Exact Lower Bounds for Some Equilibrium Properties of a Classical One-Component Plasma*

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(Received 2 February 1968)

It is shown that the internal energy, Helmholtz free energy, and Fourier-transformed static structure factor $S(\mathbf{k})$, for a classical electron gas with uniform positive background, are all bounded below by their Debye-Hückel values. This is true whether the equilibrium state is uniform or crystalline and whether periodic or impenetrable-wall boundary conditions are used.

CONSIDER N classical electrons in thermal equilibrium in the cubical[1] box $0\leq x,\ y,\ z,\ \leq L$ of volume $\Omega=L^3$, uniformly filled with positive charge of density $|e|N/\Omega=|e|n$.

The static structure factor for the system is defined by

$$S(\mathbf{k})=\lim_{\substack{N,\Omega\to\infty\\ N/\Omega=n}}\frac{1}{N}\langle|\sum_{i=1}^{N}e^{i\mathbf{k}\cdot\mathbf{r}_i}|^2\rangle, \tag{1}$$

or, alternatively,

$$S(\mathbf{k})=\lim_{\substack{N,\Omega\to\infty\\ N/\Omega=n}}\frac{1}{N}\int d\mathbf{r}\,d\mathbf{r}'e^{i\mathbf{k}\cdot(\mathbf{r}-\mathbf{r}')}\langle\hat{n}(\mathbf{r})\hat{n}(\mathbf{r}')\rangle, \tag{2}$$

where

$$\hat{n}(\mathbf{r})=\sum_{i=1}^{N}\delta(\mathbf{r}-\mathbf{r}_i), \tag{3}$$

$$\langle f\rangle=\frac{1}{Q}\int d\mathbf{r}_1\cdots d\mathbf{r}_N e^{-\beta U}f,\quad Q=\int d\mathbf{r}_1\cdots d\mathbf{r}_N e^{-\beta U}, \tag{4}$$

$\beta=1/k_BT$, and U is the potential energy.

The main purpose of this paper is to demonstrate[2] that for any $\mathbf{k}$

$$S(\mathbf{k})\geq k^2/(k^2+k_D^2),\quad k_D^2=4\pi ne^2/k_BT. \tag{5}$$

Immediate corollaries of (5) are exact lower bounds on the internal energy per particle u and the Helmholtz free energy per particle f:

$$u=\tfrac{3}{2}k_BT+\lim_{\substack{N\to\infty\\ N/\Omega\to n}}(1/N)\langle U\rangle\geq\tfrac{3}{2}k_BT-\tfrac{1}{2}e^2k_D, \tag{6}$$

$$f\geq f_0-\tfrac{1}{3}e^2k_D, \tag{7}$$

where f_0 is the Helmholtz free energy per particle of an ideal gas of the same density.

Since inequalities (5)–(7) are derived as equalities in the linear Debye-Hückel theory, what has been shown is that the exact $S(\mathbf{k})$, u, and f, are bounded below[3] by their Debye-Hückel values. This is consistent with currently known approximate results[4–6] and a criterion that future calculations can be tested against.

The demonstration of these inequalities depends to some extent on whether periodic or impenetrable-wall boundary conditions are chosen. Periodic boundary conditions lead directly to a proof that does not assume a spatially homogeneous equilibrium state, and therefore applies even when the electron gas crystallizes. Because, however, periodic boundary conditions are particularly clumsy for a classical Coulomb potential and because the customary assumption that results are independent of boundary conditions is not only unproved but, in the Coulomb case, even unobvious, a separate discussion is given in the case of impenetrable walls.

