Lower bounds for thermodynamic quantities of two- and three-dimensional one-component plasmas

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Exact lower bounds for the correlation energy of the one-component plasmas (OCP) with the r^{-1} potential are given in d dimensions $1 < d \leq 3$. For classical OCP's with $d = 2$ and 3, this lower bound contains most of the correlation energy in the high-density domain, and the residue is given by two integrals of positive-definite functions, including the pair correlation function and the structure factor. For the classical OCP with $d = 3$, a lower bound which improves upon known ones due to Mermin and to Lieb and Narnhofer in the domain $\Gamma < 15.3$ is given.

Exact bounds for thermodynamic quantities are useful when there exist no well-defined methods to calculate these quantities. For the correlation energy of the one-component plasma (OCP), the system of charged particles in the uniform background of opposite charges, lower bounds have been given by Dyson and Lenard,[1] Mermin,[2] and Lieb and Narnhofer.[3] For the classical three-dimensional OCP, the lower bound due to Mermin,[2] which is applicable only to the classical case, is effective in the low-density domain and that due to Lieb and Narnhofer[3] in the high-density domain. In addition to these three-dimensional plasmas, two-dimensional plasmas on the surface of liquid helium and in metal-oxide-semiconductor (MOS) inversion layers have recently become the subject of experimental and theoretical studies. For two-dimensional plasmas, where particles interact via the ordinary Coulomb potential, no exact bounds of thermodynamic quantities are known; three-dimensional derivations by Mermin[2] or Lieb and Narnhofer[3] which use the properties of the r^{-1} potential in three dimensions do not work in two dimensions.

In this paper, we show that simple arguments applicable to both three- and two-dimensional cases lead to exact lower bounds of the correlation energy of OCP, and compare them with former exact bounds[2,3] and the results of numerical experiments on classical OCP's in three[4,5] and two dimensions.[6] We also point out that these lower bounds reproduce most of the correlation energy of classical OCP's in the high-density domain without essential information on the pair-correlation function or the structure factor, and may be used as a useful zeroth-order approximation in calculations of thermodynamic quantities. In order to show the dimensionality-independent applicability, we give the result for the d-dimensional case ($1 < d \leq 3$), extending the number of dimensions to noninteger values.[7]

The correlation energy per particle e_c is given by

$$e_c = \frac{ne^2}{2}\int \frac{d\vec{r}\,h(\vec{r})}{r}, \tag{1}$$

where $h(\vec{r})$ denotes the pair-correlation function, n and e the number density and unit charge, and $d\vec{r}$ the d-dimensional volume element. The pair-correlation function is related to the structure factor $S(\vec{k})$ and the density fluctuation $\rho_{\vec{k}}$ by

$$S(\vec{k}) = \langle |\rho_{\vec{k}}|^2\rangle / N, \tag{2}$$

$$\rho_{\vec{k}} = \sum \exp(-i\vec{k}\cdot\vec{r}_i), \tag{3}$$

$$nh(\vec{r}) = \int d\vec{k}(2\pi)^{-d}[S(\vec{k}) - 1]\exp(i\vec{k}\cdot\vec{r}), \tag{4}$$

N being the number of particles. Equation (1) is then rewritten

$$e_c = \frac{e^2}{2}\int d\vec{k}(2\pi)^{-d}\phi(k)[S(\vec{k}) - 1]. \tag{5}$$

Here $\phi(k)$ is the Fourier transform of the Coulomb interaction:

$$\begin{aligned}\phi(k) &= \int \frac{d\vec{r}\exp(-i\vec{k}\cdot\vec{r})}{r} \\ &= \frac{2\pi^{(d-1)/2}}{\Gamma(\frac{1}{2}(d-1))}\int_0^\infty dr\, r^{d-1} r^{-1} \\ &\quad \times \int_0^\pi d\theta \sin^{d-2}\theta \exp(-ikr\cos\theta) \\ &= (2\pi^{1/2})^{d-1}\Gamma(\tfrac{1}{2}(d-1))k^{1-d}, \quad 1 < d \leq 3\end{aligned} \tag{6}$$

and $d\vec{k}$ denotes the d-dimensional volume element in the Fourier space. Rewriting the Coulomb interaction as

$$\frac{1}{r} = \int_0^\infty dt f(r,t) = \left(\int_0^G + \int_G^\infty\right) dt f(r,t) \tag{7}$$

with an arbitrary parameter $G \geq 0$, we obtain the Ewald-type hybrid expression for the correlation

