lambda(\mathbf{y}) = kT\rho_\Lambda^{(1)}(\mathbf{y})$ we are led to define the "*kinetic pressure*" as

$$p_\Lambda^{(k)} = \frac{kT}{\nu}\frac{1}{|\Lambda|}\int_{\partial\Lambda} d\boldsymbol{\sigma}(\mathbf{y})\,\mathbf{y}\rho_\Lambda^{(1)}(\mathbf{y}) \tag{3}$$

Property 1. (a) For any convex domain Λ, the kinetic pressure $p_\Lambda^{(k)}$ is nonnegative.

(b) For $\mathbf{E} = 0$ and $\Lambda = -\Lambda$, $p_\Lambda^{(k)} = 0$ at $T = 0$.

The proof of (a) follows immediately from Eq. (3). To establish part (b), and to compare different definitions of the pressure, we make use of the

BBGKY hierarchy to express $p_\Lambda^{(k)}$ in terms of the one- and two-point correlation functions.

From Eq. (1) with $\mathbf{E} = 0$ and $\Lambda = -\Lambda$ we obtain

$$kT\,\nabla\rho_\Lambda^{(1)}(\mathbf{x}) = \int_\Lambda dy\,\mathbf{F}(x-y)[\rho_\Lambda^{(2)}(x,y) - \rho_b\rho_\Lambda^{(1)}(x)]$$

which yields

$$kT\int_\Lambda dx\,\mathbf{x}\nabla\rho_\Lambda^{(1)}(x) = kT\int_{\partial\Lambda} d\sigma(y)\,\mathbf{y}\rho_\Lambda^{(1)}(y) - v|\Lambda|\rho kT$$
$$= \int_\Lambda dx\,\mathbf{x}\int_\Lambda dy\,\mathbf{F}(x-y)[\rho_\Lambda^{(2)}(x,y) - \rho_b\rho_\Lambda^{(1)}(x)]$$

where $\rho = N/|\Lambda|$.

Therefore

$$p_\Lambda^{(k)} = \rho kT + \frac{1}{v}\frac{1}{|\Lambda|}\int_\Lambda dx\int_\Lambda dy\,\mathbf{x}\mathbf{F}(x-y)[\rho_\Lambda^{(2)}(x,y) - \rho_b\rho_\Lambda^{(1)}(x)]$$

At $T = 0$ the RE states are defined by the solutions of the corresponding BBGKY hierarchy and the first equation yields

$$0 = \int_\Lambda dy\,\mathbf{F}(x-y)[\rho_\Lambda^{(2)}(x,y) - \rho_b\rho_\Lambda^{(1)}(x)]$$

which implies $p_\Lambda^{(k)} = 0$.

Remarks. For Coulomb systems in one and three dimensions, Monte Carlo computer simulations indicate that a stronger result, namely $\lim_{T\to 0} p_\Lambda^{(k)} = 0$, should also be valid.[9,10] However, it should be recalled that the limit $T \to 0$ must be taken after the thermodynamic limit $\Lambda \to \infty$.

Using the truncated function

$$\rho_{\Lambda,T}^{(2)} = \rho_\Lambda^{(2)}(x,y) - \rho_\Lambda^{(1)}(x)\rho_\Lambda^{(1)}(y)$$

we obtain

$$p_\Lambda^{(k)} = \rho kT + \frac{1}{v}\frac{1}{|\Lambda|}\int_\Lambda dx\int_\Lambda dy\,\mathbf{x}\mathbf{F}(x-y)[\rho_{\Lambda,T}^{(2)}(x,y) + c_\Lambda(x)c_\Lambda(y)]$$
$$+ \frac{1}{v}\frac{\rho_b}{|\Lambda|}\int_\Lambda dx\int_\Lambda dy\,\mathbf{x}\mathbf{F}(x-y)c_\Lambda(y) \tag{4}$$

This last expression will be useful in the following to compare the different definitions of the pressure.

3.2. Virial Pressure

In the virial equation of state the pressure is introduced as

$$p_\Lambda^{(v)} = \frac{2}{v}\overline{E^{\text{cin}}}^t + \frac{1}{v}\frac{1}{|\Lambda|}\sum_{i=1}^{N}\overline{\mathbf{x}_i\mathbf{F}_i}^t$$

where $\mathbf{F}_i$ represents the force on the ith particle due to the other particles *and* the bath (not the wall).

We shall thus define the "virial pressure" as

$$p_\Lambda^{(v)} = \rho kT + \frac{1}{v}\frac{1}{|\Lambda|}\sum_{i=1}^{N}\langle\mathbf{x}_i\mathbf{F}_i\rangle \tag{5}$$

which yields

$$p_\Lambda^{(v)} = \rho kT + \frac{1}{v}\frac{1}{|\Lambda|}\left[\left\langle\sum_{i\neq j}\mathbf{x}_i\mathbf{F}(x_i - x_j)\right\rangle - \left\langle\sum_i \mathbf{x}_i\int_\Lambda dy\,\mathbf{F}(x_i - y)\rho_b\right\rangle\right]$$

i.e.,

$$p_\Lambda^{(v)} = \rho kT + \frac{1}{v}\frac{1}{|\Lambda|}\int_\Lambda dx\int_\Lambda dy\,\mathbf{x}\mathbf{F}(x-y)[\rho_\Lambda^{(2)}(x,y) - \rho_b\rho_\Lambda^{(1)}(x)]$$

In conclusion, we have

$$\rho_\Lambda^{(k)} = p_\Lambda^{(v)} \tag{6}$$

3.3. Thermal Pressure (Canonical Ensemble)

The thermal pressure has been introduced using the idea that the OCP is the limiting case of a two-component system. Since for the two-component system the pressure is defined by

$$p_\Lambda = -\frac{\partial F}{\partial V}(T, V, N, N_b)$$

it seems reasonable to introduce a "thermal pressure" for the OCP as

$$p_\Lambda^{(\theta)} = kT\,(\partial/\partial V)\ln Q(T, V, N, N_b)$$

where $Q(T, V, N, N_b)$ is the partition function associated with

$$H_\Lambda = \sum_{i=1}^{N}\frac{\mathbf{p}_i^{\,2}}{2m} + u_\Lambda(\mathbf{x}_1,\ldots,\mathbf{x}_N)$$

$$u_\Lambda(\mathbf{x}_1,\ldots,\mathbf{x}_N) = \frac{1}{2}\sum_{i\neq j}\phi(\mathbf{x}_i - \mathbf{x}_j) - \frac{N_b}{V}\sum_i\int_\Lambda dy\,\phi(\mathbf{x}_i - \mathbf{y}) + \frac{1}{2}\left(\frac{N_b}{V}\right)^2\int_\Lambda dx\int_\Lambda dy\,\phi(\mathbf{x}-\mathbf{y})$$

and $\rho_b = N_b/V$.

Using the standard dilatation method,

$$\frac{\partial}{\partial V}\ln Q(T, V, N, N_b) = \frac{1}{Q}\frac{1}{v}\frac{1}{V}\left(\frac{\partial Q(\xi)}{\partial \xi}\right)_{\xi=1}$$

$$Q(\xi) = \frac{1}{N!}\lambda^{-vN}\xi^{vN}\int_\Lambda d\mathbf{x}_1 \cdots d\mathbf{x}_N \exp[-\beta u_\xi(\mathbf{x}_1,\ldots,\mathbf{x}_N)]$$

$$u_\xi(\mathbf{x}_1,\ldots,\mathbf{x}_N) = \frac{1}{2}\sum_{i\neq j}\phi[\xi(\mathbf{x}_i-\mathbf{x}_j)] - \frac{N_b}{V}\sum_i\int_\Lambda dy\,\phi[\xi(\mathbf{x}_i-\mathbf{y})] + \frac{1}{2}\left(\frac{N_b}{V}\right)^2\int_\Lambda dx\int_\Lambda dy\,\phi[\xi(\mathbf{x}-\mathbf{y})]$$

we have

$$\begin{aligned} kT\frac{\partial}{\partial V}\ln Q(T, V, N, N_b) &= \rho kT - \frac{1}{vV}\left\langle\left(\frac{\partial u_\xi}{\partial\xi}\right)_{\xi=1}\right\rangle \\ &= \rho kT + \frac{1}{vV}\left\langle\sum_{i\neq j}\frac{\mathbf{x}_i-\mathbf{x}_j}{2}\mathbf{F}(\mathbf{x}_i-\mathbf{x}_j)\right\rangle \\ &\quad - \frac{1}{v}\frac{N_b}{V}\left\langle\sum_i\int_\Lambda dy\,(\mathbf{x}_i-\mathbf{y})\mathbf{F}(\mathbf{x}_i-\mathbf{y})\right\rangle \\ &\quad + \frac{1}{vV}\left(\frac{N_b}{V}\right)^2\frac{1}{2}\int_\Lambda dx\int_\Lambda dy\,(\mathbf{x}-\mathbf{y})\mathbf{F}(\mathbf{x}-\mathbf{y}) \end{aligned}$$

Therefore

$$\begin{aligned} p_\Lambda^{(\theta)} &= \rho kT + \frac{1}{vV}\left\langle\sum_i \mathbf{x}_i\mathbf{F}_i\right\rangle + \frac{\rho_b{}^2}{v}\frac{1}{V}\int_\Lambda dx\int_\Lambda dy\,\mathbf{x}\mathbf{F}(\mathbf{x}-\mathbf{y}) \\ &\quad + \frac{1}{vV}\rho_b\left\langle\sum_i\int_\Lambda dy\,\mathbf{y}\mathbf{F}(\mathbf{x}_i-\mathbf{y})\right\rangle \end{aligned}$$

i.e.,

$$p_\Lambda^{(\theta)} = p_\Lambda^{(k)} - \frac{\rho_b}{v}\frac{1}{V}\int_\Lambda dx\int_\Lambda dy\,\mathbf{x}\mathbf{F}(\mathbf{x}-\mathbf{y})c_\Lambda(\mathbf{y}) \tag{7}$$

Using Eq. (4), we thus have

$$p_\Lambda^{(\theta)} = \rho kT + \frac{1}{v}\frac{1}{|\Lambda|}\int_\Lambda dx\int_\Lambda dy\,\mathbf{x}\mathbf{F}(\mathbf{x}-\mathbf{y})[\rho_{\Lambda,T}^{(2)}(x,y) + c_\Lambda(\mathbf{x})c_\Lambda(\mathbf{y})] \tag{8}$$

3.4. Mechanical Pressure (Canonical Ensemble)

For a fluid parametrized by the parameters (T, V, N, ρ_b) the mechanical pressure—or partial pressure due to the particles—is introduced as

$$p_\Lambda^{(m)} = -\frac{\partial F}{\partial V}(T, V, N, \rho_b) = \rho^2 \frac{\partial}{\partial \rho}\left[\frac{1}{\rho} f(T, \rho, N, \rho_b)\right]$$

We then define the "*mechanical pressure*" as

$$p_\Lambda^{(m)} = kT(\partial/\partial V) \ln Q(T, V, N, \rho_b)$$

Using again the dilatation method, we have

$$p_\Lambda^{(m)} = \rho kT + \frac{1}{v}\frac{1}{|\Lambda|}\left\langle \sum_i \mathbf{x}_i \mathbf{F}_i \right\rangle + \frac{\rho_b}{v}\frac{1}{|\Lambda|}\int_\Lambda dx \int_\Lambda dy\, \nabla_x[x\phi(x-y)]c_\Lambda(y)$$

which yields [assuming $\phi(x) = O(1/|x|^\alpha)$, $\alpha < v$ as $x \to 0$]

$$p_\Lambda^{(m)} = \rho kT + \frac{1}{v}\frac{1}{|\Lambda|}\left\langle \sum_i \mathbf{x}_i \mathbf{F}_i \right\rangle + \frac{\rho_b}{v}\frac{1}{|\Lambda|}\int_\Lambda dy\, c_\Lambda(y) \int_{\partial\Lambda} d\sigma(x)\, \mathbf{x}\phi(x-y) \quad (9)$$

This definition of the pressure for OCP was first introduced in Ref. 11 and called "mechanical" since in the grand canonical ensemble

$$p_\Lambda^{(m)}(z, T, \rho_b) = (\partial/\partial|\Lambda|) \ln Q_\Lambda(z, T, \rho_b)$$

while

$$p_\Lambda^{(\theta)} = [\ln Q_\Lambda(z, T, \rho_b)]/|\Lambda|$$

4. RELATIONS AMONG THE DIFFERENT PRESSURES

4.1. Arbitrary Interactions

(i) We have already obtained the relation (7),

$$p_\Lambda^{(k)} = p_\Lambda^{(\theta)} + \frac{\rho_b}{v}\frac{1}{|\Lambda|}\int_\Lambda dx \int_\Lambda dy\, \mathbf{x}\mathbf{F}(x-y)c_\Lambda(y) \quad (10)$$

Using Eq. (1), we thus have for $\mathbf{E} = 0$ and $\Lambda = -\Lambda$

$$p_\Lambda^{(k)} = p_\Lambda^{(\theta)} + \frac{\rho_b}{v}\frac{1}{|\Lambda|}\int_\Lambda dx\, \mathbf{x}\mathbf{E}_{\rho_\Lambda}(x) \quad (11)$$

(ii) From Eqs. (9), (5), and (6)

$$p_\Lambda^{(m)} = p^{(k)} + \frac{\rho_b}{v}\frac{1}{|\Lambda|}\int_\Lambda dy\, c_\Lambda(y) \int_{\partial\Lambda} d\sigma(x)\, \mathbf{x}\phi(x-y) \quad (12)$$

(iii) It follows from the equation preceding Eq. (9), together with Eq. (10) that

$$p_\Lambda^{(m)} = p_\Lambda^{(\theta)} + \rho_b \frac{1}{|\Lambda|} \int_\Lambda dx \int_\Lambda dy\, \phi(x-y) c_\Lambda(y) = p_\Lambda^{(\theta)} - \frac{1}{|\Lambda|} \langle u_{pb} + 2u_{bb} \rangle \quad (13)$$

Property 2. (a) $p_\Lambda^{(k)} = p_\Lambda^{(v)}$.