The results in both cases follow from a judicious choice of functions $A(\mathbf{r}_1\cdots\mathbf{r}_N)$ and $\mathbf{B}(\mathbf{r}_1\cdots\mathbf{r}_N)$ in the inequality

$$\langle|\mathbf{B}-A\langle A^*\mathbf{B}\rangle/\langle|A|^2\rangle|^2\rangle\geqq 0, \tag{8}$$

which in turn implies the Schwartz inequality[7]

$$\langle|A|^2\rangle\geq|\langle A^*\mathbf{B}\rangle|^2/\langle|\mathbf{B}|^2\rangle. \tag{9}$$

We take the vector function $\mathbf{B}$ to be of the form

$$\mathbf{B}(\mathbf{r}_1\cdots\mathbf{r}_N)=\sum_{i=1}^{N}\left[\varphi(\mathbf{r}_i)\frac{\partial U}{\partial\mathbf{r}_i}-\frac{1}{\beta}\nabla\varphi(\mathbf{r}_i)\right] \tag{10}$$

* Work supported by the National Science Foundation under Contract No. GP-5517.

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[1] The generalization to an arbitrary parallelepiped will be obvious.

[2] "A demonstration convinces a reasonable man; a proof, a stubborn one." (An approximation of a remark of M. Kac in a recent public disputation with M. Black, while at large at Cornell.)

[3] S. F. Edwards [Phil. Mag. 4, 1171 (1959)] gives a bound for a thermodynamic potential in terms of Debye-Hückel theory by formulating an electron-ion problem in terms of functional integrals. His work, however, has no evident relation to the results demonstrated here. The Debye-Hückel form, for example, is an upper bound in Edwards's paper. We have not been able to derive any of the Debye-Hückel lower bounds by such functional integration techniques.

[4] D. L. Bowers and E. E. Salpeter [Phys. Rev. **119**, 1180 (1960)] give analytic corrections to the Debye-Hückel internal energy.

[5] S. G. Brush, H. L. Sahlin, and E. Teller [J. Chem. Phys. **45**, 2102 (1966)] give numerical calculations of the internal energy and free energy.

[6] J. Coste [Nucl. Fusion **5**, 284 (1965)] gives an analytic calculation of the static structure factor.

[7] The apparently *ad hoc* procedure that follows is a special application of a very general method for bounding certain correlation functions. See N. D. Mermin, J. Math. Phys. **8**, 1061 (1967).

or, equivalently,

$$\mathbf{B}=-\frac{e^{\beta U}}{\beta}\sum_{i=1}^{N}\frac{\partial}{\partial \mathbf{r}_i}(\varphi(\mathbf{r}_i)e^{-\beta U}), \tag{11}$$

where the function $\varphi(\mathbf{r})$ is any twice differentiable function that either has the period of the cube of side L, or vanishes on the surfaces of the cube, depending on whether we are using the periodic or impenetrable-wall boundary conditions.

For A we choose

$$A=\sum_{i=1}^{N}\psi(\mathbf{r}_i), \tag{12}$$

where $\psi(\mathbf{r})$ is any differentiable function that has the period of the cube of side L if we are using the periodic boundary conditions and is unrestricted if the impenetrable-wall conditions are used.

Note first that for any differentiable (and periodic, if the periodic boundary conditions are being used) function $X(\mathbf{r}_1\cdots\mathbf{r}_N)$

$$\langle \mathbf{B}X\rangle=-\frac{1}{\beta Q}\int_{\Omega}d\mathbf{r}_1\cdots d\mathbf{r}_N\sum_{i=1}^{N}X\frac{\partial}{\partial \mathbf{r}_i}(e^{-\beta U}\varphi(\mathbf{r}_i))$$
$$=\frac{1}{\beta}\sum_{i=1}^{N}\langle\varphi(\mathbf{r}_i)\partial X/\partial \mathbf{r}_i\rangle. \tag{13}$$

(The integration by parts leads to no surface term either because the integrand is periodic, or because φ vanishes on the surface.) In particular, (13) implies

$$\langle \mathbf{B}A^*\rangle=\frac{1}{\beta}\sum_{i=1}^{N}\langle\varphi(\mathbf{r}_i)\nabla\psi^*(\mathbf{r}_i)\rangle \tag{14}$$

and

$$\langle|\mathbf{B}|^2\rangle=\langle\mathbf{B}\cdot\mathbf{B}^*\rangle=\frac{1}{\beta}\sum_{i=1}^{N}\left\langle\varphi(\mathbf{r}_i)\frac{\partial}{\partial \mathbf{r}_i}\cdot\mathbf{B}^*\right\rangle. \tag{15}$$

