Eur. Phys. J. D **8**, 145–149 (2000)

THE EUROPEAN PHYSICAL JOURNAL D

EDP Sciences

One-component-plasma: Going beyond Debye-Hückel

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Received 12 April 1999

Abstract. Using field-theoretic methods, we calculate the internal energy for the One-Component Plasma (OCP). We go beyond the recent calculation by Brilliantov [N. Brilliantov, Contrib. Plasma Phys. **38**, 489 (1998)] by including non-Gaussian terms. We show that, for the whole range of the plasma parameter Γ, the effect of the higher-order terms is small and that the final result is not improved relative to the Gaussian theory when compared to simulations.

PACS. 52.25.Kn Thermodynamics of plasmas – 61.20.Gy Theory and models of liquid structure – 05.20.-y Classical statistical mechanics

1 Introduction

In its simplest form, the One-Component Plasma (OCP) consists of a collection of n equally charged point-particles immersed in a neutralizing background that assures global charge neutrality of the system. The OCP is important in several areas of physics as a starting point from where concepts or more refined theories are derived. For instance, in astrophysics both OCP and its quantum-mechanical counterpart (the electron gas or "jellium") are used in the description of degenerate stellar matter (interior of white dwarfs and outer layer of neutron stars) and the interior of massive planets like Jupiter [1]. In condensed matter physics, jellium is often used as a reference state when calculating the electronic structure of solids. When generalized to a Two-Component Plasma (or Primitive Model, if hard-core interactions are taken into account), it can describe electrolytes and electrostatically stabilized colloidal solutions. For reviews see [1,2].

Different analytical techniques were employed in order to understand the OCP. These were, in most cases, based on integral equations (as for instance in [3–5]) or modified Mayer expansions [6,7], *i.e.*, low density expansions that used infinite resummation of diagrams that accounted for the long range character of the Coulomb interaction. Comparison of the theoretical results with experimental data is usually not possible. It is here where simulations (or "computer experiments" [2]) play a particularly important role, by providing a test ground where the suitability and range of validity of the different approaches can be checked. In general, the simulations use Monte Carlo technique [8–11] and yield quantities like the internal energy or the pair distribution function $g(r)$.

In a recent paper [12], a field-theoretic approach was used to treat the OCP. The introduction of a cut-off at small wavelength (large-k) related to the mean distance between particles led to a good agreement, for all values of the plasma parameter Γ, between the calculated internal energy and simulation results. The field-theoretic action used in [12] neglects terms other than the Gaussian ones, *i.e.*, it goes up to second order in the fluctuating field. Here we extend this by including more terms in the action and calculating consistently, using the same cut-off, their contribution to the internal energy. As our main result, we show that the higher order terms do not affect significantly the results obtained with the Gaussian theory derived in [12].

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2 The field-theoretic model

Let us assume a classical system where n positively charged particles are immersed in a neutralizing negatively charged background. The partition function of this system is

$$Z = \frac{1}{n!}\left[\prod_{j=1}^{n}\int\frac{\mathrm{d}\mathbf{r}_j}{\lambda^3}\right]\exp\Bigg\{E_{\mathrm{self}} - \frac{1}{2}\int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}'\hat{\rho}_{\mathrm{c}}(\mathbf{r})v(\mathbf{r}-\mathbf{r}')\hat{\rho}_{\mathrm{c}}(\mathbf{r}')\Bigg\} \tag{1}$$

where λ is an arbitrary constant, $v(\mathbf{r}) = \ell_{\mathrm{B}}/r$ is the bare Coulomb operator and $\ell_{\mathrm{B}} \equiv e^2/4\pi\epsilon k_{\mathrm{B}}T$ is the Bjerrum length (the length at which two elementary charges have an interaction energy equal to the thermal energy). The charge density $\hat{\rho}_{\mathrm{c}}(\mathbf{r})$ is defined as