(b) For a fluid, i.e., $\rho_b = 0$, we have $p_\Lambda^{(k)} = p_\Lambda^{(v)} = p_\Lambda^{(m)} = p_\Lambda^{(\theta)}$.

(c) If the potential ϕ is $\mathscr{L}^1$ and if ρ_Λ converges to a RE state locally neutral and invariant under some translation subgroup $\mathscr{T}$ of $\mathbb{R}^\nu$ in such a manner that

$$\lim_{\Lambda \to \mathbb{R}^\nu} \frac{1}{|\Lambda|} \int_\Lambda dx\, |\rho_\Lambda^{(1)}(x) - \rho_\infty^{(1)}(x)| = 0$$

then

$$\lim_{\Lambda \to \mathbb{R}^\nu} p_\Lambda^{(m)} = \lim_{\Lambda \to \mathbb{R}^\nu} p_\Lambda^{(\theta)}$$

i.e., $p^{(m)} = p^{(\theta)}$ and

$$\lim_{\Lambda \to \mathbb{R}_\nu} \frac{1}{|\Lambda|} \langle u_{pb} + 2u_{bb} \rangle = 0$$

Proof. Parts (a) and (b) have been already established.

$$p_\Lambda^{(m)} - p_\Lambda^{(\theta)} = \frac{\rho_b}{|\Lambda|} \int_\Lambda dx \int_\Lambda dy\, \phi(x-y)[c_\infty(y) + \rho_\Lambda^{(1)}(y) - \rho_\infty^{(1)}(y)]$$

but $\phi(x-y)c_\infty(y) \in \mathscr{L}^1(dx)$, and $\phi(x-y)c_\infty(y)$ periodic in (x, y) implies[8]

$$\lim_{\Lambda \to \mathbb{R}^\nu} \rho_b \frac{1}{|\Lambda|} \int_\Lambda dx \int_\Lambda dy\, \phi(x-y) c_\infty(y) = \rho_b \frac{1}{\Delta_0} \int_{\Delta_0} dy \int_{\mathbb{R}^\nu} dx\, \phi(x-y) c_\infty(y)$$
$$= 0 \quad \text{(by neutrality)}$$

(where Δ_0 denotes a "unit cell" and $\{\Lambda\}$ is a sequence of volumes defined as the union of unit cells $\tau_a \Delta_0$, $a \in \mathscr{T}$) and

$$\frac{\rho_b}{|\Lambda|} \int_\Lambda dx \int_\Lambda dy\, |\phi(x-y)| |\rho_\Lambda^{(1)}(y) - \rho_\infty^{(1)}(y)|$$
$$\leqslant \rho_b \|\phi\|_{\mathscr{L}^1} \frac{1}{|\Lambda|} \int_\Lambda dy\, |\rho_\Lambda^{(1)}(y) - \rho_\infty^{(1)}(y)| \to 0 \quad \text{by assumption}$$

To conclude this discussion, we consider the special case

$$\mathbf{F}(\mathbf{x}) = e^2(\mathbf{x}/|\mathbf{x}|^{\gamma+1})$$

Then

$$\mathbf{x}\mathbf{F}(\mathbf{x}) = e^2\delta_{\gamma,1} + (\gamma - 1)\phi(\mathbf{x})$$

and

$$\begin{aligned} p_\Lambda^{(\theta)} &= \rho kT + \frac{1}{v}\frac{1}{|\Lambda|}\int_\Lambda dx \int_\Lambda dy\, \tfrac{1}{2}[e^2\delta_{\gamma,1} + (\gamma-1)\phi(x-y)] \\ &\quad \times [\rho_{\Lambda,T}^{(2)}(x,y) + c_\Lambda(x)c_\Lambda(y)] \\ &= \rho kT + \frac{1}{v}\frac{1}{|\Lambda|}\frac{e^2}{2}\delta_{\gamma,1}\left\{\int_\Lambda dx \int_\Lambda dy\, \rho_{\Lambda,T}^{(2)}(x,y) + \left[\int_\Lambda dx\, c_\Lambda(x)\right]^2\right\} \\ &\quad + (\gamma-1)\frac{1}{v}\frac{1}{|\Lambda|}\langle u_\Lambda\rangle \end{aligned}$$

which yields

$$p_\Lambda^{(\theta)} = \rho kT + \frac{\gamma-1}{v}\frac{1}{|\Lambda|}\langle u_\Lambda\rangle + \delta_{\gamma,1}\left[-\frac{\rho e^2}{2v} + \frac{e^2}{2v}|\Lambda|(\rho-\rho_b)^2\right], \qquad \rho = \frac{N}{|\Lambda|} \tag{14}$$

Expression (14) is erroneously called the "virial pressure" in the literature.

4.2. Coulomb Systems

Property 3. For *Coulomb systems* with *spherical domain* Λ (radius R)

(a) $$p_\Lambda^{(k)} - p_\Lambda^{(\theta)} = -\frac{\rho_b e^2}{2R^v}\int_\Lambda dy\, c_\Lambda(y)|\mathbf{y}|^2 + \rho_b(\rho-\rho_b)\frac{e^2}{2}\frac{\omega_v}{v}R^2$$

(b) $$p_\Lambda^{(k)} - p_\Lambda^{(m)} = -\rho_b\phi(R)(N - N_b)$$

where $N_b = \rho_b|\Lambda|$, $\omega_1 = 2$, $\omega_2 = 2\pi$, and $\omega_3 = 4\pi$.

Corollary. For *Neutral Coulomb systems* with *spherical domain*

$$p_\Lambda^{(k)} - p_\Lambda^{(\theta)} = -\frac{1}{|\Lambda|}\langle u_{pb} + 2u_{bb}\rangle = -\frac{\rho_b e^2}{2R^v}\int_\Lambda dy\, c_\Lambda(y)|\mathbf{y}|^2, \qquad p_\Lambda^{(k)} - p_\Lambda^{(m)} = 0$$

Proof. (a) We have

$$\begin{aligned} &\int_{\partial\Lambda} d\sigma(x)\, \mathbf{x}\phi(x-y) \\ &\quad = v\int_\Lambda dx\, \phi(x-y) - \int_\Lambda dx\, \mathbf{x}\mathbf{F}(x-y) \\ &\quad = v\int_\Lambda dx\, \phi(x-y) - \int_\Lambda dx\, (\mathbf{x}-\mathbf{y})\mathbf{F}(x-y) - \mathbf{y}\int_\Lambda dx\, \mathbf{F}(x-y) \end{aligned}$$

But for Coulomb systems

$$\mathbf{x}\mathbf{F}(\mathbf{x}) = [e^2\delta_{\nu,2} + (\nu - 2)\phi(x)]$$

Therefore

$$\int_{\partial\Lambda} d\sigma(x)\, \mathbf{x}\phi(x-y) = 2\int_\Lambda dx\, \phi(x-y) - \mathbf{y}\int_\Lambda dx\, \mathbf{F}(x-y) - e^2|\Lambda|\delta_{\nu,2}$$

Since

$$\frac{1}{|\Lambda|}\int_\Lambda dx\, \phi(x-y) = -\frac{e^2}{2}\frac{y^2}{R^\nu} + \frac{\nu}{2}\phi(R) + \frac{e^2}{2}\delta_{\nu,2} \tag{15}$$

if Λ is a sphere of radius R and $y \in \Lambda$, we obtain

$$\int_{\partial\Lambda} d\sigma(x)\, \mathbf{x}\phi(x-y) = |\Lambda|\nu\phi(R) \tag{16}$$

$$|\Lambda| = \omega_\nu R^\nu/\nu; \qquad \omega_1 = 2, \quad \omega_2 = 2\pi, \quad \omega_3 = 4\pi \tag{17}$$

and thus it follows from Eq. (11) that

$$p_\Lambda^{(k)} - p_\Lambda^{(m)} = -\rho_b\phi(R)(N - N_b)$$

(b) It follows from Eqs. (13) and (15) that for spherical domains

$$\begin{aligned} p_\Lambda^{(m)} - p_\Lambda^{(\theta)} &= \rho_b \int_\Lambda dy\, c_\Lambda(y)\left[-\frac{e^2|\mathbf{y}|^2}{2R^\nu} + \frac{\nu}{2}\phi(R) + \frac{e^2}{2}\delta_{\nu,2}\right] \\ &= -\frac{\rho_b e^2}{2R^\nu}\int_\Lambda dy\, c_\Lambda(y)|\mathbf{y}|^2 + \rho_b(N - N_b)\left[\phi(R)\frac{\nu}{2} + \frac{e^2}{2}\delta_{\nu,2}\right] \end{aligned}$$

which concludes the proof.

From Eq. (14), we have

$$p_\Lambda^{(\theta)} = \rho kT + \frac{\nu-2}{\nu}\frac{1}{|\Lambda|}\langle u_\Lambda\rangle + \delta_{\nu,2}\left[-\frac{\rho e^2}{4} + \frac{e^2}{4}|\Lambda|(\rho - \rho_b)^2\right] \tag{18}$$

where

$$\langle u_\Lambda\rangle = u_{pp} + u_{pb} + u_{bb}, \qquad u_{bb} = \tfrac{1}{2}\rho_b{}^2\int_\Lambda dx \int_\Lambda dy\, \phi(x-y)$$

Using property 3(b) with Eqs. (13) and (18), we obtain for a *spherical domain* Λ with radius R [4]

$$\nu = 1 \qquad p_\Lambda^{(k)} = \rho kT - \frac{1}{2R}\langle u_{pp} + 2u_{pb}\rangle - N\rho_b\phi(R)$$

$$\nu = 2 \qquad p_\Lambda^{(k)} = \rho kT - \frac{\rho e^2}{4} + \frac{\rho^2 e^2|\Lambda|}{4} - \frac{e^2\rho\rho_b|\Lambda|}{2} - \frac{1}{|\Lambda|}\langle u_{pb}\rangle - N\rho_b\phi(R)$$

$$\nu = 3 \qquad p_\Lambda^{(k)} = \rho kT + \frac{1}{3|\Lambda|}\langle u_{pp} - 2u_{pb}\rangle - N\rho_b\phi(R)$$

Combining these expressions with the expression for $p_\Lambda^{(k)}$ given by Property 3(a), we have

$$u_{pb} = \frac{\rho_b e^2}{2}\frac{\omega_\nu}{\nu}\int_\Lambda dy\, \rho_\Lambda^{(1)}(y)y^2 - \frac{\nu}{2}NN_b\left[\phi(R) + \delta_{\nu,2}\frac{e^2}{2}\right]$$

and

$$\begin{aligned} p_\Lambda^{(k)} &= \rho kT - \frac{\rho_b e^2}{\nu R^\nu}\int_\Lambda dy\, \rho_\Lambda^{(1)}(y)y^2 \\ &\quad + \frac{\nu - 2}{\nu}\frac{\langle u_{pp}\rangle}{|\Lambda|} + \delta_{\nu,2}\frac{e^2\rho}{4}(N-1) \qquad (19) \\ \rho &= \frac{N}{|\Lambda|} \end{aligned}$$

4.3. Conclusions

1. Let $\mathbf{F}(\mathbf{x}) = e^2(\mathbf{x}/|\mathbf{x}|^{\gamma+1})$; for $\gamma = 1$ (e.g., Coulomb in two dimensions or pseudo-Coulomb in one-dimension), we have

$$p_\Lambda^{(\theta)} = \rho kT - \frac{\rho e^2}{2\nu} + |\Lambda|\frac{e^2}{2\nu}(\rho - \rho_b)^2 \qquad (20)$$

which shows that the *thermal pressure becomes negative at low temperature* for neutral systems.

This same property also holds for Coulomb systems in one and three dimensions; for example, in one dimension

$$p_\Lambda^{(\theta)} = \rho kT - \frac{1}{|\Lambda|}\langle u_\Lambda\rangle \leqslant \rho kT - \frac{e^2}{12}[1 - 3(N - N_b)^2]$$

This remark shows that the thermal pressure cannot represent the "pressure" exerted by the particles on the surface of the container, which is a positive quantity; on the other hand, *the kinetic pressure has this positivity property.*

[4] The expression for $\nu = 3$ was derived and studied by computer simulation in Ref. 10.

2. Let us consider a spherical Coulomb system; in the limit $\Lambda \to \infty$ with N and ρ_b fixed it is expected that the "pressure" exerted by the particles on the wall should tend to zero.

Now, it follows from Eq. (19) that $p_\Lambda^{(k)}$ *will tend to zero in this limit* [if $(1/|\Lambda|)\langle u_{pp}\rangle$ tends to zero for[5] $\nu = 3$]; furthermore, this result implies that $(1/|\Lambda|) \int_\Lambda dy\ \rho_\Lambda^{(1)}(y)|\mathbf{y}|^2$ also tends to zero.