Substituting (10) in (15) gives

$$\langle|\mathbf{B}|^2\rangle=\frac{1}{\beta}\sum_{i,j=1}^{N}\langle\varphi(\mathbf{r}_i)\varphi^*(\mathbf{r}_j)\nabla_i\cdot\nabla_j U\rangle$$
$$+\frac{1}{\beta}\sum_{i=1}^{N}\left\langle\varphi(\mathbf{r}_i)\left[\nabla\varphi^*(\mathbf{r}_i)\cdot\frac{\partial U}{\partial \mathbf{r}_i}-\frac{1}{\beta}\nabla^2\varphi^*(\mathbf{r}_i)\right]\right\rangle. \tag{16}$$

The second term in (16) can be written

$$-\frac{1}{\beta^2 Q}\int d\mathbf{r}_1\cdots d\mathbf{r}_N\sum_{i=1}^{N}\varphi(\mathbf{r}_i)\frac{\partial}{\partial \mathbf{r}_i}\cdot(e^{-\beta U}\nabla\varphi^*(\mathbf{r}_i))$$
$$=\frac{1}{\beta^2}\sum_{i=1}^{N}\langle|\nabla\varphi(\mathbf{r}_i)|^2\rangle; \tag{17}$$

again, there is no surface contribution in the integration by parts, for the same reasons as earlier.

We therefore have

$$\langle|\mathbf{B}|^2\rangle=\frac{1}{\beta}\sum_{i,j=1}^{N}\langle\varphi(\mathbf{r}_i)\varphi^*(\mathbf{r}_j)\nabla_i\cdot\nabla_j U\rangle$$
$$+\frac{1}{\beta^2}\sum_{i=1}^{N}\langle|\nabla\varphi(\mathbf{r}_i)|^2\rangle. \tag{18}$$

At this point the two boundary conditions require separate discussions.

CASE 1. PERIODIC BOUNDARY CONDITIONS

For a given configuration of the $\mathbf{r}_1\cdots\mathbf{r}_N$, the potential energy U is just

$$\sum_{i=1}^{N}e\phi(\mathbf{r}_i), \tag{19}$$

where $\phi(\mathbf{r}_i)$ is the periodic electrostatic potential at $\mathbf{r}_i$ due to (a) the uniform positive background, (b) the other N-1 particles at $\mathbf{r}_k$, $k\neq i$, and (c) all the periodic images of the other particles, i.e., particles at $\mathbf{r}_k+\mathbf{R}$, $\mathbf{k}\neq i$ for all $\mathbf{R}$ of the form $(n_1, n_2, n_3)L$, with the n_i positive or negative integers.

The reason U has been described in this roundabout way rather than writing it explicitly in terms of the appropriate pair and single particle potentials is that, as is well known,[8] the explicit series is only conditionally convergent and must be summed in the correct order in order to yield the correct result. Rather than worrying about the possible hazards of differentiating term by term a series so delicately convergent, it is preferable to evaluate the first term in (18) using only properties of U that the complete summed series must certainly satisfy.

To begin with $-\nabla_i U$ must be the force acting on the ith particle, and therefore

$$\nabla_i U=-e\mathbf{E}_i. \tag{20}$$

Gauss's law then gives

$$\nabla_i^2 U=-4\pi e\rho_i,$$

where ρ_i is the charge density at the site of the ith particle;

$$\rho_i=e\sum_{\mathbf{R}}\sum_{k\neq i}\delta(\mathbf{r}_i-\mathbf{r}_k-\mathbf{R})-en.$$

We thus have

$$\nabla_i\cdot\nabla_j U=-4\pi e^2\sum_{\mathbf{R}}\sum_{k\neq i}\delta(\mathbf{r}_i-\mathbf{r}_k-\mathbf{R})+4\pi ne^2,\quad i=j. \tag{21}$$

