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« Virial » pressure of the classical one-component plasma (*)

M. Navet, E. Jamin and M. R. Feix

CRPE/CNRS, 45045 Orléans Cedex, France

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Résumé. — En appliquant le théorème du viriel à un système coulombien de N particules neutralisées par un fond continu, on définit très naturellement une pression cinétique « virielle » du système de particules, qui est une quantité essentiellement positive. Le lien est fait, dans un cas particulier, avec la définition thermodynamique de la pression utilisée dans les travaux précédents, qui a l'inconvénient de donner des valeurs négatives quand le paramètre de couplage est suffisamment grand.

Abstract. — Application of the virial theorem to a Coulomb system of N particles neutralized by a continuous background, leads quite naturally to the definition of a « virial » kinetic pressure for the system of particles, which is fundamentally positive. This definition is related, in a particular case, to the thermodynamic one used in previous works, which has the drawback to give negative values for sufficiently strong coupling.

1. The system : definition and related problems. — We consider a finite classical system of N particles of charge $-e$, imbedded in a homogeneous, non moving, neutralizing background of charge density $\rho_B e$. Particles interact between each other and with the background according to Coulomb's law. We emphasize that this one-component plasma (OCP) is composed of the sole N particles, the background being considered as extraneous.

Such a system has been considered in a classical paper by Brush, Sahlin and Teller (BST) [1], an extensive work by Hansen [2], a theoretical paper by Lieb and Narnhofer [3] (establishing the existence of the thermodynamic limit) and many others.

A somewhat strange point in these previous works is that the system is found to have a negative pressure for values of the coupling parameter

$$\Gamma = e^2(4\pi\rho_B/3)^{1/3}(kT)^{-1}$$

greater than about 4. This anomaly is usually justified by two types of arguments :

1. — The negative pressure of the OCP is, when considering a real system with two or more components, over-compensated by the positive pressure of the real background. In adopting this point of view,

one loses however the intrinsic self-consistency of the OCP model, since some of its essential features (like stability) depend on the physical properties of the background — which we precisely want to ignore. Moreover it seems to us that, according to kinetic theory, a pressure, even a partial one, i.e. the pressure exerted by one component in presence of the others, should always correspond to the mean exchange of momentum by units of time and surface with a limiting wall, and thus be positive, at least for systems in equilibrium [4]. A recent experiment [5] with electrons confined in a plane gives consistency to our point of view. The stable system of electrons realized in this experiment, in which the background is made up by a metallic anode, should indeed exhibit a well defined pressure, measurable in principle and thus positive. The usual thermodynamic definition of the pressure in this two-dimensional case, however, also predicts negative values for strong enough coupling.

2. — The negative pressure of the OCP is a characteristic anomaly of a canonical theory of the system — for which the grand-canonical ensemble is not equivalent to the canonical ensemble ([3]). Actually the definition of the pressure in the canonical theory by means of a derivative of the free energy *versus* the volume raises a lot of difficulties, due to the existence of a background and the interpretation of its compression — even if those difficulties may not

(*) This is a revised version of a note submitted to the C.R.A.S. (Paris).

always appear clearly in the usual case of an infinite periodic system.

In the work which is briefly reported here we show that it is possible to define, using the simplest and oldest concepts of kinetic theory, an essentially positive pressure for the OCP, by considering a finite system with free boundary conditions and taking into account all effects due to the presence of this boundary.

The problem of the existence of a thermodynamic limit for this pressure is considered in a forthcoming paper by Choquard *et al.* [6].

In the particular case of a spherical geometry we have been able :

1. — To express the pressure as a time average of very simple functions of the coordinates of the particles.

2. — To obtain in a Monte Carlo canonical simulation the approximate values of the pressure for $\Gamma \leq 10$ and to verify that it is equal to $\rho_w kT$, where ρ_w is the density of the OCP at the wall.

3. — To show that our expression of the pressure can be obtained in a Helmholtz formalism provided one modifies the usual hypothesis on the way the system is compressed.

4. — To check that the results of our simulations on a finite system are in good agreement with those of previous works and thus that our result on the pressure is based on a different interpretation of perfectly compatible measures.