On the other hand, by Property 3(b), $p_\Lambda^{(m)}$ will tend to $+\infty$ if $\nu = 1, 2$ and to $-\infty$ if $\nu = 3$.

Finally, using Property 3(a), we see that $p_\Lambda^{(\theta)}$ will behave as

$$-\frac{\rho_b e^2}{2}\frac{\omega_\nu}{\nu} R^2 \frac{\rho - 2\rho_b}{\nu + 2}$$

and will tend to $+\infty$.

This shows that *the kinetic pressure is the only pressure that exhibit the expected property to tend to zero in the limit $\Lambda \to \infty$, with N, ρ_b fixed.*

3. The result that the different definitions of the pressure are not equivalent is directly related to the fact that we have a fixed background $\rho_b > 0$; this result will also hold if the fixed background is not uniform. On the other hand, as we shall see for two-component systems (without background), all definitions are equivalent.

The mathematical origin of the result goes back to the fact that the integrand in the definition of $p_\Lambda^{(k)}$,

$$\mathbf{F}(\mathbf{x} - \mathbf{y})[\rho_\Lambda^{(2)}(x, y) - \rho_b \rho_\Lambda^{(1)}(x)]$$

is not symmetric in (x, y).

4. The consequence of the above result is that one should be careful in the definition of the "pressure." In fact, *the pressure one wants to consider in the equation of state of the OCP is the pressure due to the positive particles with the background considered as strictly passive.*

It appears that the thermal pressure does not have the properties required by the stability conditions of thermodynamics and is thus not the right quantity. As we have seen, both the thermal and the mechanical pressures do not have the expected property to tend to zero in the limit $\Lambda \to \infty$ with N and ρ_b fixed. We shall see in Section 6 that $p^{(k)} = \lim_{\Lambda\to\infty} p_\Lambda^{(k)}$ is also well defined for nonneutral systems (with Yukawa interactions), which is not the case of $p^{(m)}$. Finally, it is expected that $p^{(k)}$ will tend to zero as T tends to zero (as it should), while this is not the case of $p^{(\theta)}$.

In conclusion, *the kinetic pressure is the only pressure that has all the required properties*; it should be stressed that *it is defined in terms of the force and not in terms of the potential.*

[5] For $\nu = 1$ it is possible to see that this condition is satisfied.

5. The virial theorem, which is usually written for *Coulomb* systems as

$$2\langle E_\Lambda^{\text{cin}}\rangle + (\nu - 2)\langle u_\Lambda\rangle + \delta_{\nu,2}[\cdots] = \nu|\Lambda|p$$

should thus be written in terms of the physical pressure $p_\Lambda^{(k)}$ [Eqs. (12), (13)] as

$$\begin{aligned} &2\langle E_\Lambda^{\text{cin}}\rangle + (\nu - 2)\langle u_\Lambda\rangle + \delta_{\nu,2}[\cdots] \\ &\quad = \nu|\Lambda|\left\{p_\Lambda^{(k)} - \frac{\rho_b}{|\Lambda|}\int_\Lambda dx\,[\varphi(x) - \varphi_0] + \frac{\rho_b}{\nu}\frac{1}{|\Lambda|}\int_{\partial\Lambda} d\boldsymbol{\sigma}\,\mathbf{x}[\varphi(x) - \varphi_0]\right\} \end{aligned} \tag{21}$$

where $\varphi(x) - \varphi_0 = \int_\Lambda dy\, \phi(x-y)c_\Lambda(y)$.

Let us note that it is possible to compare Eq. (21) with the equation derived in Ref. 12 for quantum systems at $T = 0$. Indeed, at $T = 0$, $p_\Lambda^{(k)} = 0$ and thus for $\nu = 3$

$$2\langle E_\Lambda^{\text{cin}}\rangle + \langle u_\Lambda\rangle = -3\rho_b\int_\Lambda dx\,[\varphi(x) - \varphi_0] + \rho_b\int_{\partial\Lambda} d\boldsymbol{\sigma}\,\mathbf{x}[\varphi(x) - \varphi_0]$$

which is identical with the starting point, Eq. (6) of Ref. 12.

6. Let us consider a "*two-component system*" ($\mathbf{E} = 0$, $\rho_b = 0$). From the BBGKY equation[8]

$$\nabla\rho_\sigma(\mathbf{x}) = \beta\sigma\int_{\mathbb{R}^\nu} dy\,\mathbf{F}(x-y)[\rho_{\sigma+}^{(2)}(x,y) - \rho_{\sigma-}^{(2)}(x,y)], \qquad \sigma = \pm 1$$

with

$$\rho(x) = \rho_+(x) + \rho_-(x)$$

we obtain

$$\nabla\rho(x) = \beta\int_{\mathbb{R}^\nu} dy\,\mathbf{F}(x-y)(\rho_{++}^{(2)} + \rho_{--}^{(2)} - \rho_{+-}^{(2)} - \rho_{-+}^{(2)})(x,y)$$

$$\begin{aligned} p_\Lambda^{(k)} &= \rho kT + \frac{kT}{\nu}\frac{1}{|\Lambda|}\int_\Lambda dx\,\mathbf{x}\nabla\rho(x) \\ &= \rho kT + \frac{1}{\nu}\frac{1}{|\Lambda|}\int_\Lambda dx\int_\Lambda dy\,\mathbf{x}\mathbf{F}(x-y) \\ &\qquad \times (\rho_{++}^{(2)} + \rho_{--}^{(2)} - \rho_{+-}^{(2)} - \rho_{-+}^{(2)})(x,y) \end{aligned}$$

On the other hand, the thermal pressure is given by

$$\begin{aligned} p_\Lambda^{(\theta)} = \rho kT &+ \left\langle \sum_{i\neq j}\mathbf{F}(x_i - x_j)\mathbf{x}_i\right\rangle + \left\langle\sum_{k\neq l}\mathbf{F}(y_k - y_l)\mathbf{y}_k\right\rangle \\ &- \left\langle\sum_i\sum_k \mathbf{F}(x_i - y_k)(\mathbf{x}_i - \mathbf{y}_k)\right\rangle \end{aligned}$$

($\mathbf{x}_i$, $\mathbf{y}_k$ denote, respectively, positive and negative particles). We thus have

$$p_\Lambda^{(k)} = p_\Lambda^{(v)} = p_\Lambda^{(\theta)}$$

and we notice that the integrand in the definition of $p_\Lambda^{(k)}$

$$\mathbf{F}(x, y)(\rho_{++}^{(2)} + \rho_{--}^{(2)} - \rho_{+-}^{(2)} - \rho_{-+}^{(2)})(x, y)$$

is symmetric in (x, y).

5. PRESSURE IN THE THERMODYNAMIC LIMIT

In this section, we study the definitions of the pressure in the thermodynamic limit $\Lambda \to \mathbb{R}^\nu$ and we assume that the state obtained in this limit is a *RE state with respect to β, $\{\Lambda\}$, invariant under some (discrete) translation group $\mathscr{T}$.*

To simplify the discussion, we take $\mathbf{E} = 0$ and we consider only sequences $\{\Lambda\}$ invariant under inversion around $x = 0$, i.e., the state obtained in the limit is *invariant under the transformation* $\mathbf{x} \to -\mathbf{x}$; furthermore, we shall consider only *sequences of domains Λ which are unions of "cells" $\tau_a\Delta_0$, $a \in \mathscr{T}$*, with Δ_0 a "cell" centered around the origin[6]; the indices r, s, t will represent the center of these cells. Finally, we shall restrict our discussion to systems which are *neutral*,[7] so that

$$\int_\Lambda dy\, c_\Lambda(y) = 0, \qquad \int_\Lambda dy\, y c_\Lambda(y) = 0$$

$$\int_{\Delta_0} dy\, c_\infty(y) = 0, \qquad \int_{\Delta_0} dy\, y c_\infty(y) = 0$$

and in some cases we shall introduce the additional assumption that the state has *no quadrupole moment*, i.e.,

$$\int_{\Delta_0} dy\, (|\mathbf{y}|^2\, \delta_{\alpha\beta} - \nu y_\alpha y_\beta) c_\infty(y) = 0$$

As we shall now see, the analytic form of the pressure will depend strongly on the asymptotic behavior of the force at infinity. We shall then introduce the following conditions on the force:

$$\lim_{\lambda\to\infty} \lambda^\gamma F(\lambda\hat{x}) = \mathbf{d}(\hat{x}) \neq 0 \qquad \text{with } \gamma \geqslant \nu - 1$$

$$|\mathbf{x}|^{\gamma+1}|\partial_i F_\alpha(x)| = O(1)$$

$$|\mathbf{x}|^{\gamma+2}|\partial_i\partial_j F_\alpha(x)| = O(1) \qquad \text{as } |\mathbf{x}| \to \infty$$

[6] At this stage Δ_0 can be any "cell"; it is not necessarily the parallelepiped centered on the translation vectors and does not necessarily have a volume equal to ρ_b^{-1}.

[7] For nonneutral systems see Section 4 and the examples in Section 6.

The first two conditions were introduced in Ref. 8 to discuss equilibrium properties of systems with long-range forces. We recall that for $\gamma = \nu - 1$ (e.g., Coulomb systems) the RE are always locally neutral.

The "*excess pressure*" with respect to $p^{(\theta)}$, i.e.,

$$\Delta p^{(k)} = p^{(k)} - p^{(\theta)} = \lim_{\Lambda \to \mathbb{R}^\nu} [p_\Lambda^{(k)} - p_\Lambda^{(\theta)}]$$

$$\Delta p^{(m)} = p^{(m)} - p^{(\theta)} = \lim_{\Lambda \to \mathbb{R}^\nu} [p_\Lambda^{(m)} - p_\Lambda^{(\theta)}]$$

can be seen as the result of two contributions: first a "*bulk contribution*" given by

$$\begin{aligned} \Delta p_{\text{bulk}}^{(k)} &= \lim_{\Lambda \to \mathbb{R}^\nu} \frac{\rho_b}{\nu} \frac{1}{|\Lambda|} \int_\Lambda dx \int_\Lambda dy\, \mathbf{x}\mathbf{F}(x-y) c_\infty(y) \\ \Delta p_{\text{bulk}}^{(m)} &= \lim_{\Lambda \to \mathbb{R}^\nu} \rho_b \frac{1}{|\Lambda|} \int_\Lambda dx \int_\Lambda dy\, \phi(x-y) c_\infty(y) \end{aligned} \tag{22}$$

where $c_\infty(y) = \rho_\infty^{(1)}(y) - \rho_b$ is the *charge density* in the infinite system; and a "*surface contribution*" given by

$$\begin{aligned} \Delta p_{\text{surf}}^{(k)} &= \lim_{\Lambda \to \mathbb{R}^\nu} \frac{\rho_b}{\nu} \frac{1}{|\Lambda|} \int_\Lambda dx \int_\Lambda dy\, \mathbf{x}\mathbf{F}(x-y)[\rho_\Lambda^{(1)}(y) - \rho_\infty^{(1)}(y)] \\ \Delta p_{\text{surf}}^{(m)} &= \lim_{\Lambda \to \mathbb{R}^\nu} \rho_b \frac{1}{|\Lambda|} \int_\Lambda dx \int_\Lambda dy\, \phi(x-y)[\rho_\Lambda^{(1)}(y) - \rho_\infty^{(1)}(y)] \end{aligned} \tag{23}$$

We note that the "bulk contribution" can be obtained from the knowledge of the state of the infinite system *where the limit $\Lambda \to \mathbb{R}^\nu$ is taken in the same manner as the limit defining the state*; furthermore, this contribution is zero if the state is locally neutral and invariant under translation, i.e., Δp_{bulk} *appears as an "order parameter" for the crystalline state.*

On the other hand, the "surface contribution" will depend on the limiting process $\rho_\Lambda \to \rho_\infty$ and cannot be obtained from the knowledge of the state of the infinite system. We thus arrive at the conclusion that for a system with fixed background *a knowledge of the state of the infinite system is not sufficient to characterize its thermodynamic properties.*

Let us note that it is expected that $\Delta p_{\text{bulk}}^{(k)}$ increases as the temperature decreases, while $\Delta p_{\text{surf}}^{(k)}$ decreases; moreover, it is expected that $p^{(k)}$ tends to zero as $T \to 0$.

Finally, we remark that for Coulomb systems $\Delta p^{(k)}$ is strictly positive at low temperatures.

5.1. One-Dimensional Coulomb Systems (Radius R)

To gain some insight into the problem, it is useful to discuss first the Coulomb system in one dimension.

5.1.1. Bulk Contribution. By definition of the bulk contribution (22) and using Property 3, we have

$$\Delta p^{(k)}_{\text{bulk}} = \Delta p^{(m)}_{\text{bulk}} = \Delta p_{\text{bulk}}, \qquad \Delta p_{\text{bulk}} = -\lim_{R\to\infty} \frac{\rho_b e^2}{2R} \int_{-R}^{R} dr\, c_\infty(r)|r|^2$$

Assuming the state has some periodic structure, i.e., $c_\infty(r) = c_\infty(r+a)$, and is obtained taking the limit $R \to \infty$ as $R = (N + \frac{1}{2})a$, with N integer, we have

$$\Delta p_{\text{bulk}} = -\lim_{N\to\infty} \frac{\rho_b e^2}{2R} \sum_{k=-N}^{N} \int_{-a/2}^{a/2} dr\, c_\infty(r)|r+ka|^2$$

Using neutrality and invariance under inversion, we obtain

$$\Delta p_{\text{bulk}} = -\rho_b e^2 \frac{1}{a} \int_{-a/2}^{a/2} dr\, c_\infty(r) r^2 \tag{24}$$

Remarks. (a) It is expected that $\int_0^{a/2} dr\, c_\infty(r) r^2$ is negative, i.e., $\Delta p_{\text{bulk}} \geqslant 0$.

