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Asymptotic form of the classical one-component plasma fluid equation of state*

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(Received 23 February 1976)

The Monte Carlo data of Hansen for the internal energy of the classical one-component plasma in the fluid state is found to satisfy accurately a simple functional form, $U/NkT = a\Gamma + b\Gamma^{1/4} + c$, for $\Gamma > 1$. The fluid static energy is very close to the bcc lattice energy of the solid, and the fluid thermal energy varies as $T^{3/4}$. Simple and accurate expressions for other thermodynamic functions for the plasma fluid are given.

Hansen[1] has reported very accurate Monte Carlo calculations for the equilibrium thermodynamic properties of the classical one-component plasma (OCP) in the fluid state. In a second paper of the series Pollock and Hansen[2] reported similar calculations for the OCP in the solid phase, and the fluid-solid phase transition was studied. These "numerical experiments" are considerably more accurate and complete than the results in the pioneering work of Brush, Sahlin, and Teller[3] (BST). In terms of the conventional Coulomb coupling parameter,

$$\Gamma = (Ze)^2/kT\bar{r}, \tag{1}$$

where $\bar{r}$ is the ion-sphere radius,

$$\bar{r} = (\tfrac{4}{3}\pi N/V)^{-1/3}.$$

Hansen gives results for the fluid OCP internal energy for 23 values[4] of Γ from 1 to 160, each obtained with Monte Carlo chains of 10^6 configurations of 128 point charges. These results map out almost the entire fluid branch of the OCP below the fluid-solid transition at $\Gamma \sim 155$. The data indicate that the fluid internal energy function, $U/NkT = f(\Gamma)$, can be divided into a fluid static energy portion and a thermal energy portion,

$$U/NkT = (U_0 + U_{th})/NkT = f(\Gamma) = a\Gamma + g(\Gamma). \tag{2}$$

In this note the fluid OCP data of Hansen will be used to deduce a simple analytical form for the fluid thermal energy function, $g(\Gamma)$.

In the solid phase the static energy has a clear meaning,[2] namely, the lowest lattice energy at $T = 0\,^{\circ}\mathrm{K}$; this is the bcc lattice for which the Madelung constant is $a = a_{bcc} = -0.895\,929$. The solid-phase thermal-energy function was found to be[2] $g(\Gamma) = \frac{3}{2} + 3500/\Gamma^2$, due to harmonic vibrations plus an anharmonic correction. The term OCP fluid static energy here means the $a\Gamma$ term in Eq. (2); it is the dominant portion of the total energy for $\Gamma > 1$, and this fact complicates the task of finding a functional form of the fluid thermal energy from Hansen's 23 data points. The thermal energy is approximately 35% of the static energy at $\Gamma = 1$, about 15% at $\Gamma = 40$, and less than 2% at $\Gamma = 160$. Consequently the Monte Carlo results for the total energy must be accurate to 0.1% in order to obtain the thermal-energy portion to an accuracy of a few percent, particularly for large Γ. Hansen states that his thermal-energy results are expected to be accurate to about 1% for all values of Γ. Our analysis of his data suggests that his results are indeed this accurate or better for the ten data points in the smaller Γ range $1 \leq \Gamma \leq 40$, but that the 13 data points in the larger Γ range $50 \leq \Gamma \leq 160$ are less accurate due to much larger Monte Carlo noise and a possible systematic error due to number dependence that becomes more pronounced near the phase transition.

Hansen fitted his entire range of data, listed in Table I, by the form

$$\frac{U}{NkT} = \Gamma^{3/2}\left(\frac{a_{bcc}}{(b_1+\Gamma)^{1/2}} + \frac{a_2}{b_2+\Gamma} + \frac{a_3}{(b_3+\Gamma)^{3/2}} + \frac{a_4}{(b_4+\Gamma)^2}\right)$$

and found six free parameters by least-squares optimization. Other fitting functions may represent the data better, and it was found that a four-parameter function,

$$U/NkT = a\Gamma + b\Gamma^s + c, \tag{3}$$

TABLE I. Monte Carlo OCP data, fits to the MC data, and HNC results. The $\Gamma=0.5$ MC value is from BST, with a center-of-mass correction. The 23 values from $\Gamma=1$ to 160 are from Hansen (Ref. 1) for $N=128$; the additional MC values at $\Gamma=70$, 100, and 140 are for $N=250$. The MC fits use Eqs. (6), (7), and (9). The HNC energy values for $\Gamma=0.5$ to 10 are from Ref. 6; the remainder are from Ref. 7. The HNC values for C_V/Nk are computed from Eq. (11).

