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On the lower bound of the internal energy of the one-component-plasma

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A new simple yet accurate analytical estimate for the internal energy of the classical one-component-plasma is proposed. In the limit of weak coupling, it reduces to the Debye-Hückel result. In the opposite limit of strong coupling, the ion sphere approximation is recovered. The agreement with the accurate numerical results in the intermediate coupling regime is fairly good.
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The one-component-plasma (OCP) is an idealized model system of point charges immersed in a uniform background of opposite charge to ensure overall charge neutrality.[1,2] This model is of considerable interest from the fundamental point of view and has wide interdisciplinary applications. Not surprisingly, various topics such as thermodynamics, structural and transport properties, phase transitions have been extensively investigated, both analytically and numerically.

The thermodynamics of the OCP in three dimensions is characterized by the coupling parameter $\Gamma = Q^2/aT$, where Q is the particle charge, T is the temperature (in energy units), $a = (4\pi n/3)^{-1/3}$ is the Wigner-Seitz radius, and n is the particle density. As Γ increases, the OCP shows a transition from a weakly coupled gaseous regime ($\Gamma \ll 1$) to a strongly coupled fluid regime ($\Gamma \gg 1$) and crystallizes into the bcc lattice at $\Gamma \simeq 170 - 175$.[3,4] Monte Carlo (MC) and molecular dynamics (MD) simulations have been extensively used to obtain the OCP equation of state in a very wide range of Γ.[3,5–9] Very accurate numerical results as well as their fits for the internal energy are available in the literature.

There has been considerable continuous interest in deriving physically motivated analytical estimates or bounds on the internal energy (and other related thermodynamic quantities) of the OCP. Analytical approaches of various complexity and accuracy have been discussed in Refs. 10–21 (see also references therein). Below, we briefly remind some of the results particularly relevant to the present study. Mermin[10] demonstrated that the internal energy of the OCP is bounded below by the Debye-Hückel (DH) value. In terms of reduced excess energy per particle, this can be written as $u_{\rm OCP} \gtrsim -\frac{\sqrt{3}}{2}\Gamma^{3/2}$. This bound is a reasonable measure of the actual energy at weak coupling. Lieb and Narnhofer[11] derived another exact lower bound on the excess energy of the OCP, which reads $u_{\rm OCP} \gtrsim -\frac{9}{10}\Gamma$. This result is often refereed to as the ion sphere model[2] (ISM) and provides rather good estimate of $u_{\rm OCP}$ at strong coupling. Nordholm[16] proposed a simple modification of the DH theory, called "DH + hole" (DHH) based on the recognition that the exponential particle density must be truncated close to the particles so as not to become negative.[22] It improves considerably the DH theory at moderate coupling, $\Gamma \lesssim 1$, but exhibits improper scaling ($\propto -\frac{3}{4}\Gamma$) in the high-$\Gamma$ limit. More recently, Caillol[20] derived two other exact lower bounds[23,24] for $u_{\rm OCP}$, which have been demonstrated to be in better agreement than those obtained previously in a wide range of Γ. The purpose of this Brief Communication is to discuss yet another simple analytical scheme to estimate $u_{\rm OCP}$, which is based on the hybrid DHH + ISM consideration formulated below. This scheme produces an expression, which reduces to the DH result at weak coupling and to the ISM result at strong coupling and provides reasonable interpolation between these limits. The accuracy of the approximation is particularly good at $\Gamma \gtrsim 1$.

In the DHH approach, one solves the spherically symmetric Poisson equation, $\Delta\phi = -4\pi\rho(r)$, where ϕ is the electric potential and $\rho(r)$ is the charge density satisfying

$$\rho(r) = \begin{cases} Q\delta(\mathbf{r}) - Qn, & r < h, \\ -Q^2 n\phi/T, & r \geq h. \end{cases} \tag{1}$$

Here, the key parameter h is the radius of the hole around the test central particle, where all other particles are excluded. The solution has two branches, $\phi_{\rm in}(r)$ for $r < h$ and $\phi_{\rm out}(r)$ for $r \geq h$, which should be matched at $r = h$, requiring $\phi_{\rm in}(h) = \phi_{\rm out}(h) = T/Q$ and $\nabla\phi_{\rm in}(h) = \nabla\phi_{\rm out}(h)$. The procedure is straightforward and yields the following expression for h:[16]

$$\frac{h}{a} = \frac{1}{\sqrt{3\Gamma}}\left\{\left[1 + (3\Gamma)^{3/2}\right]^{1/3} - 1\right\} = f(\Gamma). \tag{2}$$

The function $f(\Gamma)$ has the following asymptotes: $f(\Gamma) \simeq 1 - 1/\sqrt{3\Gamma} + \mathcal{O}(\Gamma^{-3/2})$ at strong coupling ($\Gamma \gg 1$) and $f(\Gamma) \simeq \Gamma + \mathcal{O}(\Gamma^{5/2})$ at weak coupling ($\Gamma \ll 1$). The distribution of the electrical potential beyond the hole in the DHH approximation is

$$\phi_{\rm out}(r) = \frac{hT}{Qr}e^{-k_{\rm D}(r-h)}, \tag{3}$$

where $k_{\rm D} = \sqrt{4\pi Q^2 n/T}$ is the inverse screening (Debye) length associated with the particle component.