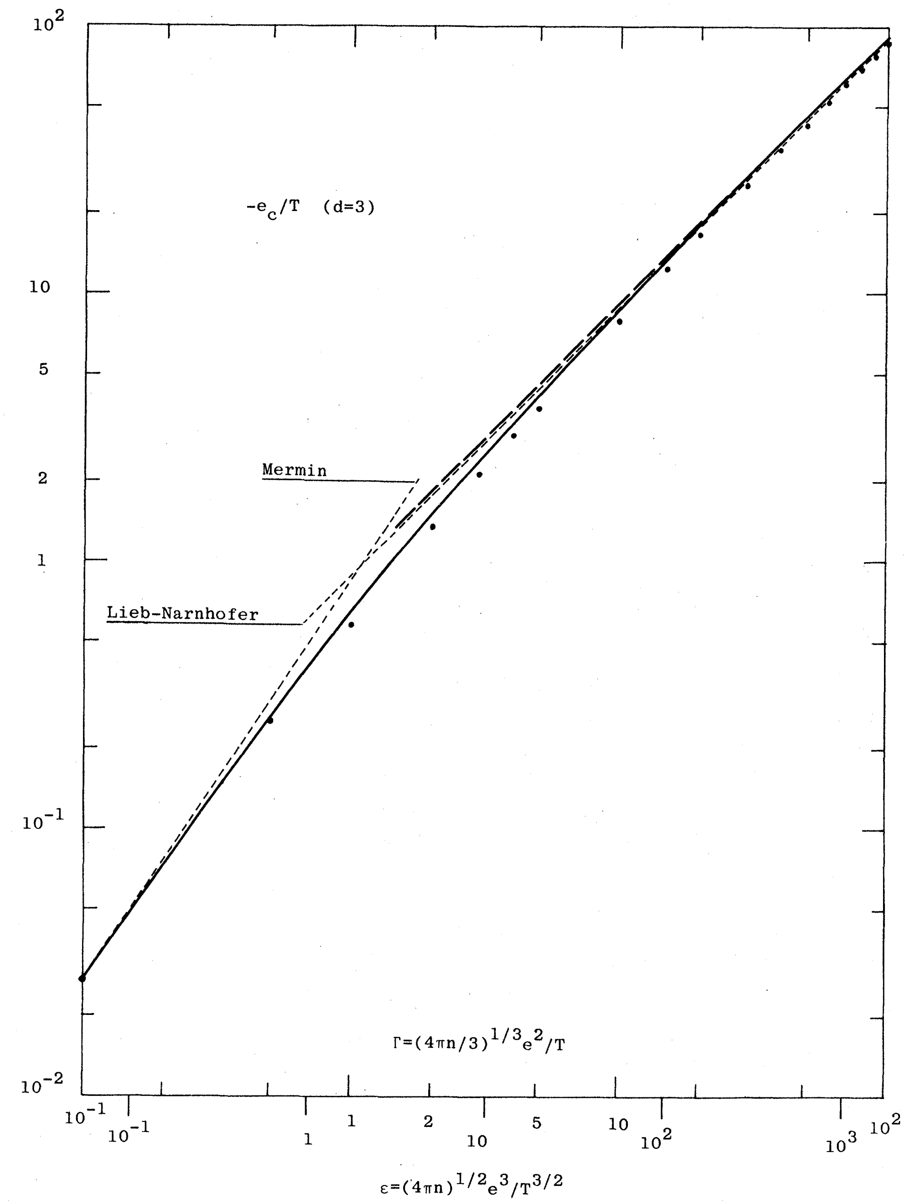

FIG. 1. Correlation energy of the three-dimensional classical one-component plasma. Closed circles are experimental values.[4,5] The dashed and solid lines describe the lower bounds (22) and (27), respectively, and the dotted lines those due to Mermin[2] and to Lieb and Narnhofer.[3]