$$\hat{\rho}_{\mathrm{c}}(\mathbf{r}) = -\rho_- + q\sum_{j=1}^{n}\delta(\mathbf{r}-\mathbf{r}_j), \tag{2}$$

where q is the valency of the particles and ρ_- is the uniform density of the neutralizing background. Global charge neutrality implies that $\rho_- = qn/V$, where V is the volume of the system. The Coulomb self-interaction of the particles is given by

$$E_{\rm self} = \frac{q^2 n}{2} v(0) = \frac{q^2 n}{2} \int \frac{{\rm d}\mathbf{k}}{(2\pi)^3} \frac{4\pi\ell_{\rm B}}{k^2} \,. \tag{3}$$

This corresponds to an infinite shift in the chemical potential, which is unimportant for the thermodynamics of the system. We keep this term for reasons that will become clear later (*cf.* Eq. (10) below).

We can apply the Hubbard-Stratonovich transformation and obtain a partition function that depends on a fluctuating field ϕ. This follows closely what has been done in [13], and so we state here the final expression

$$Z^{\rm ex} \equiv Z{\rm e}^{-S} = \int \frac{D\phi}{Z_0} \exp\biggl\{ E_{\rm self} - \frac{1}{2} \int {\rm d}\mathbf{r}{\rm d}\mathbf{r}' \phi(\mathbf{r}) v_{\rm DH}^{-1}(\mathbf{r}-\mathbf{r}') \phi(\mathbf{r}') + W[\phi] \biggr\}, \tag{4}$$

where $S = -n\ln(c\lambda^3)$ is the ideal entropy of the particles ($c = n/V$) and

$$Z_0 = \int D\phi \exp\biggl\{ -\frac{1}{2} \int {\rm d}\mathbf{r}{\rm d}\mathbf{r}' \phi(\mathbf{r}) v^{-1}(\mathbf{r}-\mathbf{r}') \phi(\mathbf{r}') \biggr\}. \tag{5}$$

We defined $Z^{\rm ex}$ as the "excess partition function", the part of Z that accounts only for the interactions between the particles. The propagator v^{-1} in (5) is the inverse of the bare Coulomb operator and $v_{\rm DH}^{-1}$ in (4) is given by

$$v_{\rm DH}^{-1}(\mathbf{r}) = -\frac{\nabla^2 \delta(\mathbf{r})}{4\pi\ell_{\rm B}} + q^2 c \delta(\mathbf{r}). \tag{6}$$

It is easy to show that this propagator is the inverse of the Debye-Hückel operator $v_{\rm DH}(\mathbf{r}) = \ell_{\rm B}{\rm e}^{\kappa r}/r$, where κ^{-1} is the screening length given by $\kappa^2 = 4\pi\ell_{\rm B} q^2 c$. The $W[\phi]$ is an infinite series in ϕ that contains only non-Gaussian terms. Up to eighth order it reads

$$\begin{aligned} W[\phi] =& \frac{{\rm i}I_3 V}{3!} \overline{\phi^3} + \frac{I_4 V}{4!} \Bigl(\overline{\phi^4} - 3\overline{\phi^2}^2 \Bigr) \\ & - \frac{{\rm i}I_5 V}{5!} \Bigl(\overline{\phi^5} - 10 \overline{\phi^2\phi^3} \Bigr) \\ & - \frac{I_6 V}{6!} \Bigl(\overline{\phi^6} - 15\overline{\phi^4\phi^2} - 10\overline{\phi^3}^2 + 30\overline{\phi^2}^3 \Bigr) \\ & + \frac{{\rm i}I_7 V}{7!} \Bigl(\overline{\phi^7} - 21\overline{\phi^2\phi^5} - 70\overline{\phi^3\phi^4} + 210\overline{\phi^2}^2\overline{\phi^3} \Bigr) \\ & + \frac{I_8 V}{8!} \Bigl(\overline{\phi^8} - 28\overline{\phi^6\phi^2} - 56\overline{\phi^5\phi^3} - 35\overline{\phi^4}^2 \\ & + 420\overline{\phi^4\phi^2}^2 + 560\overline{\phi^2\phi^3}^2 - 630\overline{\phi^2}^4 \Bigr) \end{aligned} \tag{7}$$

with $I_m \equiv q^m c$ and ${\rm i}^2 = -1$; to simplify the notation, we use $\overline{\phi^n} = \int {\rm d}\mathbf{r}\phi^n/V$.