	MC data				MC fits		HNC	
Γ	U/NkT	$\Delta U/NkT$	$f_1(\Gamma)$	C_V/Nk	$\Delta U/NkT$	C_V/Nk	U/NkT	C_V/Nk
0.5	− 0.246	0.202		0.061	0.186	0.014	− 0.236	0.027
1	− 0.580	0.316		0.11	0.317	0.111	− 0.570	0.116
2	− 1.318	0.474	−0.158	0.22	0.472	0.227		0.222
3	− 2.111	0.577		0.28	0.577	0.305	− 2.103	0.294
4	− 2.926	0.658	−0.290	0.35	0.659	0.365		0.350
6	− 4.590	0.786	−0.368		0.785	0.457		0.440
10	− 7.996	0.963		0.55	0.964	0.588	− 7.935	0.573
15	− 12.313	1.125		0.75	1.125	0.704		0.697
20	− 16.667	1.252	−0.675	0.80	1.252	0.794	− 16.537 71	0.799
30	− 25.429	1.449	−0.803	1.0	1.449	0.932		0.963
40	− 34.232	1.605	−0.898	1.06	1.605	1.039	− 33.999 23	1.098
50	− 43.094	1.702		1.16	1.736	1.127		1.214
60	− 51.936	1.820	−1.078	1.30	1.850	1.203	− 51.597 35	1.318
70	− 60.807	1.908		1.40	1.953	1.270		1.412
		1.928		1.37				
80	− 69.690	1.984	−1.226	1.25	2.046	1.330	− 69.263 88	1.500
90	− 78.569	2.065		1.6	2.132	1.385		1.581
100	− 87.480	2.113	−1.292	1.5	2.213	1.435	− 86.973 42	1.658
		2.148		1.55				
110	− 96.360	2.192		1.5	2.288	1.482		1.730
120	−105.284	2.227	−1.412	1.8	2.359	1.526	−104.713 14	1.799
125	−109.732	2.259		1.6	2.394	1.546		1.832
130	−114.182	2.289		1.5	2.428	1.566		1.865
140	−123.095	2.335	−1.481	1.8	2.492	1.605	−122.475 61	1.928
		2.37		2.15				
155	−136.44	2.43		1.9	2.584	1.659		2.018
160	−140.89	2.46	−1.510	1.9	2.614	1.677	−140.255 62	2.047

with a, b, c, and s found by a nonlinear least-squares program, did in fact fit the entire range of data with a considerably smaller standard deviation than Hansen's fit. The exponent s is a small number, $s\sim\frac{1}{4}$, whereas Hansen's function for large Γ gives an expansion in inverse powers of $\Gamma^{1/2}$. Also, in Hansen's function the static energy term for the OCP fluid was *assumed* to be the static energy for the bcc lattice. In our work the constant a for the fluid static energy is left as a free parameter to be determined by the data.

In principle the form of the thermal-energy function could be found by integrating the heat capacity at constant volume,

$$\frac{C_V}{Nk}=\frac{d(U/Nk)}{dT}$$
$$=-\Gamma^2\frac{d}{d\Gamma}\left(\frac{f(\Gamma)}{\Gamma}\right)$$
$$=-\Gamma^2\frac{d}{d\Gamma}\left(\frac{g(\Gamma)}{\Gamma}\right). \tag{4}$$

Unfortunately the Monte Carlo noise in the C_V/Nk data (obtained from a difference of large numbers, $\langle U^2\rangle-\langle U\rangle^2$), is too large to allow the C_V data to be useful for obtaining the form of $g(\Gamma)$. However, one can use the much more accurate data for U/NkT directly to find $g(\Gamma)$ by forming the function

$$f_1(\Gamma)=f(\Gamma)-2f(\tfrac{1}{2}\Gamma)$$
$$=g(\Gamma)-2g(\tfrac{1}{2}\Gamma). \tag{5}$$

Hansen's 23 data points for $f(\Gamma)$ give the 12 values of $f_1(\Gamma)$ shown in Fig. 1, and this function has the form $B\Gamma^s+C$, with $s=\frac{1}{4}$. In this way the thermal-energy function was found directly from the data without needing the exact value of the fluid static energy constant a.