2. The equation of state. — The virial theorem (see e.g. [7]) is written :

$$2 \langle K \rangle = - \left\langle \sum_i \mathbf{F}_i \cdot \mathbf{r}_i \right\rangle \quad (1)$$

where the angular brackets indicate the time average for a system in equilibrium. K is the kinetic energy (in our case $3 NkT/2$), \mathbf{r}_i the position vector of the i th particle and \mathbf{F}_i the total force acting on this particle; which may be decomposed in $\sum_{j \neq i} \mathbf{F}_{ji}$ (force due to the other particles), \mathbf{F}_{bi} (force due to the background) and \mathbf{F}_{pi} (force exerted by the wall on the colliding particle).

For our Coulomb system the three contributions to the virial read :

$$\begin{aligned} a) \quad \left\langle \sum_i \sum_{j \neq i} \mathbf{F}_{ji} \cdot \mathbf{r}_i \right\rangle &= \left\langle \sum_i \sum_{j < i} \mathbf{F}_{ji} \cdot (\mathbf{r}_i - \mathbf{r}_j) \right\rangle = \\ &= e^2 \left\langle \sum_i \sum_{j < i} r_{ij}^{-1} \right\rangle = \langle U_{pp} \rangle \quad (2) \end{aligned}$$

where $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ and U_{pp} is the potential energy of the particle-particle interactions.

b)

$$\left\langle \sum_i \mathbf{F}_{bi} \cdot \mathbf{r}_i \right\rangle = e^2 \rho_B \left\langle \sum_i \iiint_V \frac{\mathbf{r}_i \cdot (\mathbf{r} - \mathbf{r}_i) d^3r}{|\mathbf{r} - \mathbf{r}_i|^3} \right\rangle \quad (3)$$

which depends, of course, on the shape of the container, is not equal in general to the average of the potential energy of the particle-background interactions

$$U_{pb} = - e^2 \rho_B \sum_i \iiint_V \frac{d^3r}{|\mathbf{r} - \mathbf{r}_i|}. \quad (4)$$

c)

$$\left\langle \sum_i \mathbf{F}_{pi} \cdot \mathbf{r}_i \right\rangle = \left\langle \iint_S \left\{ \frac{\delta^2 mv}{\delta t \cdot \delta S} (r) \right\} \mathbf{r} \cdot d\mathbf{S} \right\rangle. \quad (5)$$

There is no *a priori* reason that the term

$$\langle \delta^2 mv / \delta t \cdot \delta S \rangle,$$

the average transfer of momentum from the wall to the colliding particles at the point \mathbf{r} of the surface, i.e. the local pressure, should in general be uniform on the surface. But in all cases it is a positive quantity provided the wall is purely passive and perfectly reflecting.

In the case of uniformity of the local pressure, (5) reads :

$$\left\langle \sum_i \mathbf{F}_{pi} \cdot \mathbf{r}_i \right\rangle = - 3 PV \quad (6)$$

where P is the kinetic pressure and V the volume of the container.

In the case of non-uniformity of the local pressure, (6) may be considered as the « virial » definition of the pressure.

The equation of state is thus written :

$$\frac{PV}{NkT} = 1 + \left\{ \langle U_{pp} \rangle + \left\langle \sum_i \mathbf{F}_{bi} \cdot \mathbf{r}_i \right\rangle \right\} / 3 NkT. \quad (7)$$

At this point of the analysis it is important to notice that the usual form of the virial theorem

$$PV/NkT = 1 + \langle U \rangle / 3 NkT \quad (8)$$

where U is the total potential energy

$$(U_{pp} + U_{pb} + \text{constant}),$$

is not identical to (7). This expression (8) strictly holds only for a system of particles ($U = U_{pp}$) and does not in general take correctly into account the particle-background interactions, at least in the finite case.