(b) It is important to take the limiting procedure in the same way for the limit $\rho_\Lambda \to \rho_\infty$ and the limit in the integral; otherwise Δp_{bulk} will depend on the limiting procedure.

For example, the state of the infinite system could have been obtained taking the limit $R \to \infty$ as $R = Na$, which would have given $c_\infty'(r) = c_\infty(r - a/2)$ and

$$\Delta p'_{\text{bulk}} = -\lim_{N\to\infty} \frac{\rho_b e^2}{2R} \sum_{k=0}^{N} \int_0^a dr\, c_\infty'(r)(r+ka)^2$$

Using neutrality and invariance under inversion, then

$$\int_0^a dr\, c_\infty'(r) = 0, \qquad \int_0^a dr\, c_\infty'(r) r = \int_{-a/2}^{a/2} dr\, c_\infty(r)(r + a/2) = 0$$

which yields

$$\Delta p'_{\text{bulk}} = -\rho_b e^2 \frac{1}{a} \int_0^a dr\, c_\infty'(r) r^2 \qquad \text{and} \qquad \Delta p'_{\text{bulk}} = \Delta p_{\text{bulk}}$$

On the other hand, if we had taken expression (24), we would have obtained

$$\Delta \tilde{p}_{\text{bulk}} = -\rho_b e^2 \frac{1}{a} \int_{-a/2}^{a/2} dr\, c_\infty'(r) r^2 = \Delta p_{\text{bulk}} - 2a \int_0^{a/2} dr\, c_\infty(r) r \neq \Delta p_{\text{bulk}}$$

(c) Note that for ν-dimensional systems with spherical symmetry

$$\Delta p_{\text{bulk}} = -\lim_{R\to\infty} \frac{\rho_b e^2}{2R^\nu}\,\omega_\nu \int_0^R dr\, c_\infty(r) r^{\nu+1}$$

5.1.2. Surface Contribution. To evaluate the surface contribution, we have to consider first a finite system. Since ν-dimensional Coulomb systems with spherical domains can be treated in the same manner, we shall directly consider this more general case,

$$\Delta p_{\text{surf}} = \lim_{\Lambda\to\mathbb{R}_\nu} \frac{\rho_b}{\nu}\frac{1}{|\Lambda|}\int_\Lambda dy\,[\rho_\Lambda^{(1)}(y) - \rho_\infty^{(1)}(y)]\int_\Lambda dx\,\mathbf{x}\mathbf{F}(x-y)$$

But for a *Coulomb system*

$$\begin{aligned}
\int_\Lambda dx\,\mathbf{x}\mathbf{F}(x-y) &= \int_\Lambda dx\,(\mathbf{x}-\mathbf{y})\mathbf{F}(x-y) + \mathbf{y}\int_\Lambda dx\,\mathbf{F}(x-y)\\
&= \int_\Lambda dx\,[e^2\delta_{\nu,2} + (\nu-2)\phi(x-y)] + \mathbf{y}\int_\Lambda dx\,\mathbf{F}(x-y)\\
&= e^2|\Lambda|\delta_{\nu,2} + \nu\int_\Lambda dx\,\phi(x-y)\\
&\quad + \left[-2\int_\Lambda dx\,\phi(x-y) + \mathbf{y}\int_\Lambda dx\,\mathbf{F}(x-y)\right]
\end{aligned}$$

which yields for Λ a *sphere of radius R*

$$\int_\Lambda dx\,\mathbf{x}\mathbf{F}(x-y) = e^2|\Lambda|\delta_{\nu,2} + \psi(R) - \tfrac{1}{2}e^2\omega_\nu|\mathbf{y}|^2$$

Using the *neutrality condition*

$$\int_0^R dr\,(R-r)^{\nu-1}[\rho_\Lambda^{(1)}(R-r) - \rho_\infty^{(1)}(R-r)] = 0$$

we have

$$\begin{aligned}
\Delta p_{\text{surf}} &= -\lim_{R\to\infty}\frac{\rho_b}{2\nu}\frac{\omega_\nu}{|\Lambda|}e^2\int_\Lambda dy\,[\rho_\Lambda^{(1)}(y) - \rho_\infty^{(1)}(y)]|\mathbf{y}|^2\\
&= -\frac{\rho_b}{2}\omega_\nu e^2\lim_{R\to\infty}\frac{1}{R^\nu}\int_0^R dr\,r^{\nu+1}[\rho_\Lambda^{(1)}(r) - \rho_\infty^{(1)}(r)]\\
&= -\frac{\rho_b}{2}\omega_\nu e^2\lim_{R\to\infty}\frac{1}{R^\nu}\int_0^R dr\,(R-r)^{\nu+1}[\rho_\Lambda^{(1)}(R-r) - \rho_\infty^{(1)}(R-r)]\\
&= \rho_b\omega_\nu e^2\lim_{R\to\infty}\int_0^R dr\,r\left(1-\frac{r}{R}\right)^{\nu-1}\left(1-\frac{r}{2R}\right)[\rho_\Lambda^{(1)}(R-r) - \rho_\infty^{(1)}(R-r)]
\end{aligned}$$

If the thermodynamic limit is reached in such a manner that

$$|\rho_\Lambda(r) - \rho_\infty(r)| < \varphi(R - r) \qquad \text{with} \int_0^\infty dr\, r\varphi(r) < \infty$$

then by dominated convergence

$$\Delta p_{\text{surf}} = e^2 \rho_b \omega_v \int_0^\infty dr\, r\, \delta\rho_w(r)$$

where $\delta\rho_w(r)$ is the difference between the density for the semiinfinite system and the infinite system (from the boundary).[8]

5.1.3. Concluding Remarks. (a) This simple example has shown that Δp_{bulk} is entirely defined by the state of the infinite system and is proportional to the "moment of inertia" of the neutral dipole free charge density of the unit cell. On the other hand, to obtain Δp_{surf} it is necessary to know the density function of the *semiinfinite* system and the contribution appears as the "*dipole moment*" of $\delta\rho_w(r)$.

(b) Let us consider the one-dimensional system at $T = 0$, i.e.,

$$c_\infty(r) = \sum_n \delta(r - na) - \rho_b, \qquad a = \rho_b^{-1}$$

Then

$$\Delta p_{\text{bulk}} = \rho_b{}^2 e^2 \frac{1}{a} \int_{-a/2}^{a/2} dr\, r^2 = \rho_b{}^2 e^2 \frac{a^2}{12} = \frac{e^2}{12} > 0$$

$$\Delta p_{\text{surf}} = 0, \qquad p^{(k)}(T = 0) = p^{(\theta)} + e^2/12 = 0$$

We thus see that $p^{(k)}$ *at* $T = 0$ *is identically zero*, while $p^{(\theta)} = -e^2/12$ is negative at $T = 0$.[5]

5.2. Bulk Contribution (Arbitrary Interactions)

5.2.1. Bulk Contributions to $\Delta p^{(k)}$ We have

$$\begin{aligned}
\Delta p^{(k)}_{\text{bulk}} &= \lim_{\lambda\to\infty} \frac{\rho_b}{v} \frac{1}{|V_\lambda|} \int_{V_\lambda} dx \int_{V_\lambda} dy\, \mathbf{x}\mathbf{F}(x - y) c_\infty(y) \\
&= \lim_{N\to\infty} \Bigg[\frac{\rho_b}{v} \frac{1}{N} \sum_{t,r} \frac{1}{|\Delta_0|} \int_{\Delta_0} dx \int_{\Delta_0} dy\, \mathbf{x}\mathbf{F}(x - y + t - r) c_\infty(y) \\
&\quad + \frac{\rho_b}{v} \frac{1}{N} \sum_{t,r} \mathbf{t} \frac{1}{|\Delta_0|} \int_{\Delta_0} dx \int_{\Delta_0} dy\, \mathbf{F}(x - y + t - r) c_\infty(y) \Bigg]
\end{aligned}$$

[8] For $v = 1$ the result of Ref. 13 gives an explicit expression for $\delta\rho_w$.

Introducing the fields

$$\mathbf{e}(x) = \int_{\Delta_0} dy\, \mathbf{F}(x-y)c_\infty(y) \tag{25}$$

$$\mathscr{F}(u) = \frac{\rho_b}{|\Delta_0|}\int_{\Delta_0} dx\, \mathbf{e}(x+u) = \frac{\rho_b}{|\Delta_0|}\int_{\Delta_0} dx \int_{\Delta_0} dy\, \mathbf{F}(x+u-y)c_\infty(y) \tag{26}$$

which have a straightforward physical interpretation, we obtain

$$\Delta p^{(k)}_{\text{bulk}} = \lim_{N\to\infty}\left[\frac{\rho_b}{v}\frac{1}{N}\sum_{t,r}\frac{1}{|\Delta_0|}\int_{\Delta_0} dx\, \mathbf{x}\mathbf{e}(x+t-r) + \frac{1}{v}\frac{1}{N}\sum_{t,r}\mathbf{t}\mathscr{F}(t-r)\right]$$

Since

$$e_\alpha(x) = \int_{\Delta_0} dy\, c_\infty(y)[F_\alpha(x) - \mathbf{y}\,\nabla F_\alpha(x) + (1-\theta_x)y^i y^j\, \partial_i\partial_j F_\alpha(x+\theta_x y)]$$

$$\theta_x \in [0, 1]$$

we have $e_\alpha(x) = O(1/|x|^{\gamma+2})$ *for neutral systems, invariant under inversion* (i.e., no dipole moment), and thus

$$\lim_{N\to\infty}\frac{1}{N}\sum_{t,r}\frac{1}{|\Delta_0|}\int_{\Delta_0} dx\, \mathbf{x}\mathbf{e}(x+t-r) = \sum_u \frac{1}{|\Delta_0|}\int_{\Delta_0} dx\, \mathbf{x}\mathbf{e}(x+u)$$

Furthermore, the invariance under inversion around the origin implies

$$\mathscr{F}(u) = \mathscr{F}(-u)$$

In conclusion, for *neutral systems, invariant under inversion*,[9]

$$\Delta p^{(k)}_{\text{bulk}} = \frac{\rho_b}{v}\frac{1}{|\Delta_0|}\int_{\Delta_0} dx\, \mathbf{x}\mathbf{E}_\rho(x) + \frac{1}{2v}\sum_u \mathbf{u}\mathscr{F}(u) \tag{27}$$

where[10]

$$\mathbf{E}_\rho(x) = \mathit{lim}_{\lambda\to\infty}\int_{V_\lambda} dy\,[\mathbf{F}(x-y) - \mathbf{F}(-y)]c_\infty(y)$$

[9] We have assumed that

$$\lim \frac{1}{N}\sum_{t,r}(\mathbf{t}-\mathbf{r})\mathscr{F}(t-r) = \sum_u \mathbf{u}\mathscr{F}(u);$$

we know this is true for $\gamma > v - 1$ and for Coulomb systems without quadrupole moment.

[10] V_λ can be taken as *any union* of unit cells Δ_0.

On the other hand, we can also write

$$\Delta p_{\text{bulk}}^{(k)} = \lim \Bigg[\frac{\rho_b}{v} \frac{1}{|V_\lambda|} \int_{V_\lambda} dx \int_{V_\lambda} dy\, (\mathbf{x} - \mathbf{y}) \mathbf{F}(x - y) c_\infty(y)$$

$$+ \frac{\rho_b}{v} \frac{1}{N} \sum_{t,r} \frac{1}{|\Delta_0|} \int_{\Delta_0} dy\, c_\infty(y)\, \mathbf{y} \int_{\Delta_0} dx\, \mathbf{F}(x - y + t - r)$$

$$+ \frac{\rho_b}{v} \frac{1}{N} \sum_{t,r} \frac{\mathbf{r}}{|\Delta_0|} \int_{\Delta_0} dx \int_{\Delta_0} dy\, \mathbf{F}(x - y + t - r) c_\infty(y) \Bigg]$$

Writing the first term as

$$\frac{1}{N} \sum_{t,r} \frac{1}{\Delta_0} \int_{\Delta_0} dy\, c_\infty(y) \int_{\Delta_0} dx\, (\mathbf{x} - \mathbf{y} + \mathbf{t} - \mathbf{r}) \mathbf{F}(\mathbf{x} - \mathbf{y} + \mathbf{t} - \mathbf{r})$$

we see that for *neutral systems, invariant under inversion* (i.e., no dipole moment) the first two terms are of the order $|t - r|^{-(\gamma+1)}$ or $|t - r|^{-(v+2)}$ for a Coulomb system without a quadrupole moment; indeed

(a) $$\int_{\Delta_0} dy\, c_\infty(y) \int_{\Delta_0} dx\, (\mathbf{x} - \mathbf{y} + \mathbf{u}) \mathbf{F}(x - y + u)$$

$$= \int_{\Delta_0} dy\, c_\infty(y) \int_{\Delta_0} dx\, [(\mathbf{x} + \mathbf{u}) \mathbf{F}(x + u) - \mathbf{y}\, \nabla(xF)(x + u)$$

$$+ (1 - \theta_x) y^i y^j\, \partial_i \partial_j (xF)(x + u + \theta_x y)]$$

(b) *Coulomb*

$$\mathbf{x}\mathbf{F} = [e^2 \delta_{v,2} + (v - 2)\phi(x)]$$

and

$$\int_{\Delta_0} dy\, c_\infty(y) y^\alpha \int_{\Delta_0} dx\, F_\alpha(x - y + u)$$

$$= \int_{\Delta_0} dy\, c_\infty(y) y^\alpha \int_{\Delta_0} dx\, [F_\alpha(x + u) - y^i\, \partial_i F_\alpha(x + u)$$

$$+ (1 - \theta_x) y^i y^j\, \partial_i \partial_j F_\alpha(x + u + \theta_x y)]$$

Therefore, if $\gamma > (\nu - 1)$ (*neutral, no dipole moment*) or *Coulomb* ($\gamma = \nu - 1$) *without quadrupole moment,*

$$\Delta p_{\text{bulk}}^{(k)} = \frac{\rho_b}{\nu} \frac{1}{|\Delta_0|} \int_{\Delta_0} dy\, c_\infty(y) \times \left\{ \lim_{\lambda \to \infty} \int_{V_\lambda} dx\, [(x - y)F(x - y) - xF(x) + y\, \nabla(xF)(x)] \right\} + \frac{\rho_b}{\nu} \frac{1}{|\Delta_0|} \int_{\Delta_0} dy\, c_\infty(y)\mathbf{y} \times \left\{ \lim_{\lambda \to \infty} \int_{V_\lambda} dx\, [\mathbf{F}(x - y) - F(x)] \right\} - \frac{1}{2\nu} \sum_u \mathbf{u}\mathscr{F}(u) \tag{28}$$

To state our next property, we need the following definition.