If we define

$$Z_{\rm DH} = \int D\phi \exp\biggl\{ -\frac{1}{2} \int {\rm d}\mathbf{r}{\rm d}\mathbf{r}' \phi(\mathbf{r}) v_{\rm DH}^{-1}(\mathbf{r}-\mathbf{r}') \phi(\mathbf{r}') \biggr\}, \tag{8}$$

then the excess free energy of the OCP is given by

$$\frac{F^{\rm ex}}{k_{\rm B}T} = -\log Z^{\rm ex} = -E_{\rm self} - \log\biggl(\frac{Z_{\rm DH}}{Z_0}\biggr) - \log\bigl\langle {\rm e}^{W[\phi]} \bigr\rangle. \tag{9}$$

The angular brackets correspond to a Gaussian average where the the inverse Debye-Hückel operator (6) is used as propagator. The term

$$\begin{aligned} \frac{F_{\rm DH}^{\rm ex}}{k_{\rm B}T} &\equiv -E_{\rm self} - \log\biggl(\frac{Z_{\rm DH}}{Z_0}\biggr) \\ &= -\frac{V}{2\pi^2} \int_0^\infty {\rm d}k\, k^2 \biggl[\frac{\kappa^2}{2k^2} - \frac{1}{2} \log\biggl(1 + \frac{\kappa^2}{k^2} \biggr) \biggr] \end{aligned} \tag{10}$$

is the Debye-Hückel contribution to the free energy. Notice that $E_{\rm self}$ automatically regularizes this integral in the ultra-violet, allowing its evaluation without the need of a small wave-length (large-k) cut-off.

Using (10) and neglecting the term $\log\bigl\langle {\rm e}^{W[\phi]} \bigr\rangle$ in (9), we get the excess free energy per particle

$$f^{\rm ex} \equiv \frac{F^{\rm ex}}{nk_{\rm B}T} = -\frac{1}{\sqrt{3}} \Gamma^{3/2} \tag{11}$$

where $\Gamma \equiv q^2\ell_{\rm B}\bigl(4\pi c/3\bigr)^{1/3}$ is the (dimensionless) plasma parameter. From the excess free energy, we can get the internal energy per particle

$$u \equiv \frac{U}{nk_{\rm B}T} = \Gamma \frac{\partial f^{\rm ex}}{\partial \Gamma} = -\frac{\sqrt{3}}{2} \Gamma^{3/2}. \tag{12}$$

This is the resulting u for what we call from now on the "Gaussian theory without cut-off".

Equation (11) is the well known Debye-Hückel limiting law, which is asymptotically exact for vanishing Γ. At $\Gamma \sim O(1)$ the expression (12) already yields poor results when compared to simulations (*cf.* Fig. 1b). At large Γ (*cf.* Fig. 1a) this inadequacy is particularly clear: fits to simulation data show a linear behavior [11,14] in the internal energy, and not a 3/2 power law.

Brilliantov [12] calculated the Gaussian theory as depicted above but introduced a modification, namely a large-k cut-off. This is justified with ideas that follow the Debye theory for the specific heat in solids, stating a direct relation between the number of allowed $\mathbf{k}$ modes in the system and the number of degrees of freedom $3n$. The allowed wave vectors would be approximately inside a spheres of radius $k_{\rm o} = \bigl(9c\pi^2\bigr)^{1/3}$, which is used to substitute the ∞ in the integral in (10). The agreement between the internal energy obtained with this cut-off and the results from Monte Carlo simulations [10,11] are good (*cf.* Figs. 1 and 2). What we will show next is that the

inclusion of contributions up to eighth order in ϕ coming from the term $\log\langle e^{W[\phi]}\rangle$ does not change significantly this result.