Now, we treat each particle surrounded by a spherical piece of background charge of radius h as a new compound particle, which has an effective charge $Q_{\rm eff} = Q[1 - (h/a)^3]$. The internal energy of such a compound particle consists of two parts: Energy of a uniformly charged sphere of radius h and charge $-Q(h/a)^3$ and the energy of a charge Q placed in the center of such a sphere. The first (background) component is

$$u_{\rm b} = \frac{3}{5}\left(Q^2/h\right)(h/a)^6 = \frac{3}{5}\Gamma f(\Gamma)^5. \tag{4}$$

The second (particle) component is

$$u_{\rm p} = -\frac{3}{2}\left(Q^2/h\right)(h/a)^3 = -\frac{3}{2}\Gamma f(\Gamma)^2. \tag{5}$$

The total reduced energy of a compound particle is thus

$$u_{\rm cp}(\Gamma) = \Gamma\left[\frac{3}{5}f(\Gamma)^5 - \frac{3}{2}f(\Gamma)^2\right]. \tag{6}$$

In the limit of strong coupling, we have $h \to a$, $Q_{\rm eff}$ tends to zero and, therefore, $u_{\rm cp}$ should be an adequate measure of the excess energy of the whole system (per particle). We get in this limit $u_{\rm cp} \simeq -\frac{9}{10}\Gamma + \frac{3}{2}$, which coincides with the static ISM result plus vibrational correction.[21,25] This is not very surprising, since essentially ISM arguments are used and only the sphere radius is allowed to vary. At $\Gamma \ll 1$, the scaling $u_{\rm cp} \propto \Gamma^3$ implies negligible contribution compared to the DH asymptote.

The compound particles are not charge neutral, except in the limiting case $\Gamma \to \infty$. The energy associated with the remaining interaction between them can be estimated from the energy equation

$$u_{\rm pp} = (2\pi n/T)\int_h^\infty r^2 V(r)[g(r)-1]dr, \tag{7}$$

where $V(r) = Q_{\rm eff}^2/r$ is the Coulomb interaction potential and $g(r)$ is the radial distribution function. Since $Q_{\rm eff}$ is considerably reduced compared to Q, especially in the strong coupling regime, it is nor very unreasonable to use an expression origination from the linearized Boltzmann relation, $g(r) = 1 - Q_{\rm eff}\phi_{\rm out}(r)/T$, where $\phi_{\rm out}$ is given by Eq. (3) in the DHH approximation. The integration is then straightforward and yields

$$u_{\rm pp}(\Gamma) = -(\sqrt{3\Gamma}/2)f(\Gamma)[1-f(\Gamma)^3]^3. \tag{8}$$

The resulting $u_{\rm pp}$ scales as $\propto \Gamma^{-1}$ for large Γ and reduces to the Debye-Hückel result, $u_{\rm pp} \simeq -\frac{\sqrt{3}}{2}\Gamma^{3/2}$, in the limit of weak coupling $\Gamma \ll 1$.

Our estimate of the OCP excess energy is then

$$u_{\rm OCP}(\Gamma) = u_{\rm cp}(\Gamma) + u_{\rm pp}(\Gamma). \tag{9}$$

We have already demonstrated that it reduces to the DH and ISM asymptotes in respective limits of weak and strong couplings. The quality of the interpolation between these two limits is illustrated in Fig. 1. The agreement with the accurate numerical data is fairly good. The present approach provides lower bounds for the internal energy in the limits of weak and strong couplings. Figure 1 also shows that it underestimates the actual $u_{\rm OCP}$ in the transitional regime. In this sense, it can be associated with the lower bond, although we have used no exact inequalities in the derivation and thus this should not be regarded as a solid mathematical proof.

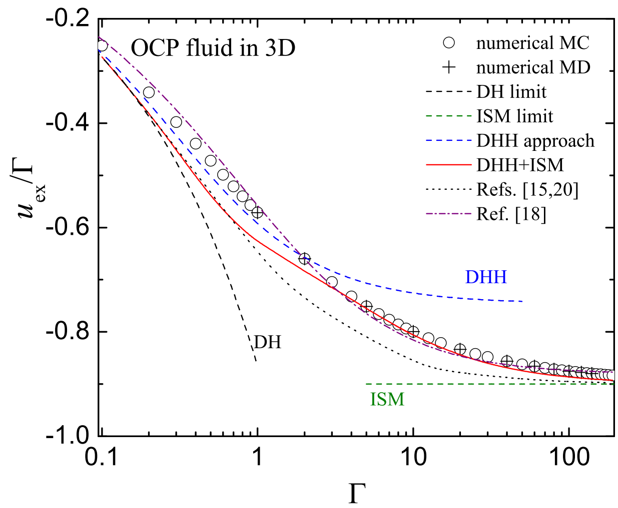

FIG. 1. Reduced excess energy of the OCP model, $u_{\rm ex}$, versus the coupling parameter Γ. Symbols are the results from MC[8,9] and MD[3] simulations. Various dashed curves correspond to the DH, DHH, and ISM approximations, as indicated in the figure. The (black) dotted curve shows the lower bound proposed in Refs. 15 and 20. The (purple) dashed-dotted curve corresponds to the "first-principle" expression derived in Ref. 18. The (red) solid curve is the present estimate of Eq. (9).

Compared to the earlier results, our present estimate represents a considerable improvement over that of Refs. 15 and 20 for $\Gamma \gtrsim 1$. For $\Gamma \lesssim 1$, the latter is slightly more accurate, but in this regime the DHH approach demonstrates better performance. The "first-principle" expression derived in Ref. 18 is only slightly less accurate than our estimate in the regime $3 \lesssim \Gamma \lesssim 30$ but is closer to the numerical data for $\Gamma \sim \mathcal{O}(1)$ (in this regime, it overestimate the actual energy). Clearly, more accurate fits for the dependence $u(\Gamma)$ in the classical OCP fluid do exist.[3,4,8,21] However, since the DHH and ISM approaches can be relatively easily generalized to the case of Yukawa systems,[26,27] present results can possibly find applications beyond the OCP.

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