Furthermore, when $i\neq j$,

$$\nabla_j\cdot\mathbf{E}_i=\nabla_j\cdot\mathbf{E}_i^j,$$

where $\mathbf{E}_i^j$ is the field acting on the ith particle due to the

[8] The Coulomb sum problem in the context of the electron gas is discussed in Ref. 5.

jth particle and its periodic extensions only. Since $\mathbf{E}_i{}^j = -\mathbf{E}_j{}^i$,

$$\nabla_j \cdot \mathbf{E}_i = -\nabla_j \cdot \mathbf{E}_j{}^i = -4\pi e \sum_{\mathbf{R}} \delta(\mathbf{r}_i - \mathbf{r}_j - \mathbf{R})$$

and hence

$$\nabla_i \cdot \nabla_j U = 4\pi e^2 \sum_{\mathbf{R}} \delta(\mathbf{r}_i - \mathbf{r}_j - \mathbf{R}), \quad i \neq j. \tag{22}$$

The contribution of (22) to the first term in (18) precisely cancels the contribution from the δ-function terms in (21). All that remains is the contribution from the constant term in (21) and therefore

$$\begin{aligned}\langle |B|^2\rangle &= \frac{4\pi n e^2}{\beta} \sum_{i=1}^{N} \langle |\varphi(r_i)|^2\rangle + \frac{1}{\beta^2} \sum_{i=1}^{N} \langle |\nabla\varphi(\mathbf{r}_i)|^2\rangle \\ &= \frac{1}{\beta^2} \sum_{i=1}^{N} \langle |\nabla\varphi(\mathbf{r}_i)|^2 + k_D{}^2 |\varphi(\mathbf{r}_i)|^2\rangle.\end{aligned} \tag{23}$$

Evaluating the Schwartz inequality (9) with the forms given in (12), (14), and (23), we find

$$\langle |\sum_{i=1}^{N} \psi(\mathbf{r}_i)|^2\rangle \geq \frac{|\sum_{i=1}^{N} \langle \varphi(\mathbf{r}_i) \nabla\psi^*(\mathbf{r}_i)\rangle|^2}{\sum_{i=1}^{N} \langle |\nabla\varphi(\mathbf{r}_i)|^2 + k_D{}^2 |\varphi(\mathbf{r}_i)|^2\rangle}. \tag{24}$$

The choice

$$\varphi(\mathbf{r}) = \psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}, \quad \mathbf{k} = (2\pi/L)(n_1, n_2, n_3)$$

is consistent with the periodicity requirements and reduces (24) to

$$\langle |\sum_{i=1}^{N} e^{i\mathbf{k}\cdot\mathbf{r}_i}|^2\rangle \geq \frac{Nk^2}{(k^2 + k_D{}^2)}. \tag{25}$$

If both sides of (25) are divided by N, the desired inequality (5) follows in the thermodynamic limit.

CASE 2. IMPENETRABLE-WALL BOUNDARY CONDITIONS

Equation (23) remains valid. It can be derived as earlier or, less fussily, directly from the explicit form for U:

$$U = \tfrac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} - \frac{N}{\Omega} \sum_{i=1}^{N} \int_{\Omega} d\mathbf{r} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}|}. \tag{26}$$

We again choose

$$\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}, \quad \mathbf{k} \text{ arbitrary}, \tag{27}$$

but now pick

$$\varphi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} f(\mathbf{r}), \tag{28}$$

where $f(\mathbf{r})$ is a real continuous differentiable function that vanishes on the walls of the box, as required to justify the integrations by parts. Equations (27) and (28) now reduce (24) to

$$(1/N)\langle |\sum_{i=1}^{N} e^{i\mathbf{k}\cdot\mathbf{r}_i}|^2\rangle \geq \frac{k^2 \langle (1/N) \sum_{i=1}^{N} f(\mathbf{r}_i)\rangle^2}{(k^2 + k_D{}^2)\langle (1/N) \sum_{i=1}^{N} f(\mathbf{r}_i)^2\rangle + \langle (1/N) \sum_{i=1}^{N} |\nabla f(\mathbf{r}_i)|^2\rangle}. \tag{29}$$