When the cut-off k_o is used in (10), we get the Debye-Hückel excess free energy per particle

$$f_{\rm DH}^{\rm ex} = -\frac{3}{2}\big(b\Gamma\big)^{3/2}\arctan\left(\frac{1}{\sqrt{b\Gamma}}\right) - \frac{3}{4}\left(b\Gamma - \log\big(1+b\Gamma\big)\right) \tag{13}$$

where Γ is the plasma parameter and $b \equiv \big(2/\pi^2\big)^{1/3} 2/3$ (keeping the notation used in [12]). Notice that in the limit $\Gamma \to 0$ this expression reduces to (11), as it should. This is the excess free energy used in [12] to calculate the internal energy.

In order to go beyond the Debye-Hückel level, we do the cumulant expansion

$$\log\langle e^{W[\phi]}\rangle = \langle W[\phi]\rangle + \frac{1}{2}\left(\langle W^2[\phi]\rangle - \langle W[\phi]\rangle^2\right) + \cdots \tag{14}$$

Using (7) and going up to eighth order in ϕ, we obtain

$$-\frac{\log\langle e^{W[\phi]}\rangle}{n} = \frac{\pi}{108}\left[\chi_3 + \frac{3}{2}\langle\phi^2\rangle^2\chi_1\right] + \frac{\pi}{144}\langle\phi^2\rangle^3\chi_1 - \frac{\pi}{432}\chi_4 \tag{15}$$

where

$$\langle\phi^2\rangle = \frac{\ell_{\rm B}}{2\pi^2}\int_0^{k_o} {\rm d}k \frac{k^2}{k^2+\kappa^2} = \frac{9b\Gamma}{2}\left[1 - \sqrt{b\Gamma}\arctan\left(\frac{1}{\sqrt{b\Gamma}}\right)\right] \tag{16}$$

and

$$\chi_m \equiv 4\pi\int_a^\infty {\rm d}r\langle\phi(0)\phi(r)\rangle^m = \frac{4}{\pi^2}\left(\frac{9\pi}{4}\right)^m m^{m-3}\big(b\Gamma\big)^{3(m-1)/2}\overline{\Gamma}\big(3-m, m\pi\sqrt{b\Gamma}\big). \tag{17}$$

$\overline{\Gamma}(m,x)$ is the incomplete gamma function [15] and $a = \pi/\big(9c\pi^2\big)^{1/3}$ is a small distance cut-off. Ideally, the integrals χ_m should be performed in k-space with the momentum cut-off given by k_o. However, for $m \geq 3$, the Fourier transformed integrals cannot be solved in a closed form; on the other hand, the integrals, when written in real space are not difficult to calculate exactly, provided a small distance cut-off. Since a large-k cut-off corresponds in real space roughly to a small distance cut-off, we introduced as an approximation the small-r limit a such that $k_o = \pi/a$.

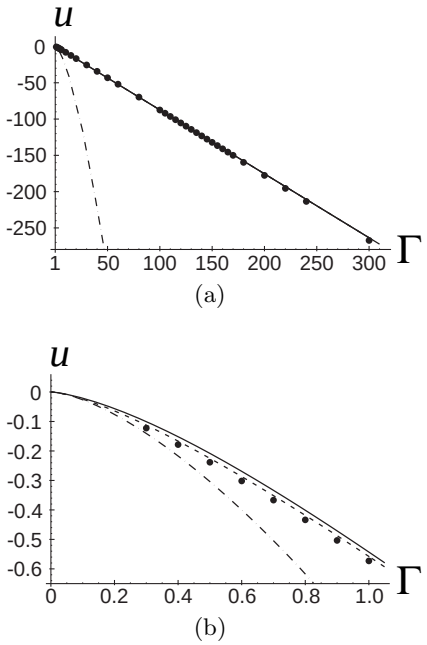

Fig. 1. Internal energy (u) as function of the plasma parameter Γ in the range (a) $1 < \Gamma < 300$ and (b) $0 < \Gamma \leq 1$. The full line denotes the result obtained here, the dashed line the Gaussian theory with cut-off [12], the dash-dotted line the u obtained from the Debye-Hückel limiting law (Eq. (12)). The points denote simulation results from references [10] ($0 < \Gamma < 1$) and [11] ($1 < \Gamma < 300$).