Let us now specialize to a particular geometry where the forces and potentials are easily expressed :

the container is a sphere of radius R . Of course (6) is valid by symmetry, and (3) and (4) become respectively, using Gauss's theorem and without any approximation :

$$\begin{aligned} \left\langle \sum_i \mathbf{F}_{bi} \cdot \mathbf{r}_i \right\rangle &= -\frac{4}{3} \pi \rho_B e^2 \left\langle \sum_i r_i^2 \right\rangle = \\ &= - (N + s) e^2 R^{-3} \left\langle \sum_i r_i^2 \right\rangle \quad (9) \end{aligned}$$

where $(N + s) e$ is the total charge of the background, allowance being made for an excess charge s , and

$$U_{pb} = \frac{(N + s) e^2}{2 R^3} \sum_i r_i^2 - \frac{3 N(N + s) e^2}{2 R}. \quad (10)$$

Notice that in this particular case there appears a simple relation between U_{pb} and the corresponding term of the virial, but with the unexpected factor -2 , so that the equation of state is written :

$$\frac{PV}{NkT} = 1 + \{ \langle U_{pp} \rangle - 2 \langle U_{pb} \rangle - 3 N(N + s) e^2 R^{-1} \} / 3 NkT. \quad (11)$$

We stress that the analysis above is completely independent of any hypothesis on the properties (e.g. rigidity or compressibility) of the background. The « virial » kinetic pressure defined by (11) may hence be considered as the partial pressure of the sole particles. It has been derived only from the forces applied on the system, and is here expressed in terms of the potential energies introduced in fine, only to compare it more easily to the usual expression (8). It is of course independent of the arbitrary constants allowed in the definition of the potential energies.

As U_{pp} and U_{pb} are not extensive quantities, we may « normalize » them by introducing, for example, their values at infinite temperature (ideal fluid limit), in which case the equation is written :

$$\frac{PV}{NkT} = 1 + \{ \langle U_{pp} \rangle - U_{pp}^\infty - 2(\langle U_{pb} \rangle - U_{pb}^\infty) \} / 3 NkT - e^2(s + 1) / 5 RkT \quad (12)$$

where

$$U_{pp}^\infty = 3 e^2 N(N - 1) / 5 R$$

and

$$U_{pb}^\infty = - 6 e^2 N(N + s) / 5 R \quad (13)$$

are calculated in the limit where the one-particle distribution function is constant in the sphere and no correlations occur between the positions of two particles. Another « normalization » would be to introduce the values of the energies at zero temperature, but this would require the knowledge of the fundamental equilibrium state, known only in one dimension [8].

It is worthwhile to notice that now the last term of (12) is less than intensive and thus disappears in the thermodynamic limit, provided the absolute value of the excess charge s increases more slowly than $N^{1/3}$, and also that it is identically zero for $s = -1$. This quite remarkable case, as already noticed by Baxter [9] in one dimension, corresponds to a situation where every particle, considered as a test-particle interacts with a vanishing total external charge.

3. Numerical simulation. — We have used the Monte Carlo method of Metropolis *et al.* [10], which generates a Markov chain simulating the canonical ensemble, also used by BST and by Hansen. The pressure is obtained from (11), by replacing time averages by ensemble averages. As in our case

we do not benefit from the periodicity of the basic cubic cell, whose homogeneous coverage is easily realized by the unweighted Markov chain, we have adopted, after careful testing, a slightly modified scheme to properly take the wall effects into account : each time the Markov chain leads a particle outside our spherical vessel, the previous state is recounted, and the chain is restarted from this state.

The initial state is taken either at random or with a crystalline structure. The equilibrium state has been checked to be attained in both cases and for all values of the coupling parameter considered, after some 10^4 steps in the Markov chain. Each trial consists in an average over the 10^5 states following this relaxation ; in this way we obtain a reasonable convergence for not excessively large values of the coupling parameter.

The preliminary results shown in the figure were obtained for a neutral ($s = 0$) system of 256 particles whose centre of gravity is constrained to stay fixed at the centre of the sphere. This (not very important) constraint is imposed by choosing an initial state which satisfies it and by generating each successive state by moving two randomly chosen particles with displacements $\Delta \mathbf{r}$ and $-\Delta \mathbf{r}$. Our method, unless radically modified, does not allow to obtain precise values of the « virial » pressure for large values of Γ : indeed, since the numerator of (12) includes two large terms ($\langle U_{pp} - U_{pp}^\infty \rangle$ and $2 \langle U_{pb} - U_{pb}^\infty \rangle$) with correspondingly large absolute errors, the rela-

tive error on their difference, which tends to zero with decreasing temperature, becomes quickly inordinately large. Actually it seems that this feature is a characteristic of the physics of the system and not of the simulation. In a « molecular dynamics » simulation the collisions against the wall would become, at these low temperatures, extremely rare and thus the determination of the kinetic pressure would be very rough.