In order to fix the exponent s as exactly as possible, various ranges of the U/NkT data were fitted by Eq. (5) with a nonlinear least-squares program giving a, b, c, and s and also a linear program giving a, b, and c for assumed values of s; the standard deviation $\sigma(s)$ was computed for all

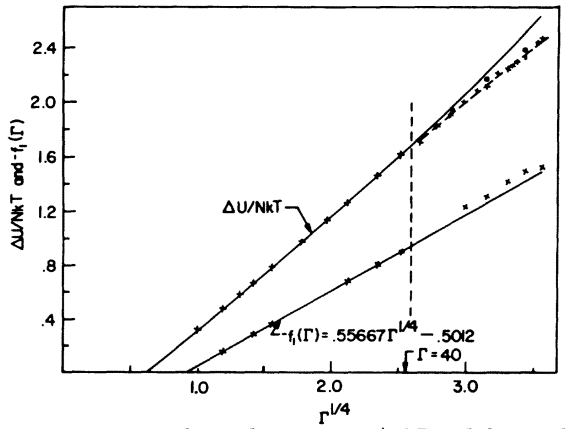

FIG. 1. Excess thermal energy $\Delta U/NkT$ and the auxiliary function $-f_1(\Gamma)$ vs $\Gamma^{1/4}$. The $-f_1(\Gamma)$ points up to $\Gamma = 40$ lie on a perfect straight line. The solid line for $\Delta U/NkT$ is computed with Eq. (6), and has a positive curvature because of the positive $\Delta a\Gamma$ term in Eq. (7). The dashed line through the larger Γ values of $\Delta U/NkT$ is a plot of Eq. (8), and has a negative curvature.

fits. The ten data points in the lower range, $1 \leq \Gamma \leq 40$, fell on a very smooth curve with a small $\sigma(s)$ that had a sharp minimum near $s = 0.25$; the best value of s was $s = 0.247 \pm 0.009$. Thus within statistical error the Monte Carlo (MC) data for the smaller Γ range give $s = \frac{1}{4}$; consequently, the dominant temperature dependence of the thermal energy is $U_{\text{th}} \sim T^{3/4}$. With $s = 0.25$ the best fit to the ten data points is

$$U/NkT = -(0.894\,61 \pm 0.000\,03)\Gamma + (0.8165 \pm 0.0008)\Gamma^{1/4} - (0.5012 \pm 0.0016), \quad (6)$$

with $\sigma = 0.0009$. The fluid static energy obtained in this manner from the data is

$$U_0/NkT\Gamma = a = a_{\text{bcc}} + \Delta a = -0.894\,61,$$

which is above the bcc lattice energy by $\Delta a = 0.001\,32$, or 0.15%. The excess thermal energy (the energy above the bcc lattice value at $T = 0\,^\circ\text{K}$)

$$\Delta U/NkT = (U_{\text{MC}} - U_{\text{bcc}})/NkT = \Delta a\Gamma + g(\Gamma) \quad (7)$$

obtained from Eq. (6) for the $\Gamma \leq 40$ range is shown in Fig. 1. When extended to the large-Γ range, Eq. (6) gives results for $\Delta U/NkT$ a few percent larger than Hansen's results.

The 11 data points in the large-Γ range, $50 \leq \Gamma \leq 140$, had too much noise to determine the exponent s to better than $s = 0.3 \pm 0.1$. With s assumed to be 0.25, the best fit to the data gave

$$U/NkT = -(0.8966 \pm 0.0001)\Gamma + (0.874 \pm 0.009)\Gamma^{1/4} - (0.568 \pm 0.023), \quad (8)$$

with $\sigma = 0.0060$. The coefficients a, b, and c are significantly different from the values in Eq. (6), and the difference is far greater than the estimated statistical errors. Thus there appears to be a kink in Hansen's data at $\Gamma = 50$. A possible explanation is that 128 charges is insufficient to accurately represent the $N = \infty$ system for large Γ. Hansen gives results for $\Delta U/NkT$ obtained with 250 charges at $\Gamma = 70$, 100, and 140 that are, respectively, 1.0%, 1.5%, and 1.3% larger than the corresponding results for $N = 128$. These differences, although small, account for about half of the difference between Eqs. (6) and (8) for $\Gamma = 70$ and 100. The calculation of the Ewald potential with five Kubic harmonics rather than four may also lead to about 1% increase in $\Delta U/NkT$ for large Γ. The values of $\Delta U/NkT$ for $\Gamma = 155$ and 160 are three or four standard deviations above the values expected from Eq. (8) (see Fig. 1), and were not used.