energy

$$e_c=\frac{ne^2}{2}\int_G^\infty dt\int d\vec{r}\, h(\vec{r})f(r,t)+\frac{e^2}{2}\int_0^G dt\int d\vec{k}(2\pi)^{-d}[S(\vec{k})-1]f(k,t)$$
$$=\frac{ne^2}{2}\int_G^\infty dt\int d\vec{r}[h(\vec{r})+1]f(r,t)+\frac{e^2}{2}\int_0^G dt\int d\vec{k}(2\pi)^{-d}S(\vec{k})f(k,t)+B[f,G], \quad (8)$$

where $f(k,t)$ is the Fourier transform of $f(r,t)$ and

$$B[f,G]=-\frac{ne^2}{2}\int_G^\infty dt f(k=0,t)-\frac{e^2}{2}\int_0^G dt f(r=0,t)\,. \quad (9)$$

Noting the trivial inequalities

$$h(\vec{r})\geq -1\,, \quad (10)$$
$$S(\vec{k})\geq 0\,, \quad (11)$$

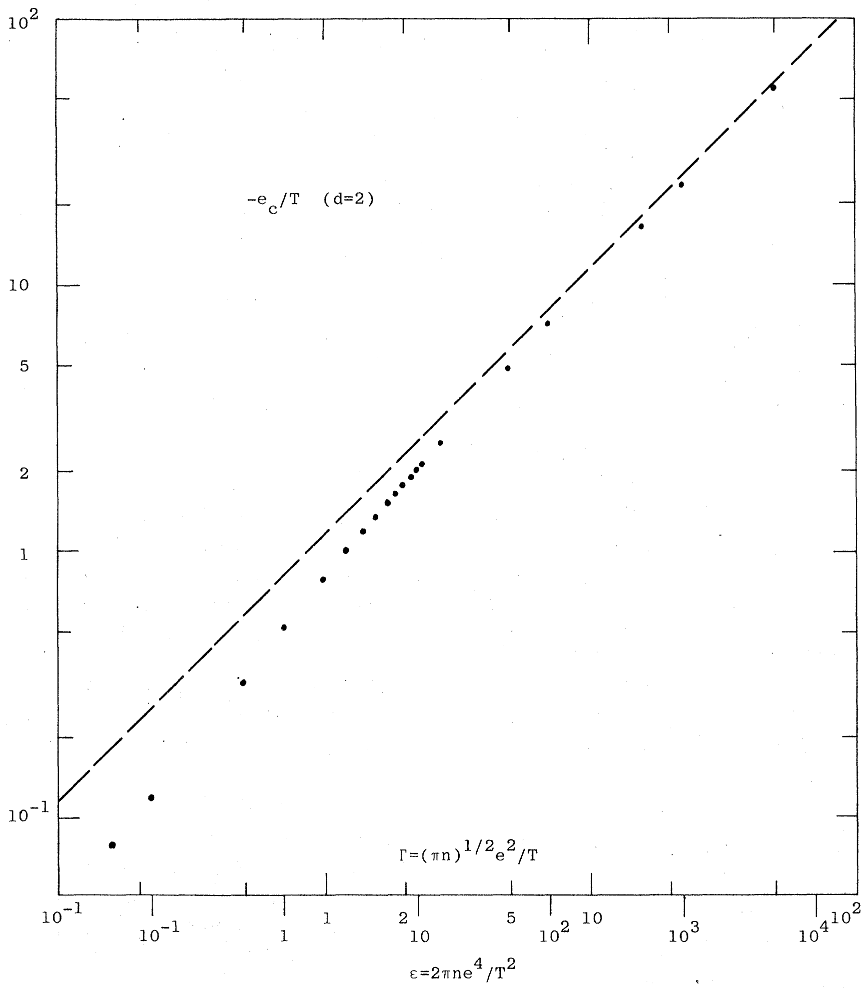

FIG. 2. Correlation energy of the two-dimensional classical one-component plasma. Closed circles are experimental values,[6] and the dashed line describes the lower bound (23).