Putting (13, 15) into (9), we finally obtain the expression for the excess free energy of the OCP with contributions up to eighth order in ϕ. The internal energy follows as in (12).

3 Results and discussion

In Figures 1a and 1b we show u obtained from simulations [10,11] (black circles), from the Gaussian theory *with* [12] and *without* (Eq. (12)) cut-off (respectively dashed line and dash-dotted line) and from the results obtained here with the higher order terms (full line).

In the strongly coupled regime ($\Gamma > 1$, Fig. 1a), the inclusion of higher order terms does not affect the results obtained with the Gaussian theory with cut-off; both results are indistinguishable on this scale. We also calculate the relative error in u, defined as

$$R_{\rm err} = \frac{u - u_{\rm s}}{|u_{\rm s}|}, \tag{18}$$

where the subscript s stands for simulation. In Figure 2a we show, for $\Gamma > 1$, $R_{\rm err}$ for the Gaussian theory with cut-off (black circles) and for u with the higher order terms calculated here (white circles). The agreement between theory and simulation is good, with deviations between -2% and 2% [16]. Notice however that for $\Gamma \lesssim 10$ the inclusion of the higher order terms make the results worse,

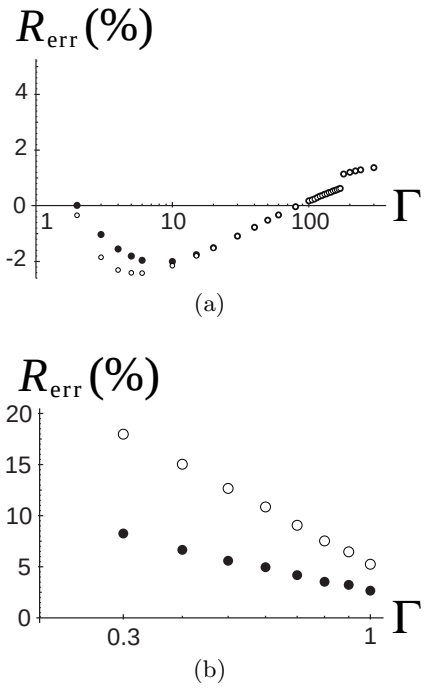

Fig. 2. The relative error $R_{\rm err}$ (Eq. (18)) as function of Γ for (a) $1 < \Gamma < 300$ and (b) $0.3 < \Gamma \leq 1$. The white circles represent the relative error for the u obtained here with the higher order corrections; the black circles represent the relative error for the Gaussian theory with cut-off [12].

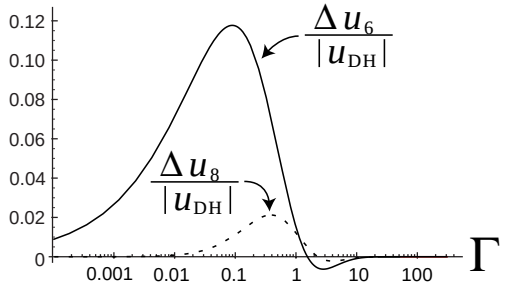

Fig. 3. Comparison of the sixth order and eighth order corrections with $u_{\rm DH}$. Notice that Δu_6 is roughly one order of magnitude smaller than $u_{\rm DH}$ and Δu_8 is two orders smaller than $u_{\rm DH}$.

relative to the Gaussian theory with cut-off, when compared to simulation.