Definition. Two sequences of volumes $\{V_\lambda\}$ and $\{V_\lambda'\}$ are said to be "equivalent" if $|V_\lambda \blacktriangle V_\lambda'| = o(|V_\lambda \cap V_\lambda'|)$, where $V_\lambda \blacktriangle V_\lambda' = (V_\lambda \cup V_\lambda')\backslash(V_\lambda \cap V_\lambda')$ is the symmetric difference.

It was shown in Ref. 8 that if a state (of the infinite system) is a RE state with respect to $\{V_\lambda\}$, then it is also a RE state with respect to $\{V_\lambda'\}$ whenever $\{V_\lambda\}$ and $\{V_\lambda'\}$ are equivalent (for $\gamma \geqslant \nu - 1$).

Property 4. (a) We have

$$\Delta p_{\text{bulk}}^{(k)} = \frac{\rho_b}{\nu} \frac{1}{|\Delta_0|} \int_{\Delta_0} dx\, \mathbf{x}\mathbf{E}_\rho(x) + \frac{1}{2\nu} \sum_u \mathbf{u}\mathscr{F}(u) \tag{29}$$

(b) Furthermore, if the sequence $\{V_\lambda\}$ is equivalent to the dilatation of some fixed volume V_0, i.e., $V_\lambda \approx \{\lambda x; x \in V_0\}$, then, for $\gamma > \nu - 1$,

$$\Delta p_{\text{bulk}}^{(k)} = \frac{1}{2} \frac{\rho_b}{\nu} \frac{1}{|\Delta_0|} \int_{\Delta_0} dx\, \mathbf{x}E_\rho \tag{30}$$

for Coulomb systems without quadrupole moment (with respect to Δ_0),

$$\Delta p_{\text{bulk}}^{(k)} = \frac{1}{2} \frac{\rho_b}{\nu} \frac{1}{|\Delta_0|} \int_{\Delta_0} dx\, \mathbf{x}\mathbf{E}_\rho(x) - \frac{\rho_b e^2}{4} \frac{\omega_\nu}{\nu} \frac{1}{\Delta_0} \int_{\Delta_0} dy\, c_\infty(y)|\mathbf{y}|^2 \tag{31}$$

Remark. The overall "macroscopic shape" defined by means of V_0 does not enter into the expressions for $\Delta p_{\text{bulk}}^{(k)}$, Eqs. (30) and (31); however, $\Delta p_{\text{bulk}}^{(k)}$ will depend on the "microscopic shape" as defined by Δ_0.

Proof. (a) Already established.

(b) For $\gamma > \nu - 1$, we have[8]

$$\lim_{\lambda \to \infty} \int_{V_\lambda} dx\,[F(x-y) - F(x)] = 0$$

$$\lim_{\lambda \to \infty} \int_{V_\lambda} dx\,[(\mathbf{x}-\mathbf{y})\mathbf{F}(x-y) - \mathbf{x}\mathbf{F}(x) + \mathbf{y}\,\nabla(xF)(x)] = 0$$

Indeed, let $\psi(x) = \mathbf{x}\mathbf{F}(x)$. Then

$$\int_{V_\lambda} dx\,[\psi(x-y) - \psi(x) + \mathbf{y}\,\nabla\psi(x)] = \mathbf{y}\int_{V_\lambda} dx\,[\nabla\psi(x) - \nabla\psi(x+\theta_x y)]$$

$$\theta_x \in [0, 1]$$

But

$$\left|\int_{V_\lambda} dx\,[(\partial_\alpha\psi)(x) - (\partial_\alpha\psi)(x+\theta_x y)]\right| \leqslant \int_{V_\lambda \blacktriangle V_\lambda'} dx\,|\partial_\alpha\psi(x)|$$

where $V_\lambda' = \tau_y V_\lambda = \{x + y;\, x \in V_\lambda\}$.

Therefore, repeating the argument of Ref. 8, we find that the difference will tend to zero if $\partial_\alpha\psi = o(1/|x|^{\nu-1})$ when $|x| \to \infty$. By the condition on the force, namely

$$F_\alpha(x) = O(1/|x|^\gamma), \qquad \partial_\alpha F_\beta(x) = O(1/|x|^{\gamma+1})$$

this condition will be satisfied for $\gamma > \nu - 1$.

It thus follows from Eqn. (28) that for $\gamma > \nu - 1$ (neutral, no dipole)

$$\Delta p^{(\mathrm{k})}_{\mathrm{bulk}} = -\frac{1}{2\nu}\sum_u \mathbf{u}\mathscr{F}(u)$$

which concludes the proof because of (a).

For Coulomb systems, we have

$$\mathbf{x}\mathbf{F} = [e^2\,\delta_{\nu,2} + (\nu-2)\phi(x)]$$

Therefore Eq. (28) yields (Coulomb system without quadrupole moment)

$$\begin{aligned}\Delta p^{(\mathrm{k})}_{\mathrm{bulk}} = {}& \rho_b \frac{\nu-2}{\nu}\frac{1}{|\Delta_0|}\int_{\Delta_0} dy\, c_\infty(y) \\ &\times \lim_{\lambda\to\infty}\int_{V_\lambda} dx\,[\phi(x-y) - \phi(x) + \mathbf{y}\,\nabla\phi(x)] \\ &+ \frac{\rho_b}{\nu}\frac{1}{|\Delta_0|}\int_{\Delta_0} dy\, c_\infty(y)\mathbf{y}\lim_{\lambda\to\infty}\int_{V_\lambda} dx\,[\mathbf{F}(x-y) - \mathbf{F}(x)] \\ &- \frac{1}{2\nu}\sum_u \mathbf{u}\mathscr{F}(u)\end{aligned}$$

Using the result of Ref. 8, we know that

$$\lim_{\lambda\to\infty}\int_{V_\lambda} dx\,[F_i(x-y)-F_i(x)] = \lim_{\lambda\to\infty}\int_{\lambda V_0} dx\,[F_i(x-y)-F_i(x)]$$
$$= -e^2\mathbb{C}_{ij}y^j$$

where

$$\mathbb{C}_{ij} = \int_{\partial V_0} d\sigma_i(y)\,\frac{y_j}{|y|^\nu} \qquad \text{if} \quad V_\lambda = \lambda V_0$$

On the other hand

$$\lim_{\lambda\to\infty}\int_{V_\lambda} dx\,[\phi(x-y)-\phi(x)+\mathbf{y}\,\nabla\phi(x)] = -\tfrac{1}{2}e^2\langle y|\mathbb{C}|y\rangle$$

We thus have

$$\Delta p^{(\mathrm{k})}_{\mathrm{bulk}} = -\frac{\rho_b e^2}{2}\frac{1}{|\Delta_0|}\int_{V_0} dy\, c_\infty(y)\langle y|\mathbb{C}|y\rangle - \frac{1}{2\nu}\sum_u \mathbf{u}\mathscr{F}(u)$$

which together with Eq. (29) yields for Coulomb systems without quadrupole moment[8]

$$\Delta p^{(\mathrm{k})}_{\mathrm{bulk}} = \frac{\rho_b}{2\nu}\frac{1}{|\Delta_0|}\int_{\Delta_0} dx\,\mathbf{x}\mathbf{E}_\rho(x) - \frac{\rho_b e^2}{4}\frac{\omega_\nu}{\nu}\frac{1}{|\Delta_0|}\int_{\Delta_0} dy\,c_\infty(y)|\mathbf{y}|^2$$

We shall now derive an explicit expression for the excess kinetic pressure, i.e., for $\int_{\Delta_0} dx\,\mathbf{x}\mathbf{E}_\rho(x)$, in terms of the Fourier transform of the one-point correlation function. For this derivation, we shall consider that the unit cell Δ_0 is a parallelepiped based on the translation vectors.

Property 5. Let Δ_0 be a parallelepiped with basis vectors $\Delta_i\mathbf{a}^{(i)}$, $|\mathbf{a}^{(i)}| = 1$.

For any locally *neutral RE state invariant under the translation group* defined by $\{\Delta_i\mathbf{a}^{(i)}\}$,

$$\frac{1}{|\Delta_0|}\int_{\Delta_0} dx\,\mathbf{x}\mathbf{E}_\rho(x) = -\sum_{j=1}^{\nu}\left[\sum_{n_j\neq 0}(-1)^{n_j}\tilde{\phi}(n_j\mathbf{Q}^{(j)})\tilde{\rho}_\infty(n_j\mathbf{Q}^{(j)})\right] \qquad (32)$$

where $\tilde{\phi}(k) = \int_{\mathbb{R}^\nu} dx\,\phi(x)e^{-ikx}$ is the Fourier transform of the potential

$$\tilde{\rho}_\infty(k) = \frac{1}{|\Delta_0|}\int_{\Delta_0} dx\,\rho^{(1)}_\infty(x)e^{-ikx}$$

and $\mathbf{Q}^{(j)}$ denotes the vectors of the reciprocal lattice.

Proof. (i) Fourier transform

$$\tilde{\varphi}(k) = \frac{1}{|\Delta_0|}\int_{\Delta_0} dx\, \varphi(x) e^{-ikx} = \mathscr{F}[\varphi], \qquad k \in \text{reciprocal lattice}$$

$$\varphi(x) = \sum_k e^{ikx}\tilde{\varphi}(k), \qquad \frac{1}{|\Delta_0|}\int_{\Delta_0} dx\, \varphi(x)\zeta(x) = \sum_k \overline{\tilde{\varphi}(k)}\,\tilde{\zeta}(k)$$

If

$$\varphi(x) = \int_{\mathbb{R}^\nu} dy\, G(x-y)h(y), \qquad h \text{ periodic over } \Delta_0$$

$$\tilde{\varphi}(k=0) = \frac{1}{|\Delta_0|}\int_{\Delta_0} dx\, \varphi(x), \qquad \tilde{\varphi}(k \neq 0) = \tilde{G}(k)\tilde{h}(k)$$

$$\tilde{G}(k) = \int_{\mathbb{R}_\nu} dx\, e^{-ikx} G(x)$$

(ii) We have[11]

$$\frac{1}{|\Delta_0|}\int_{\Delta_0} dx\, \mathbf{x}\mathbf{E}_\rho(x) = \sum_\alpha \sum_k \overline{\mathscr{F}[x_\alpha]}\mathscr{F}[E_\alpha], \qquad \mathscr{F}[x_\alpha] = \frac{1}{|\Delta_0|}\int_{\Delta_0} dx\, e^{-ikx} x_\alpha$$

Introducing

$$\mathbf{x} = u_j \mathbf{a}^{(j)}, \qquad |\mathbf{a}^{(j)}| = 1, \qquad u_j \in [-\Delta_j/2, \Delta_j/2]$$

$$\mathbf{k} = n_j \mathbf{Q}^{(j)}, \qquad n_j \in \mathbb{Z}$$

then

$$kx = \sum_j \frac{2\pi}{\Delta_j} n_j u_j$$

$$x^\alpha = e^{(\alpha)}\mathbf{x} = \sum_j (\mathbf{e}^{(\alpha)}\mathbf{a}^{(j)})u_j = T^{\alpha j}u_j$$

$$k^\alpha = \mathbf{e}^{(\alpha)}\mathbf{k} = \sum_i (\mathbf{Q}^{(i)}\mathbf{e}^{(\alpha)})n_i = n_i \tau^{i\alpha}$$

$$\sum_\alpha \tau^{i\alpha}T^{\alpha j} = \frac{2\pi}{\Delta_j}\delta_{ij}$$

[11] Notice that for $k = 0$,

$$\mathscr{F}[E_\alpha](k=0) = \frac{1}{|\Delta_0|}\int_{\Delta_0} dx\, E_\alpha(x)$$

is well defined since $E_\alpha(x)$ is bounded for a periodic RE state.