The fact that the error bars, for high values of Γ , could become compatible with a negative estimation of the pressure should not induce any confusion : the pressure defined by (11) is by definition positive. If one would obtain a negative « measure » of P for some value of Γ , one should suspect the simulation process (e.g. the legitimacy of replacing the time average by an approximate canonical average) and not the definition of P .

Of course the N dependence of our results has been carefully checked in a series of experiments with smaller values of N , which cannot be reported here. It seems that for $N = 256$ the thermodynamic limit is approached with a quite good accuracy (see below).

These initial experiments thus clearly show that the « virial » kinetic pressure, which in the high temperature limit approaches of course the ideal gas law, tends to zero with and faster than the temperature. An identical result has been found, in the framework of a broader analysis which will be reported later, for the analogous cases in one and two dimensions.

The main difference between our approach and the one followed in [1] [2] is that, while these authors use a modified Ewald potential to minimize wall effects we have chosen to treat these effects exactly, as we think that the departure of the pressure at the wall from the perfect gas one enters through the

modifications of the physical quantities (principally the density) as consequence of the interactions. Here we adopt an « operational » point of view for the measure of the pressure.

To illustrate this idea, we have measured, during the previous simulation, the average particles density on the wall of the sphere. As could be expected in a experimental simulation of the canonical ensemble, this wall density, normalized to the average density in the full sphere is equal, within the experimental error bars, to the pressure we have defined in (11), normalized to the ideal gas pressure.

Finally it should be emphasized that the computations involved here are much simpler than in [1] [2] due to the simplicity of the Coulomb potential compared to the Ewald one. The consequent gain in computer time could be, in some problems, a considerable advantage.

4. Thermodynamic definitions of the pressure. —

Choquard [11] has shown that one can define a « mechanical » pressure P_M of the Wigner model by differentiating the free energy *versus* the volume, keeping constant not the total charge of the particles + background system (as in the usual definition), but the background density, and he has given a rather general expression for the difference between these two definitions. This idea can be applied to our system.

In the classical thermodynamic definition

$$P/kT = (\partial \text{Log } Z/\partial V)_{N,T} \quad (14)$$

we express the partition function Z by means of the integration variables $\mathbf{x}_i = \mathbf{r}_i/R$ which reduce the volume to the sphere of unit radius (S)

$$Z = R^{3N} \int_S \cdots \int_S \exp \{ - (U_{pp} + U_{pb} + U_{bb})/kT \} d\mathbf{x}_1 \dots d\mathbf{x}_N . \quad (15)$$

Following Choquard we have explicitly included the self-energy of the background U_{bb} . The derivative of Z is written

$$\frac{\partial Z}{\partial V} = \frac{N}{V} Z - \frac{R^{3N+1}}{3VkT} \int_S \cdots \int_S \exp \{ - (U_{pp} + U_{pb} + U_{bb})/kT \} \frac{\partial}{\partial R} (U_{pp} + U_{pb} + U_{bb}) d\mathbf{x}_1 \dots d\mathbf{x}_N . \quad (16)$$

Let us now express the energies as functions of the reduced variables, introducing explicitly R_B , the radius of the sphere which contains the background [12]. In the infinitesimal change of volume used to compute the pressure, R_B will either remain equal to R , the radius of the sphere containing the particles (usual definition of the thermal pressure P_θ), or be kept constant (definition of the « mechanical » pressure P_M).

$$\begin{aligned} U_{pp} &= e^2 R^{-1} \sum_i \sum_{j<i} x_{ij}^{-1} \\ U_{pb} &= 2 \pi e^2 \rho_B \sum_i R^2 x_i^2/3 - 2 \pi N e^2 \rho_B R_B^2 \\ U_{bb} &= (4 \pi e \rho_B)^2 R_B^5/15 . \end{aligned} \quad (17)$$