and assuming

$$f(r,t)\geqslant 0 \quad\text{and}\quad f(k,t)\geqslant 0\,, \tag{12}$$

we have an exact lower bound for the correlation energy,

$$e_c \geqslant B[f,G]\,. \tag{13}$$

The nonideal part of the Helmholtz free energy $F_{\rm int}$ is bounded as follows:

$$F_{\rm int}\geqslant \int_0^{e^2} d(\ln e^2) B[f,G]\,. \tag{14}$$

When the function $f(r,t)$ has the form

$$f(r,t)=f(rt)\,, \tag{15}$$

the maximum of $B[f,G]$ is attained at $G=G_0$,

$$G_0=\left(n\int \frac{d\vec{r}f(r)}{f(r=0)}\right)^{1/d}, \tag{16}$$

and the best lower bound within assumption (15) is given by

$$B[f,G_0]=-\pi^{-1/2}\frac{d}{2(d-1)}\left(\Gamma(\tfrac{1}{2}d+1)\int\frac{d\vec{r}f(r)}{f(r=0)}\right)^{1/d} \times\frac{f(r=0)e^2}{a}\,. \tag{17}$$

Here the mean distance $a=\pi^{-1/2}[\Gamma(\frac{1}{2}d+1)/n]^{1/d}$ is defined by

$$n\int_{r\leqslant a} d\vec{r}=1\,. \tag{18}$$

For the function $f(r,t)$ we now take[8]

TABLE I. Comparison of exact lower bounds for the correlation energy with experimental values, e_c/T, for three-dimensional classical one-component plasmas.

Γ	ϵ	Experiments by Brush *et al.*[4] (BST) or Hansen[5] (H)	Lower bounds: Present paper [Eq. (27)]	Lower bounds: Mermin[2] (M) or Lieb and Narnhofer[3] (LN)
0.1	5.477×10^{-2}	-2.70×10^{-2} (BST)	-2.693×10^{-2}	-2.739×10^{-2} (M)
0.5	6.124×10^{-1}	-2.52×10^{-1} (BST)	-2.669×10^{-1}	-3.062×10^{-1} (M)
1	1.732	-5.80×10^{-1} (H)	-6.572×10^{-1}	-8.660×10^{-1} (M)
2	4.899	−1.318 (H)	−1.518	−1.80 (LN)
4	13.86	−2.926 (H)	−3.322	−3.60 (LN)
10	54.77	−7.996 (H)	−8.854	−9.00 (LN)
15	100.6	−12.313 (H)	−13.49	−13.50 (LN)
20	154.9	−16.667 (H)	−18.14	−18.00 (LN)

$$f(r,t)=f_0(rt)=2\pi^{-1/2}\exp(-r^2t^2)\,. \quad (19)$$

The function $f_0(rt)$ and its Fourier transform

$$f_0(k,t)=2\pi^{(d-1)/2}t^{-d}\exp(-k^2/4t^2) \quad (20)$$

satisfy conditions (12). The correlation energy is thus bounded as

$$e_c\geq B[f_0,G_0]=-\pi^{-1/2}\frac{d}{d-1}\frac{\Gamma(\tfrac{1}{2}d+1)^{1/d}e^2}{a}. \quad (21)$$

For $d=3$ and $d=2$, we have

$$e_c\geq-\frac{\tfrac{3}{2}(3/4\pi)^{1/3}e^2}{a}=-\frac{0.9305e^2}{a}\,,\quad d=3 \quad (22)$$

$$e_c\geq-\frac{2\pi^{-1/2}e^2}{a}=-\frac{1.1284e^2}{a}\,,\quad d=2\,. \quad (23)$$