$$\mathscr{F}[x^\alpha] = \frac{J}{\Delta_0}\sum_j T^{\alpha j}\int_{-\Delta_1/2}^{\Delta_1/2} du_1 \cdots \int_{-\Delta_\nu/2}^{\Delta_\nu/2} du_\nu\, u_j \exp\left(-i\frac{2\pi}{\Delta_l} n_l u_l\right)$$

$$= \sum_j T^{\alpha j}(1-\delta_{n_j,0})\frac{(-1)^{n_j}}{-i(2\pi/\Delta_j)n_j}\prod_{i\neq j}\delta_{n_i,0}$$

$$\frac{1}{|\Delta_0|}\int_{\Delta_0} dx\, \mathbf{x}\mathbf{E}_\rho(x) = \sum_\alpha\sum_j T^{\alpha j}\sum_{n_j\neq 0}\frac{(-1)^{n_j}}{i(2\pi/\Delta_j)n_j}\tilde{F}_\alpha(n_j\mathbf{Q}^{(j)})\tilde{\rho}_\infty(n_j\mathbf{Q}^{(j)})$$

But

$$\mathbf{F} = -\nabla\phi, \qquad \tilde{F}_\alpha(k) = -i\mathbf{k}\mathbf{e}^{(\alpha)}\tilde{\phi}(k)$$

$$F_\alpha(n_j\mathbf{Q}^{(j)}) = -in_j\mathbf{Q}^{(j)}\mathbf{e}^{(\alpha)}\tilde{\phi}(k) = -in_j\tau^{j\alpha}\tilde{\phi}(k)$$

Therefore

$$\frac{1}{|\Delta_0|}\int_{\Delta_0} dx\, \mathbf{x}\mathbf{E}_\rho(x) = -\sum_{j=1}^{\nu}\sum_{n_j\neq 0}(-1)^{n_j}\tilde{\phi}(n_j\mathbf{Q}^{(j)})\tilde{\rho}_\infty(n_j\mathbf{Q}^{(j)})$$

Property 6. "Coulomb systems." (a) If the basis vectors of the parallelepiped Δ_0 are orthogonal, then for any Δ_0-invariant RE states of a Coulomb system

$$\frac{1}{|\Delta_0|}\int_{\Delta_0} dx\, \mathbf{x}\mathbf{E}_\rho(\mathbf{x}) = -\frac{e^2\omega_\nu}{2}\frac{\mathbf{1}}{|\Delta_0|}\int_{\Delta_0} dy\, |\mathbf{y}|^2 c_\infty(y)$$

(b) For any *RE state with cubic symmetry*

$$\Delta p_{\text{bulk}}^{(\text{k})} = \frac{\rho_b}{\nu}\frac{1}{|\Delta_0|}\int_{\Delta_0} dx\, \mathbf{x}\mathbf{E}_\rho(x) = -\frac{\rho_b e^2}{2}\frac{\omega_\nu}{\nu}\frac{1}{|\Delta_0|}\int_{\Delta_0} dy\, |\mathbf{y}|^2 c_\infty(y) \tag{33}$$

Proof. We have

$$\tilde{\phi}(k) = e^2\frac{\omega_\nu}{|k|^2}, \qquad \tilde{\phi}(n_j\mathbf{Q}^{(j)}) = e^2\frac{\omega_\nu}{[(2\pi/\Delta_j)n_j]^2}$$

Therefore

$$\frac{1}{|\Delta_0|}\int_{\Delta_0} dx\, \mathbf{x}\mathbf{E}_\rho(x) = -e^2\omega_\nu\sum_{j=1}^{\nu}\sum_{n_j\neq 0}(-1)^{n_j}\frac{1}{[(2\pi/\Delta_j)n_j]^2}\tilde{\rho}_\infty(n_j\mathbf{Q}^{(j)})$$

$$= -e^2\omega_\nu\sum_{j=1}^{\nu}\sum_{n_j\neq 0}(-1)^{n_j}\frac{1}{[(2\pi/\Delta_j)n_j]^2}\frac{1}{|\Delta_0|}$$

$$\times\int_{\Delta_0} dx_1 \cdots \int_{\Delta_0} dx_\nu\left\{\exp\left[i\left(\frac{2\pi}{\Delta_j}\right)n_j x_j\right]\right\}c_\infty(x)$$

$$= -e^2\omega_\nu\frac{1}{|\Delta_0|}\int_{\Delta_0} dx$$

$$\times\sum_j\left\{\sum_{n_j\neq 0}\frac{(-1)^{n_j}\exp[i(2\pi/\Delta_j)n_j x_j]}{[(2\pi/\Delta_j)n_j]^2}\right\}c_\infty(x)$$

But

$$\sum_{n_j \neq 0} \frac{(-1)^{n_j} \exp[i(2\pi/\Delta_j)n_j x_j]}{[(2\pi/\Delta_j)n_j]^2} = -\frac{\Delta_j^2}{24} + \frac{x_j^2}{2}$$

which concludes the proof of (a) because of the neutrality property.

The last part of the property follows then from Eq. (31).

5.2.2. Bulk Contribution to $\Delta p^{(m)}$. We have

$$\begin{aligned}\Delta p^{(m)}_{\text{bulk}} &= \lim_{\lambda\to\infty} \frac{\rho_b}{|V_\lambda|} \int_{V_\lambda} \mathrm{dx} \int_{V_\lambda} dy\, \phi(x-y) c_\infty(y) \\ &= \lim_{\lambda\to\infty} \frac{\rho_b}{N} \sum_{t,r} \frac{1}{|\Delta_0|} \int_{\Delta_0} dx \int_{\Delta_0} dy\, c_\infty(y)\phi(x-y+t-r)\end{aligned}$$

Using neutrality and invariance under inversion, we can replace

$$\int_{\Delta_0} dx \int_{\Delta_0} dy\, c_\infty(y)\phi(x-y+t-r)$$

by

$$\int_{\Delta_0} dx \int_{\Delta_0} dy\, c_\infty(y)[\phi(x-y+u) - \phi(x+u) + \mathbf{y}\,\nabla\phi(x+u)]$$

which behaves as $|u|^{-(\gamma+1)}$ or as $|u|^{-(\nu+2)}$ for a Coulomb system without quadrupole moment.

We thus have for $\gamma > \nu - 1$ and for a Coulomb system without quadrupole moment

$$\Delta p^{(m)}_{\text{bulk}} = \rho_b \frac{1}{|\Delta_0|} \int_{\Delta_0} dy\, c_\infty(y) \left\{ \lim_{\lambda\to\infty} \int_{V_\lambda} dx\, [\phi(x-y) - \phi(x) + \mathbf{y}\,\nabla\phi(x)] \right\}$$

and therefore the results of Section 5.2.1 yield the following:

Property 7. (a) If $\gamma > \nu - 1$, then $[p^{(m)} - p^{(\theta)}]_{\text{bulk}} = 0$.

(b) (i) For Coulomb forces without quadrupole moment

$$\Delta p^{(m)}_{\text{bulk}} = -\frac{\rho_b e^2}{2} \frac{\omega_\nu}{\nu} \frac{1}{|\Delta_0|} \int_{\Delta_0} dy\, c_\infty(y)|\mathbf{y}|^2$$

i.e.,

$$[p^{(k)} - p^{(m)}]_{\text{bulk}} = -\frac{1}{2\nu} \sum_u \mathbf{u}\mathscr{F}(u)$$

(ii) For Coulomb forces with cubic symmetry

$$[p^{(k)} - p^{(m)}]_{\text{bulk}} = 0$$

5.2.3. Concluding Remarks.

1. For $\gamma > \nu - 1$ and for Coulomb systems without quadrupole moment with respect to Δ_0 it follows from the results of Sections 5.2.1 and 5.2.2 that

$$[p^{(k)} - p^{(\theta)}]_{\text{bulk}} = \frac{1}{2}\frac{\rho_b}{\nu}\frac{1}{|\Delta_0|}\int_{\Delta_0} dx\,\mathbf{x}\mathbf{E}_\rho(x) + \frac{1}{2}[p^{(m)} - p^{(\theta)}]_{\text{bulk}}$$

$$[p^{(m)} - p^{(\theta)}]_{\text{bulk}} = \frac{\rho_b}{\nu}\frac{1}{|\Delta_0|}\int_{\Delta_0} dx\,\mathbf{x}\mathbf{E}_\rho(x) + \frac{1}{\nu}\sum_u \mathbf{u}\mathscr{F}(u)$$

$$[p^{(k)} - p^{(m)}]_{\text{bulk}} = -\frac{1}{2\nu}\sum_u \mathbf{u}\mathscr{F}(u)$$

Moreover, if $\gamma > \nu - 1$, then

$$[p^{(m)} - p^{(\theta)}]_{\text{bulk}} = 0, \qquad \sum_u \mathbf{u}\mathscr{F}(u) = -\frac{\rho_b}{|\Delta_0|}\int_{\Delta_0} dx\,\mathbf{x}\mathbf{E}_\rho(x)$$

but for Coulomb systems with cubic symmetry

$$[p^{(k)} - p^{(m)}]_{\text{bulk}} = 0, \qquad \sum_u \mathbf{u}\mathscr{F}(u) = 0$$

2. One should notice the factor $\frac{1}{2}$ of difference between $\Delta p^{(k)}_{\text{bulk}}$ for $\gamma > \nu - 1$ and for $\Delta p^{(k)}_{\text{bulk}}$ for Coulomb systems with cubic symmetry.

3. For Coulomb systems without quadrupole moment $\Delta p^{(k)}_{\text{bulk}}$ is proportional to the moment of inertia of the charge density in the cell Δ_0 if and only if $\sum_u \mathbf{u}\mathscr{F}(u) = 0$.

4. Properties 4 and 7 show that for $\gamma > \nu - 1$ and for Coulomb systems without quadrupole moment with respect to Δ_0, the bulk contribution to $p^{(k)}$ and $p^{(m)}$ does not depend on the "macroscopic shape" as defined by V_0 (i.e., V_λ can be taken as any union of cells Δ_0), but will depend on the "microscopic shape" as defined by Δ_0.

On the other hand, it is possible to show[14] that for Coulomb systems with nonvanishing quadrupole moment $\Delta p^{(k)}_{\text{bulk}}$ and $\Delta p^{(m)}_{\text{bulk}}$ will also depend on the "macroscopic shape."

5. Property 7(a) extends Property 2, $p^{(m)} = p^{(\theta)}$, from $\gamma > \nu + 1$ to $\gamma > \nu - 1$, but the result is now restricted to the bulk contribution.

6. Property 7(b) extends Property 3, $p^{(m)} = p^{(k)}$, from spherical domains to domains with cubic symmetry, but is also restricted to the bulk contribution.

7. For Coulomb forces and general domains, there exists a representation of the potential by means of a double Fourier series[14] which yields the result

$$\Delta p^{(m)}_{\text{bulk}} = -\frac{\rho_b e^2}{2}\omega_\nu \frac{1}{|\Delta_0|}\int_{\Delta_0} dy\, c_\infty(y)\langle y|\mathbb{F}|y\rangle$$

where $\mathbb{F}$ is a symmetrical tensor of unit trace depending on the sequence $\{V_\lambda\}$. In the cubic case $\mathbb{F} = (1/\omega_v)\mathbb{C}$.

6. APPLICATIONS

In this section, we illustrate the previous derivation by some explicit examples. We shall see in particular that it is *not* possible to obtain the equation of state of the one-component plasma using the Yukawa potential and passing to the limit $\mu \to 0$. We shall also see that the definition of $p^{(\mathrm{k})}$ still makes sense for nonneutral systems, which is not true of $p^{(\mathrm{m})}$.

These examples show that $\Delta p^{(\mathrm{k})}_{\mathrm{bulk}}$ and $\Delta p^{(\mathrm{k})}_{\mathrm{surf}}$ can have either sign and it appears that $\Delta p^{(\mathrm{k})}_{\mathrm{surf}}$ is minimum for cells Δ_0 defined by the vectors of the translation symmetry group.

6.1. One-Dimensional Systems[12]

We assume that the state of the infinite system is periodic with period a,[13] and is obtained by means of a sequence of domains $V_\lambda = [-L, L]$ with $2L = (N+1)a$. In particular the states of the finite and infinite systems will be invariant under inversion.

For a one-dimensional system, Eq. (13) yields

$$p_\Lambda^{(\mathrm{m})} - p_\Lambda^{(\theta)} = \frac{\rho_b}{2L} \int_{-L}^{L} dy\, c_\Lambda(y) \int_{-L}^{L} dx\, [\phi(x-y) - \phi(x)] + \rho_b(\rho - \rho_b) \int_{-L}^{L} dx\, \phi(x)$$

i.e.,

$$\begin{aligned} p_\Lambda^{(\mathrm{m})} - p_\Lambda^{(\theta)} &= \frac{\rho_b}{2L} \int_{-L}^{L} dy\, c_\Lambda(y) \int_{0}^{y} dx\, [\phi(L+x) - \phi(L-x)] \\ &\quad + \rho_b(\rho - \rho_b) \int_{-L}^{L} dx\, \phi(x) \\ p_\Lambda^{(\mathrm{k})} - p_\Lambda^{(\mathrm{m})} &= -\rho_b \int_{-L}^{L} dy\, c_\Lambda(y) \phi(L-y) \end{aligned} \tag{34}$$

(expressions which are valid without assuming neutrality).