In terms of the mean number density, defined as the ensemble average of (3),

$$n(\mathbf{r}) = \langle \hat{n}(\mathbf{r})\rangle;$$

we can write (29)

$$S(\mathbf{k}) \geq \lim \frac{k^2 [(1/N) \int_{\Omega} d\mathbf{r}\, n(\mathbf{r}) f(\mathbf{r})]^2}{(1/N) \int_{\Omega} d\mathbf{r}\, n(\mathbf{r}) f^2(\mathbf{r})(k^2 + k_D{}^2) + (1/N) \int_{\Omega} d\mathbf{r}\, n(\mathbf{r}) |\nabla f(\mathbf{r})|^2}. \tag{30}$$

Let Ω_s be the set of points within a distance $aL^{1/2}$ of the walls of the box, where a is independent of L, and pick a set of f's satisfying the additional conditions: (1) $0 \leq f \leq 1$ in Ω_s, (2) $f = 1$ everywhere in Ω outside of Ω_s, (3) $|\nabla f| < bL^{-1/2}$ in Ω_s, for some b independent of L. Then

$$\begin{aligned}\frac{1}{N} \int_{\Omega} d\mathbf{r}\, n(\mathbf{r}) f(\mathbf{r}) &\geq \frac{1}{N}\left(\int_{\Omega} d\mathbf{r}\, n(\mathbf{r}) - \int_{\Omega_s} d\mathbf{r}\, n(\mathbf{r})\right) \\ &= 1 - \frac{1}{N} \int_{\Omega_s} d\mathbf{r}\, n(\mathbf{r});\end{aligned} \tag{31}$$

$$\frac{1}{N} \int_{\Omega} d\mathbf{r}\, n(\mathbf{r}) f^2(\mathbf{r}) \leq \frac{1}{N} \int_{\Omega} d\mathbf{r}\, n(\mathbf{r}) = 1; \tag{32}$$

$$\frac{1}{N} \int_{\Omega} d\mathbf{r}\, n(\mathbf{r}) (\nabla f(\mathbf{r}))^2 < \frac{b^2}{NL} \int_{\Omega_s} d\mathbf{r}\, n(\mathbf{r}). \tag{33}$$

Equations (31)–(33) reduce (30) to the desired inequality (5) in the thermodynamic limit, provided we make the additional assumption that the fraction of the total number of electrons in Ω_s vanishes in the thermodynamic limit:

$$\lim_{\substack{N \to \infty \\ N/\Omega \to n}} \frac{1}{N} \int_{\Omega_s} d\mathbf{r}\, n(\mathbf{r}) = 0. \tag{34}$$

This condition is certainly satisfied by the uniform

equilibrium state and the electron crystal, since both are electrically neutral on a macroscopic scale.[9]

INTERNAL AND FREE ENERGIES

The inequality (6) for the internal energy u follows from (5) and the general result[10]:

$$u=\tfrac{3}{2}k_BT+\frac{1}{2\Omega}\sum_{\mathbf{k}\neq 0}\frac{4\pi e^2}{k^2}(S(\mathbf{k})-1)\xrightarrow[N/V\to\Omega]{N,V\to\infty}\tfrac{3}{2}k_BT+\frac{1}{2}\int\frac{d\mathbf{k}}{(2\pi)^3}\frac{4\pi e^2}{k^2}(S(\mathbf{k})-1)\,. \quad (35)$$

Placing the lower bound (5) for $S(\mathbf{k})$ in (35) and evaluating the integral leads directly to (6).

Finally (7) follows routinely from (6) by noting that

$$\partial f/\partial e^2=(1/e^2)u\,, \quad (36)$$

replacing the right side of (36) by its lower bound for each e^2, and integrating with respect to e^2 from zero to the actual value of the electronic charge.