In the weakly coupled regime ($\Gamma \leq 1$, Fig. 1b), this trend is confirmed. In Figure 2b it is clear that the deviation between theory and simulations are larger when the higher orders are included. However, in both cases $R_{\rm err}$ increases with decreasing Γ. This is not surprising though, since u goes to zero as Γ decreases, making the relative error very sensitive to small differences between theory and simulation.

In Figure 3 we assess the importance of the higher order corrections computed here in comparison to the Gaussian theory with cut-off. The higher order terms of the excess free energy are given by (15): the first term in the rhs corresponds to the sixth order in ϕ correction and two remaining ones to the eighth order. We can then write down u as a sum of three terms, *viz.*

$$u = u_{\rm DH} + \Delta u_6 + \Delta u_8 \tag{19}$$

where $u_{\rm DH}$ is the Gaussian contribution to the internal energy coming from (13). In Figure 3 we plot $\Delta u_6/|u_{\rm DH}|$ and $\Delta u_8/|u_{\rm DH}|$. As we can see, Δu_6 is approximately one order of magnitude smaller than $u_{\rm DH}$ and Δu_8 two order of magnitude smaller than $u_{\rm DH}$. We expect that the inclusion of terms of order higher than eight will not change significantly the picture given here.

In summary, we have calculated higher order contributions to the internal energy of the OCP. We have shown that (i) the effects of these higher order terms are small relative to the previously calculated Gaussian theory [12] and (ii) they do not improve the agreement between theory and simulation This shows that the Gaussian theory with the cut-off $k_{\rm o}$ introduced such as to approximately include strong nearest-neighbor correlations in the high-Γ limit is very accurate for describing the OCP [17].

Our calculation consists of two major steps, *viz.*, the expansion of the excess free energy (9) in cumulants of ϕ and the introduction of the cut-off $k_{\rm o}$ suggested in reference [12]. In principle, the first step can be improved systematically by including higher order terms, while there is no clear recipe for improving the second one. The results we obtained here are then a consequence of the approximate way of calculating the cut-off. Since the precise value of $k_{\rm o}$ is not uniquely determined, it may be treated as a fit parameter. By fitting the theory to simulation at the high-Γ limit we obtain $k_{\rm fit} \simeq 4.417c^{1/3}$, which is close to the value $k_{\rm o} = \left(9\pi^2 c\right)^{1/3} \simeq 4.462c^{1/3}$ used by Brilliantov and also used by us.

AGM acknowledges financial support from the Portuguese FCT through the grant Praxis XXI/BD/13347/97.

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12. N.V. Brilliantov, Contrib. Plasma Phys. **38**, 489 (1998).
13. R.R. Netz, H. Orland, Europhys. Lett. **45**, 726 (1999); notice that in equation (14) of this reference (which is equivalent to Eq. (15) here) the factor $a^3 I_5 I_3/32$ should read $a^3 I_5 I_3/16$.

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16. Although the deviations are small, we should notice that they are statistically significant since the numerical error given by simulations in this range of Γ is below $\pm 0.02\%$ [11].
17. As a side remark, we note that the application of the cut-off $k_{\rm o}$ to the Two-Component Plasma (TCP) leads to unphysical results. At the Debye-Hückel level, the excess free energy per volume goes for small $c \equiv (n_+ + n_-)/V$ as $f^{\rm ex} \sim -\left(4\pi\ell_{\rm B}q^2c\right)^{3/2}/12\pi$ (the already discussed Debye-Hückel limiting law) and as $f^{\rm ex} \sim -(9/\pi)^{1/3}\ell_{\rm B}q^2c^{4/3}$ for large c; at this limit total free energy per volume is unbounded from below and non-convex. At finite temperatures, the Maxwell construction leads to the coexistence between states with a zero and an infinite density, which is clearly unphysical and signals that this approach is not appropriate for the TCP. This difference between the OCP and the TCP becomes more transparent in a recent systematic low-density expansion of the free energy, where the TCP expansion coefficients are shown to be dominated by ion-pair formation [18].
18. R.R. Netz, H. Orland, to be published.