[12] For a more detailed discussion of one-dimensional systems, see Ref. 15.

[13] In particular it could be invariant under translation.

6.1.1. Coulomb Potential: $\phi(x) = -e^2|x|$. As shown in Sections 4.2 and 5.1

$$p^{(m)} - p^{(k)} = 0$$

$$[p^{(k)} - p^{(\theta)}]_{\text{bulk}} = -\rho_b e^2 \frac{1}{a} \int_{-a/2}^{a/2} dy\, c_\infty(y) y^2$$

$$[p^{(k)} - p^{(\theta)}]_{\text{surf}} = 2\rho_b e^2 \int_0^\infty dy\, y\, \delta\rho_w(y)$$

In particular at $T = 0$, $\Delta p^{(k)}_{\text{bulk}} > 0$ and $\Delta p^{(k)}_{\text{surf}} = 0$.

6.1.2. Yukawa Potential: $\phi(x) = (e^2/\mu)(e^{-\mu|x|} - 1)$. Using the general result of Section 5, we have for *neutral* systems

$$p^{(m)} - p^{(\theta)} = 0, \qquad [p^{(k)} - p^{(\theta)}]_{\text{bulk}} = -\tfrac{1}{2}\rho_b \sum_{n\neq 0} (-1)^n \tilde{\phi}\left(\frac{2\pi}{a} n\right) \tilde{\rho}^{(1)}_\infty\left(\frac{2\pi}{a} n\right)$$

where for the Yukawa potential

$$\tilde{\phi}(k) = 2e^2/(k^2 + \mu^2)$$

Therefore

$$\Delta p^{(k)} = -\frac{\rho_b e^2}{a} \int_{-a/2}^{a/2} dy\, c_\infty(y) \sum_{n\neq 0} (-1)^n \frac{e^{i(2\pi/a)ny}}{[(2\pi/a)n]^2 + \mu^2}$$

But

$$\sum_{n\neq 0} (-1)^n \frac{e^{i(2\pi/a)ny}}{[(2\pi/a)n]^2 + \mu^2} = \frac{a}{2\mu} \frac{\operatorname{ch}(\mu y)}{\operatorname{sh}(a\mu/2)} - \frac{1}{\mu^2}$$

which yields, using the *neutrality* condition,

$$[p^{(k)} - p^{(\theta)}]_{\text{bulk}} = -\frac{\rho_b e^2}{2\mu \operatorname{sh}(\mu a/2)} \int_{-a/2}^{a/2} dy\, c_\infty(y) \operatorname{ch}(\mu y) \tag{35}$$

On the other hand $p^{(m)} = p^{(\theta)}$ implies

$$\begin{aligned} [p^{(k)} - p^{(\theta)}]_{\text{surf}} &= -\rho_b \lim_{L\to\infty} \int_{-L}^{L} dy\, (\rho^{(1)}_{(-L,+L)} - \rho^{(1)}_\infty)(y) \frac{e^2}{\mu} (e^{-\mu|L-y|} - 1) \\ &= \rho_b e^2 \int_0^\infty dy\, \delta\rho_w(y) \frac{1 - e^{-\mu y}}{\mu} \end{aligned} \tag{36}$$

$$\begin{aligned} [p^{(m)} - p^{(\theta)}]_{\text{surf}} = \lim_{L\to\infty} \frac{\rho_b e^2}{\mu^2} \frac{1}{L} \int_{-L}^{L} dy\, (\rho^{(1)}_{(-L,+L)} - \rho^{(1)}_\infty)(y) \\ \times (e^{-\mu L} - e^{-\mu(L-y)}) = 0 \end{aligned}$$

Taking the limit $\mu \to 0$, we obtain

Yukawa $\mu \to 0$	*Coulomb*
$[p^{(m)} - p^{(\theta)}]_{\text{bulk}} = 0$	$[p^{(m)} - p^{(\theta)}]_{\text{bulk}} = I(\mu = 0)$
$[p^{(m)} - p^{(\theta)}]_{\text{surf}} = 0$	$[p^{(m)} - p^{(\theta)}]_{\text{surf}} = J(\mu = 0)$
$[p^{(k)} - p^{(\theta)}]_{\text{bulk}} = \frac{1}{2}I(\mu \to 0)$	$[p^{(k)} - p^{(\theta)}]_{\text{bulk}} = I(\mu = 0)$
$[p^{(k)} - p^{(\theta)}]_{\text{surf}} = \frac{1}{2}J(\mu \to 0)$	$[p^{(k)} - p^{(\theta)}]_{\text{surf}} = J(\mu = 0)$

where

$$I(\mu) = -\frac{\rho_b e^2}{a} \int_{-a/2}^{a/2} dy\, c_\infty^{(\mu)}(y) \frac{\operatorname{ch} \mu y}{(\mu/a) \operatorname{sh}(\mu a/2)}$$

$$J(\mu) = 2\rho_b e^2 \int_0^\infty dy\, \delta\rho_w(y) \frac{1 - e^{-\mu y}}{\mu}$$

$$p^{(\theta)}(\mu = 0) = \lim_{\mu \to 0} p^{(\theta)}(\mu)$$

In conclusion, the *equation of state of the one-component plasma, i.e.*, $p^{(k)} = p^{(k)}(\rho, T)$, cannot be obtained using the Yukawa potential and passing to the limit $\mu \to 0$ after the thermodynamic limit, whereas the thermal pressure can be obtained in this manner.

To understand better the origin of the factor $\frac{1}{2}$, it may be useful to rederive explicitly the general expressions (30); we shall thus repeat the derivation *without imposing the neutrality condition.*

(i) Using the definition (34), we have

$$\begin{aligned}
p_\Lambda^{(k)} - p_\Lambda^{(m)} &= -\rho_b \int_{-L}^{L} dy\, c_\Lambda(y) \frac{e^2}{\mu} (e^{-\mu(L-y)} - 1) \\
&= -\frac{\rho_b e^2}{\mu} \sum_{n=-N}^{N} \int_{-a/2}^{a/2} dy\, c_\Lambda(y) e^{-\mu[(N-n+1/2)a - y]} + \frac{\rho_b e^2}{\mu} (N_\Lambda - N_b) \\
&= -\frac{\rho_b e^2}{\mu} \sum_{k=0}^{2N} e^{-\mu k a} \int_{-a/2}^{a/2} dy\, c_\Lambda(y) e^{-\mu(a/2 - y)} + \frac{e^2 \rho_b}{\mu} (N_\Lambda - N_b) \\
&= -\frac{e_b e^2}{\mu} e^{-\mu a/2} \left[\sum_{k=0}^{2N} e^{-\mu k a}\right] \int_{-a/2}^{a/2} dy\, c_\Lambda(y) \operatorname{ch}(\mu y) + \frac{e^2 \rho_b}{\mu} (N_\Lambda - N_b)
\end{aligned}$$

Therefore, if $N_\Lambda - N_b \to 0$ as $N \to \infty$, we obtain

$$[p^{(k)} - p^{(m)}]_{\text{bulk}} = -\frac{\rho_b e^2}{\mu} \frac{e^{-\mu a/2}}{1 - e^{-\mu a}} \int_{-a/2}^{a/2} dy\, c_\infty(y) \operatorname{ch}(\mu y)$$

which is identical with Eq. (35).

(ii) On the other hand, Eq. (34) yields

$$p_\Lambda^{(\mathrm{m})} - p_\Lambda^{(\theta)} = \frac{\rho_b}{L} \int_{-L}^{L} dy\, c_\Lambda(y) \frac{e^2}{\mu} (e^{-\mu L} - e^{-\mu(L-y)}) + \rho_b(N_\Lambda - N_b) \frac{e^2}{\mu} \left(\frac{1 - e^{-\mu L}}{\mu L} - 1 \right)$$

Therefore, if $N_\Lambda - N_b \to 0$ as $N \to \infty$, we obtain

$$[p^{(\mathrm{m})} - p^{(\theta)}]_{\mathrm{bulk}} = 0$$

(iii) Finally, following the proof of Property 4(a), we have

$$\begin{aligned} p_\Lambda^{(\mathrm{k})} - p_\Lambda^{(\theta)} &= \frac{\rho_b}{2L} \int_{-L}^{L} dy\, c_\Lambda(y) \int_{-L}^{L} dx\, xF(x-y) \\ &= \frac{\rho_b}{2L} \int_{-L}^{L} dy\, c_\Lambda(y) \int_{-L}^{L} dx\, (x-y)F(x-y) \\ &\quad + \frac{\rho_b}{2L} \sum_{n=-N}^{N} \int_{-a/2}^{a/2} dy\, c_\Lambda(y) y \int_{-L}^{L} dx\, F(x-y-na) \\ &\quad + \frac{\rho_b}{2L} \sum_{n=-N}^{N} na \int_{-a/2}^{a/2} dy\, c_\Lambda(y) \int_{-L}^{L} dx\, F(x-y-na) \end{aligned}$$

The contribution to $\Delta p_{\mathrm{bulk}}^{(\mathrm{k})}$ coming from the first term is given by

$$2\rho_b \frac{1}{a} \int_{-a/2}^{a/2} dy\, c_\infty(y) \int_0^\infty dx\, xF(x) = \frac{2\rho_b e^2}{\mu^2} (\rho - \rho_b)$$

The contribution of the second term is zero by invariance under inversion.

Finally, the last term gives

$$\begin{aligned} &\rho_b \int_{-a/2}^{a/2} dy\, c_\infty(y) \lim_{N\to\infty} \frac{1}{(2N+1)a} \\ &\quad \times \sum_{n=-N}^{N} \sum_{r=-N}^{N} \frac{(n-r)a}{2} \int_{-a/2}^{a/2} dx\, F[x - y - (n-r)a] \\ &= \rho_b \int_{-a/2}^{a/2} dy\, c_\infty(y) \sum_{k=1}^{\infty} k \int_{-a/2}^{a/2} dx\, F(x-y-ka) \\ &= e^2 \rho_b \int_{-a/2}^{a/2} dy\, c_\infty(y) \sum_{k=1}^{\infty} k e^{-\mu(ka+y)} \frac{e^{\mu a/2} - e^{-\mu a/2}}{-\mu} \\ &= -\frac{e^2 \rho_b}{\mu} e^{\mu a/2} (1 - e^{-\mu a}) \frac{e^{-\mu a}}{(1 - e^{-\mu a})^2} \int_{-a/2}^{a/2} dy\, c_\infty(y)\, \mathrm{ch}(\mu y) \end{aligned}$$

which is the same expression as Eq. (35).

Therefore

$$\Delta p_{\text{bulk}}^{(\text{k})} = -\frac{e^2 \rho_b}{2\mu \operatorname{sh}(\mu a/2)} \int_{-a/2}^{a/2} dy\, c_\infty(y) \operatorname{ch}(\mu y) + \frac{2\rho_b e^2}{\mu^2} (\rho - \rho_b)$$

This expression is well defined even for systems which are not neutral; on the other hand, for systems which are not neutral, $\Delta p_{\text{bulk}}^{(\text{m})}$ diverges as the length of the system.

6.1.3. Pseudo-Coulomb Potential: $\phi(x) = -e^2 \ln|x|$. Using Eq. (14) and the general results of Section 5, we have for *neutral* systems

$$p^{(\theta)} = \rho kT - \tfrac{1}{2} e^2 \rho, \qquad [p^{(\text{m})} - p^{(\theta)}]_{\text{bulk}} = 0$$

and

$$[p^{(\text{k})} - p^{(\theta)}]_{\text{bulk}} = -\tfrac{1}{2}\rho_b \sum_{n \neq 0} (-1)^n \tilde{\phi}\left(\frac{2\pi}{a} n\right) \tilde{\rho}_\infty^{(1)}\left(\frac{2\pi}{a} n\right)$$

with $\tilde{\phi}(k) = \pi e^2/|k|$, $k \neq 0$.