[9] Although it is highly implausible that an equilibrium state violating (34) could have lower free energy than a uniform or crystalline state, we are not aware of a proof of this.

[10] See, for example, D. Pines and P. Nozieres, *The Theory of Quantum Liquids I* (W. A. Benjamin, Inc., New York, 1966), equation on the top of p. 297 (but note that a factor of $1/\Omega$ is missing on the right). The argument works equally well for the classical internal energy in thermal equilibrium and does not assume a spatially homogeneous equilibrium state. The proof is routine for impenetrable-wall boundary conditions, following directly from the explicit form (26) for U. The legitimacy of the operations leading to (35) is somewhat less clear when periodic boundary conditions are used, but the result is widely accepted.

PHYSICAL REVIEW VOLUME 171, NUMBER 1 5 JULY 1968

Effect of the Gravitational Field on the Superfluid Transition in He^4

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(Received 27 December 1967)

It is shown experimentally that in a liquid helium sample of finite height, He II and He I coexist in thermodynamic equilibrium over a finite temperature range. This is contrary to a recent theoretical prediction. Observations made by noting the position of the boundary between the phases of high and low thermal conductivity as a function of temperature are quantitatively confirmed by high-resolution heat-capacity measurements near the transition region. The rate of movement with temperature of the interface between the two phases yields a slope for the transition line of 113.9±4.6 atm/°K at saturated vapor pressure, in quantitative agreement with recent direct measurements.

INTRODUCTION

It is the purpose of this paper to present experimental evidence which demonstrates that in the gravitational field He^4 II and He^4 I can exist as two phases in equilibrium with each other, although the transition between them is not of first order.[1,2] In homogeneous samples, the coexistence of two phases is possible only if the transition is of first order. However, for inhomogeneous samples, such as tall liquid samples, where the pressure is not constant, it is possible in principle to establish an equilibrium phase boundary even if the transition between the phases is of higher order.[3] Although the experimental demonstration of the existence of such a phase boundary in a system with a higher order transition is of some interest for its own sake, the case of the superfluid transition in helium is of particular interest at the present because it has been predicted[4] on the basis of the phenomenological theory of superfluidity[5] that coexistence of He^4 II and He^4 I is impossible even in the gravitational field. Before proceeding to the experimental section of this paper, a brief discussion of the classically expected effect and of the theoretical predictions will be given.

In a liquid sample of height H, the pressure at the bottom is larger than at the top by

$$\Delta P=\rho gH\,, \quad (1)$$

where ρ is the density and g the gravitational acceleration. In liquid helium, the temperature derivative of the transition pressure is negative. Therefore, it is to be expected that the transition temperature at the bottom ($T_\lambda{}^H$) is lower than at the liquid surface ($T_\lambda{}^S$) by

$$\Delta T_\lambda=\rho gH(dT/dP)_\lambda=aH\,. \quad (2)$$

[1] G. F. Kellers, thesis, Duke University, 1960 (unpublished); W. M. Fairbank, M. J. Buckingham, and C. F. Kellers, in *Proceedings of the Fifth International Conference on Low Temperature Physics and Chemistry*, edited by J. R. Dillinger (University of Wisconsin Press, Madison, Wisc., 1958), p. 50.

[2] G. Ahlers, Phys. Rev. **164**, 259 (1967).

[3] A. B. Pippard, *Elements of Classical Thermodynamics* (Cambridge University Press, New York, 1964), p. 155.

[4] L. V. Kiknadze, Tu. G. Mamaladze, and O. D. Cheishvili, Zh. Eksperim. i Teor. Fiz., Pis'ma v Redaktsiyu **3**, 305 (1966) [English transl.: Soviet Phys.—JETP Letters **3**, 197 (1966)].

[5] V. L. Ginzburg and L. P. Pitaevskii, Zh. Eksperim. i Teor. Fiz. **34**, 1240 (1958), [English transl.: Soviet Phys.—JETP **34**, 858 (1958)].