In the case $\partial R_B/\partial R = 1$ we get

$$\partial U/\partial R = - U/R \quad (18)$$

so that

$$P_\theta V/NkT = 1 + \langle U_{pp} + U_{pb} + U_{bb} \rangle / 3 NkT \quad (19)$$

but in the case $\partial R_B / \partial R = 0$

$$\partial U / \partial R = - \left(U_{pp} - 2 U_{pb} - 5 \frac{N}{\frac{4}{3} \pi R_B^3 \rho_B} U_{bb} \right) / R \quad (20)$$

and

$$P_M V/NkT = 1 + \left\langle U_{pp} - 2 U_{pb} - 5 \frac{N}{N+s} U_{bb} \right\rangle / 3 NkT. \quad (21)$$

Equations (19) and (21) are thus respectively identical to (8) and (11), the averages being now taken over the canonical ensemble.

From this analysis it follows that :

1. — In the case of spherical symmetry the « virial » kinetic pressure is identical to the « mechanical » pressure defined in [11] (the generalization to other geometries is not trivial).

2. — Choquard's formula is recovered in this particular case if one assumes the system neutral ($s = 0$)

$$\Delta P = P_M - P_\theta = - \langle U_{pb} + 2 U_{bb} \rangle / V. \quad (22)$$

3. — If one wants to define, using a Helmholtz formalism, a measurable pressure, it is necessary (at least in our particular case) to keep the density of the background constant rather than to let it vary, as was done in previous works.

To illustrate those differences, we have plotted in the figure, in addition to the results of our Monte Carlo simulation for P_M , the results obtained (in the same runs) for the « thermal » pressure P_θ (19). Comparison of the latter with the values given by the semi-empirical formula of De Witt [13], simultaneously serves as a check on the general validity of the simulation of a finite system. It is indeed seen that our results compare satisfactorily with previously published ones. Though the number of particles is small and the effects of finiteness of our system could be expected to be large (for $N = 256$, 40 % of the particles are, in the fluid

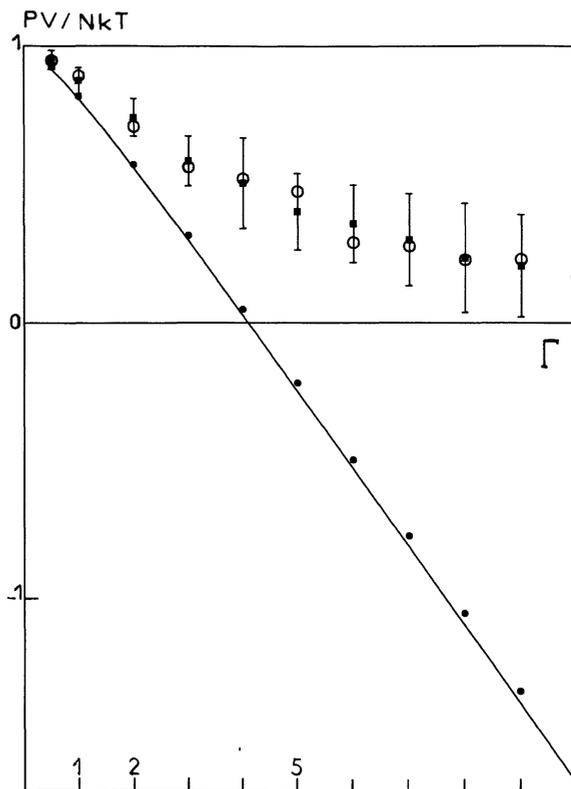


Fig. 1. — The pressure, defined in two ways, is plotted as a function of the coupling parameter.

The squares show the values of the « virial » pressure. Error bars represent $\pm \sigma$, with σ the standard deviation on the average values of 20 series of 5 000 successive states, considered for this sake as independent experiments.

The open circles show the values of the particles density at the wall $\rho(r = R) / \rho_B$.

The continuous curve corresponds to De Witt's semi-empirical interpolation formula. The black circles show the values of the « thermal » pressure, obtained from our simulation with a precision better than the diameter of the circle. The systematic difference with the continuous curve suggests that the thermodynamic limit is not completely reached.

limit, located within a distance $(4 \pi \rho_B / 3)^{-1/3}$ from the wall), our results are remarkably close to the ones calculated in the simulation of the infinite periodic OCP.

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