Our lower bound for $d=3$ is lower by 3% than the lower bound due to Lieb and Narnhofer,[3]

$$e_c\geq-\tfrac{9}{10}e^2/a\,, \quad (24)$$

which is very close to the correlation energy of the three-dimensional Wigner lattices, $e_c(\mathrm{bcc})=-0.895\,93e^2/a$, $e_c(\mathrm{fcc})=-0.895\,87e^2/a$, and $e_c(\mathrm{sc})=-0.8801e^2/a$. In the case of two dimensions, our lower bound is lower by 2% than the correlation energy of the Wigner lattices,[6] $e_c(\mathrm{hexagonal})=-1.106e^2/a$ and $e_c(\mathrm{square})=-1.100e^2/a$. Our results for $d=3$ and $d=2$ are compared with values obtained by the numerical experiments on classical OCP's[4-6] and other lower bounds for $d=3$ in Figs. 1 and 2. There the values of e_c/T are plotted as functions of the nondimensional parameter Γ defined by $\Gamma=e^2/aT$, T being the temperature in energy units. It is shown that most of the correlation energy of the classical OCP in the high-density domain is obtained by the zeroth approximation $h(\vec{r})=-1$ and $S(\vec{k})=0$ from Eq. (8), with $f(r,t)$ and G given by Eqs. (19) and (16). Equation (8) with the same $f(r,t)$ and G may thus be useful, since $B[f_0,G_0]$ is already included in the zeroth approximation and the remaining contributions from the pair-correlation function in the short-range domain and the structure factor in the long-range domain, given by the integrals of positive-definite functions, do not cancel each other.

In the case of three-dimensional classical OCP's Mermin[2] has shown that the structure factor is bounded exactly by its RPA value

$$S(\vec{k})\geq S_{\mathrm{RPA}}(k)=k^2/(k^2+k_D^2)\,, \quad (25)$$

where k_D is the Debye wave number defined by $k_D^2=4\pi ne^2/T$. Substituting this inequality instead of (11) into (8), we obtain an exact lower bound which improves upon $B[f,G]$:

$$e_c\geq\frac{e^2}{2}\int_0^G dt\int d\vec{k}(2\pi)^{-3}S_{\mathrm{RPA}}(k)f(k,t)+B[f,G]\,. \quad (26)$$

Assuming again Eq. (19), we have

$$e_c/T\geq-\tfrac{1}{2}[x^2+\epsilon\exp(x^2)\mathrm{erfc}(x)]\,,\quad x=k_D/2G \quad (27)$$

where ϵ denotes the plasma parameter defined by $\epsilon=3^{1/2}\Gamma^{3/2}$, and

$$\mathrm{erfc}(x)=2\pi^{-1/2}\int_x^\infty dt\exp(-t^2)\,. \quad (28)$$

After optimizing with respect to G for each value of ϵ, we have an exact lower bound as shown in Fig. 1 and Table I. Our result improves upon the former bounds[2,3] in the domain $\Gamma(\epsilon)<15.3(1.03\times10^2)$. When the plasma parameter is small or large,[9] this lower bound is given approximately by

$$e_c/T\geq-\tfrac{1}{2}(\epsilon-\epsilon^2/\pi)\qquad\text{for }\Gamma,\epsilon\ll1 \quad (29)$$

$$e_c/T\geq-\tfrac{3}{2}(3/4\pi)^{1/3}\Gamma+\tfrac{1}{2}\quad\text{for }\Gamma,\epsilon\gg1\,, \quad (30)$$

and reduces to Mermin's result[2] $e_c\geq-\tfrac{1}{2}\epsilon$ or Eq. (22).

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[8]Among simple functions $f_0(rt)$, $c\exp(-rt)$, and $c(r^2t^2+1)^{-\nu}$ ($\nu > \frac{1}{2}d$) which satisfy conditions (12), f_0 gives the best lower bound.
[9]The second term on the right-hand side of (8) gives $\frac{1}{2}$ in (30), while the non-negative first term may be estimated (not exactly as a lower bound) by the ion-sphere model [E. E. Salpeter, Aust. J. Phys. 7, 373 (1954)] as 0.0621Γ.