Therefore

$$\Delta p_{\text{bulk}}^{(\text{k})} = -\frac{\rho_b e^2}{a} \frac{\pi}{2} \int_{-a/2}^{a/2} dy\, c_\infty(y) \sum_{n=1}^{\infty} \frac{(-1)^n}{(2\pi/a)n} 2 \cos \frac{2\pi n y}{a}$$

and

$$\sum_{n=1}^{\infty} \frac{(-1)^n}{(2\pi/a)n} \cos\left(\frac{2\pi}{a} n y\right) = -\frac{a}{2\pi} \ln\left(2 \cos \frac{\pi y}{a}\right)$$

yields

$$\Delta p_{\text{bulk}}^{(\text{k})} = \rho_b \frac{e^2}{2} \int_{-a/2}^{a/2} dy\, c_\infty(y) \ln \cos \frac{\pi y}{a}$$

Moreover,

$$\begin{aligned}
\Delta p_{\text{surf}}^{(\text{m})} &= -\lim_{L\to\infty} \frac{e^2 \rho_b}{L} \int_{-L}^{0} dy\, [\rho_{(-L,+L)}^{(1)}(y) - \rho_\infty^{(1)}(y)] \int_0^y dx \ln \frac{L+x}{L-x} \\
&= -\lim_{L\to\infty} \frac{e^2 \rho_b}{L} \int_{-L}^{0} dy\, [\rho_{(-L,+L)}^{(1)}(y) - \rho_\infty^{(1)}(y)] \\
&\quad \times [(L-y)\ln(L-y) + (L+y)\ln(L+y) - 2L \ln L] \\
&= -\lim_{L\to\infty} e^2 \rho_b \int_0^L dy\, \delta\rho_w(y) \left[\frac{y \ln y}{L} + 2\left(1 - \frac{y}{2L}\right) \ln\left(1 - \frac{y}{2L}\right)\right]
\end{aligned}$$

Therefore, assuming that $\int_0^\infty dy\, y|\delta\rho_w(y)| < \infty$, we obtain

$$\Delta p_{\text{surf}}^{(\text{m})} = 0$$

On the other hand,

$$\Delta p_{\text{surf}}^{(\mathrm{k})} = \lim_{L\to\infty} e^2\rho_b \int_{-L}^{0} dy\, [\rho^{(1)}_{(-L,+L)}(y) - \rho^{(1)}_{\infty}(y)] \ln[(L-y)(L+y)]$$

$$= \lim_{L\to\infty} e^2\rho_b \int_{0}^{L} dy\, \delta\rho_w(y)\left[\ln y + \ln\left(1 - \frac{y}{2L}\right)\right]$$

i.e.,

$$\Delta p_{\text{surf}}^{(\mathrm{k})} = e^2\rho_b \int_0^\infty dy\, \delta\rho_w(y) \ln y$$

In conclusion,

$$p^{(\theta)} = \rho_b kT - \tfrac{1}{2}e^2\rho_b$$

$$p^{(\mathrm{m})} = p^{(\theta)}$$

$$p^{(\mathrm{k})} = \rho_b kT - \tfrac{1}{2}e^2\rho_b + \tfrac{1}{2}e^2\rho_b$$

$$\times \int_{-a/2}^{a/2} dy\, c_\infty(y) \ln[\cos(\pi y/a)] + e^2\rho_b \int_0^\infty dy\, \delta\rho_w(y) \ln y$$

Let us note that for the state at $T = 0$ given by

$$c_\infty(y) = \sum_n \delta(y - na) - \rho_b, \qquad a = \rho_b^{-1}$$

we have

$$[p^{(\mathrm{k})} - p^{(\theta)}]_{\text{bulk}}(T = 0) = \tfrac{1}{2}e^2\rho_b \ln 2 > 0$$

i.e.,

$$p^{(\mathrm{k})}(T = 0) = e^2\rho_b(-\tfrac{1}{2} + \tfrac{1}{2}\ln 2) + \Delta p_{\text{surf}}^{(\mathrm{k})} = e^2\rho_b(-0.158) + \Delta p_{\text{surf}}^{(\mathrm{k})}$$

which shows that in this case $\Delta p_{\text{surf}}^{(\mathrm{k})}$ is positive at $T = 0$, while for one-dimensional Coulomb interactions we obtained $\Delta p_{\text{surf}}^{(\mathrm{k})}(T = 0) = 0$.

Remark. The result $p^{(\mathrm{m})} = p^{(\theta)}$ extends the property established in Section 4.1 for $\gamma > \nu + 1$ to the case $\gamma = \nu$.

6.2. ν-Dimensional Systems

6.2.1. Coulomb Systems. For RE states with *cubic symmetry* and *cubic cells* Δ_0

$$[p^{(\mathrm{k})} - p^{(\mathrm{m})}]_{\text{bulk}} = 0, \qquad [p^{(\mathrm{k})} - p^{(\theta)}]_{\text{bulk}} = -\frac{\rho_b e^2}{2}\frac{\omega_\nu}{\nu}\frac{1}{|\Delta_0|}\int_{\Delta_0} dy\, c_\infty(y)|\mathbf{y}|^2$$

Let us consider the special case $T = 0$ and let us assume that the state was obtained taking the limit $V_\lambda \to \infty$ by means of rectangular parallelepipeds with sides of length $(2N_j + 1)a$, $j = 1,\ldots, \nu$ ($|\Delta_0| = a^3$).

(i) $\nu = 2$, simple cubic lattice, $\rho_b a^2 = 1$. For the RE state $c_\infty(x) = \sum_t \delta(x - t) - \rho_b$, we have

$$p^{(\theta)}(T = 0) = -e^2\rho_b/4, \qquad \Delta p^{(k)}_{\text{bulk}}(T = 0) = (e^2\rho_b/12)\pi > 0$$

$$p^{(k)}(T = 0) = 0 = e^2\rho_b(-\tfrac{1}{4} + \tfrac{1}{12}\pi) + \Delta p^{(k)}_{\text{surf}}$$

i.e.,

$$\Delta p^{(k)}_{\text{surf}}(T = 0) = -0.12e^2\rho_b = 0.05p^{(\theta)}(T = 0) < 0$$

(ii) $\nu = 3$, simple cubic lattice, $\rho_b a^3 = 1$. For the RE state $c_\infty(x) = \sum_t \delta(x - t) - \rho_b$, we have

$$\Delta p^{(k)}_{\text{bulk}}(T = 0) = e^2\rho_b^{4/3}\pi/6 > 0$$

Using the well-known inequality[6] $p^{(\theta)}(T) > -\frac{3}{10}e^2\rho_b^{4/3}(\frac{4}{3}\pi)^{1/2}$,

$$p^{(k)}(T = 0) = 0 = p^{(\theta)} + \Delta p^{(k)}_{\text{bulk}} + \Delta p^{(k)}_{\text{surf}} > e^2\rho_b^{4/3}[\tfrac{1}{6}\pi - \tfrac{3}{10}(\tfrac{4}{3}\pi)^{1/2}] + \Delta p^{(k)}_{\text{surf}}$$

i.e.,

$$\Delta p^{(k)}_{\text{surf}}(T = 0) < -0.04e^2\rho_b^{4/3} < 0$$

In fact, using a numerical estimate for $p^{(\theta)}(T = 0)$,[16] we have

$$\Delta p^{(k)}_{\text{surf}}(T = 0) \approx -0.06e^2\rho_b^{4/3} \approx 0.07p^{(\theta)}(T = 0)$$

(iii) $\nu = 3$, bcc lattice, $\rho_b a^3 = 2$. For the RE state

$$c_\infty(x) = \sum_t \left[\delta(x - t) + \frac{1}{8}\sum_{i=1}^{8} \delta(x - b_i - t)\right] - \rho_b$$

we obtain

$$\Delta p^{(k)}_{\text{bulk}} = e^2\rho_b^{4/3}\tfrac{1}{6}\pi(2)^{2/3}(1 - \tfrac{3}{2}) < 0$$

and using a numerical estimate for $p^{(\theta)}(T = 0)$,[16] we have

$$\Delta p^{(k)}_{\text{surf}} = e^2\rho_b^{4/3}[\tfrac{1}{12}\pi(2)^{2/3} + 0.298(\tfrac{4}{3}\pi)^{1/2}] = -1.68p^{(\theta)}(T = 0)$$

which shows that $\Delta p^{(k)}_{\text{surf}}(T = 0)$ is positive and is quite important.

6.2.2. Two-Dimensional Pseudo-Coulomb Systems: $\phi(x) = e^2/|x|$, $\tilde{\phi}(k) = 2\pi e^2/|k|$. Equation (14) and the results of Section 5 give for Δ_0 a parallelepiped $\{\Delta_1\mathbf{a}^{(1)}, \Delta_2\mathbf{a}^{(2)}\}$, $\mathbf{a}^{(1)}\mathbf{a}^{(2)} = \cos\varphi$,

$$p^{(\theta)} = \rho kT + u, \qquad u = \lim_{\Lambda\to\infty} \frac{\langle u_\Lambda\rangle}{|\Lambda|}, \qquad [p^{(m)} - p^{(\theta)}]_{\text{bulk}} = 0$$

$$
\begin{aligned}
[p^{(\mathrm{k})} - p^{(\theta)}]_{\mathrm{bulk}} &= -\frac{\rho_b 2\pi e^2}{4} \sum_{j=1}^{2} \sum_{n_j \neq 0} \frac{(-1)^{n_j} \sin\varphi}{(2\pi/\Delta_j)|n_j|} \tilde{\rho}_\infty(n_j \mathbf{Q}^{(j)}) \\
&= \frac{\rho_b e^2}{2} \sin\varphi \frac{1}{|\Delta_0|} \int_{\Delta_0} dy\, c_\infty(y) \sum_{j=1}^{2} \Delta_j \ln\left[\cos\left(\frac{\pi}{\Delta_j} \mathbf{y}\mathbf{a}^{(j)}\right)\right]
\end{aligned}
$$

Let us consider the RE state on the *triangular lattice* at $T = 0$.

(i) Assuming the state was obtained taking the limit $V_\lambda \to \infty$ by means of the union of cells Δ_0 such that

$$
\Delta_1 = \Delta_2 = q, \qquad \varphi = 60^\circ, \qquad \tfrac{1}{2}\rho_b a^2 \sqrt{3} = 1
$$

then

$$
c_\infty(x) = \sum_t \delta(x - t) - \rho_b, \qquad \Delta p_{\mathrm{bulk}}^{(\mathrm{k})}(T = 0) = \rho_b^{3/2} e^2 \ln 2\, (\tfrac{1}{2}\sqrt{3})^{1/2} > 0
$$

and

$$
p_{\mathrm{bulk}}^{(\mathrm{k})}(T = 0) = 0 = \tfrac{1}{2}u + \rho_b^{3/2} e^2 \ln 2\, (\tfrac{1}{2}\sqrt{3})^{1/2} + \Delta p_{\mathrm{surf}}^{(\mathrm{k})}
$$

Using the numerical estimate for u,[3] we obtain

$$
\Delta p_{\mathrm{surf}}^{(\mathrm{k})}(T = 0) \approx 0.24 e^2 \rho_b^{3/2} \approx 0.25 p^{(\theta)}(T = 0) > 0
$$

(ii) On the other hand, if the state was obtained by means of V_λ that are the union of rectangular cells Δ_0,

$$
\Delta_1 = a, \qquad \Delta_2 = \sqrt{3}\, a, \qquad \varphi = 90^\circ, \qquad \rho_b a^2 \sqrt{3} = 2
$$

then

$$
c_\infty(x) = \sum_t [\delta(x + z - t) - \delta(x - z - t)] - \rho_b, \qquad z = \left(\frac{a}{4}, \frac{\sqrt{3}}{4} a\right)
$$

which yields

$$
\tilde{\rho}_\infty(n_j \mathbf{Q}^{(j)}) = \frac{2}{|\Delta_0|} \cos\left(\frac{2\pi}{\Delta_j} n_j z_j\right) = \frac{2}{a^3\sqrt{3}} \cos\left(\frac{\pi}{2} n_j\right)
$$

Thus

$$
\Delta p_{\mathrm{bulk}}^{(\mathrm{k})}(T = 0) = \rho_b^{3/2} e^2 \ln 2 \left(\frac{\sqrt{3}}{2}\right)^{1/2} \left(\frac{1 + \sqrt{3}}{2\sqrt{3}}\right)
$$

$$
\Delta p_{\mathrm{surf}}^{(\mathrm{k})}(T = 0) \approx 0.36 \rho_b^{3/2} e^2
$$

which shows that the *surface contribution is 30% larger if the limit is reached by means of rectangles rather than with parallelepipeds* (although the total pressure is shape independent, since it is zero).

Table I

Range of force	$\Delta p^{(\mathrm{m})} = p^{(\mathrm{m})} - p^{(\theta)} = -(u_{pb} + 2u_{bb})$	$\Delta p^{(\mathrm{k})} = p^{(\mathrm{k})} - p^{(\theta)}$
$\gamma > \nu + 1$	$\Delta p^{(\mathrm{m})} = 0$	$\left\{ \Delta p^{(\mathrm{k})}_{\mathrm{bulk}} = \frac{1}{2} \frac{\rho_b}{\nu} \int_{\Delta_0} dx\, \mathbf{x} \mathbf{E}_\rho(x) \right.$
$\gamma > \nu - 1$	$\Delta p^{(\mathrm{m})}_{\mathrm{bulk}} = 0$	
$\gamma = \nu - 1$: Coulomb without quadrupole moment	$\Delta p^{(\mathrm{m})}_{\mathrm{bulk}} = \Delta p^{(\mathrm{k})}_{\mathrm{bulk}}$	$\Delta p^{(\mathrm{k})}_{\mathrm{bulk}} = \frac{1}{2} \frac{\rho_b}{\nu} \int_{\Delta_0} dx\, \mathbf{x} \mathbf{E}_\rho(x) + \frac{1}{2} I$
With cubic symmetry	i.e., $[p^{(\mathrm{m})} - p^{(\mathrm{k})}]_{\mathrm{bulk}} = 0$	$\Delta p^{(\mathrm{k})}_{\mathrm{bulk}} = \frac{\rho^b}{\nu} \int_{\Delta_0} dx\, \mathbf{x} \mathbf{E}_\rho(x) = c \int_{\Delta_0} dx\, \mathbf{x}^2 c_\infty(\mathbf{x})$
With spherical domains	$p^{(\mathrm{m})} - \mathrm{p}^{(\mathrm{k})} = 0$	—

7. SUMMARY

For a force with asymptotic behavior $|F(x)| \sim |x|^{-\gamma}$ and any periodic RE state which is neutral and invariant under inversion, we have the results shown in Table I.

Conjectures:

1. $p^{(\mathrm{m})} = p^{(\theta)}$ if $\gamma > \nu - 1$.
2. $p^{(\mathrm{k})}(T) \to_{T \to 0} 0$.
3. $\Delta p^{(\mathrm{k})}_{\mathrm{bulk}}(T)$ is decreasing with increasing temperature.

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