The $b\Gamma^{1/4} + c$ form of the OCP fluid thermal energy is evidently an asymptotic form for the stongly coupled system, $\Gamma \geq 1$. In fact Eq. (6) reproduces the MC data with great accuracy down to $\Gamma = 1$; it must clearly fail for $\Gamma < 1$, since as $\Gamma \to 0$, the energy must go over to the Debye-Huckel form, $U/NkT = -\frac{1}{2}3^{1/2}\Gamma^{3/2}$. At $\Gamma = 0.5$ the asymptotic form is about 10% below the BST value. It would be helpful to have a few more accurate MC results in the $0.3 < \Gamma < 1$ region in order to establish how the function $f(\Gamma)$ changes over to the Debye-Huckel form. The MC data of Hoover *et al.*[5] for fluids governed by inverse power potentials, $u(r) \sim 1/r^n$, can also be well fitted by this form of the thermal energy.

The heat capacity for the OCP, using Eqs. (4) and (6), is

$$C_v/Nk = (1 - s)b\Gamma^s - s = 0.670\,96\Gamma^{1/4} - 0.5012, \quad (9)$$

and this result agrees well with the noisy MC values for C_V/Nk.

The interaction part of the Helmholtz free energy obtained from Eq. (6) is

$$\frac{F}{NkT} = \int_{\Gamma_1}^{\Gamma} d\Gamma' \frac{(U/NkT)}{\Gamma'} + \frac{F(\Gamma_1)}{NkT_1} = a\Gamma + \frac{1}{s}b\Gamma^s + c\ln\Gamma + d = -0.894\,61\Gamma + 3.265\,91\Gamma^{1/4} - 0.501\,23\ln\Gamma - 2.816. \quad (10)$$

The entropy constant d is obtained with $\Gamma_1 = 1$ and $F(1)/NkT_1 = -0.445$. Hansen's fluid free-energy expression obtained from his fitting form with the

large-Γ data for $N = 128$ intersects the solid free energy[2] at $\Gamma = 158$. This estimate of the location of the fluid-solid transition is very sensitive to small changes in $\Delta U/NkT$. The three slightly higher values of $\Delta U/NkT$ obtained with 250 charges gives an estimate of the free energy that lowers the transition to about 150. Using Eq. (10), which may be a better estimate for the $N = \infty$ system, lowers the transition point to about $\Gamma = 144$.

Of the various integral equations applied to the OCP the hypernetted chain (HNC) equation gives the best results when compared to the MC data.[6] Ng[7] has solved the HNC equation for Γ up to 7000, and has obtained very accurate results for U/NkT. Since there is no noise in Ng's numerical results, the method indicated by Eq. (4) could determine the exact functional form of the thermal-energy function $g(\Gamma)$ for HNC's as $b\Gamma^{1/2} + c \ln\Gamma + d$. The results are

$$(U/NkT)_{\mathrm{HNC}} = -0.900\,470\Gamma + 0.268\,826\,3\Gamma^{1/2} + 0.071\,999\,25 \ln\Gamma + 0.053\,791\,9\,, \tag{11}$$

$$(C_V/Nk)_{\mathrm{HNC}} = 0.134\,413\,2\Gamma^{1/2} + 0.071\,992\,5 \ln\Gamma - 0.018\,200\,6\,, \tag{12}$$

for $\Gamma > 1$. These asymptotic results for the HNC's U/NkT and C_V/Nk break down for $\Gamma < 1$ is about the same way as do the analogous results obtained from the MC data, Eqs. (6) and (9). The HNC results and the MC data and fits are shown in Table I. The main reason for the apparent good agreement of HNC and MC results for the total energy is that the static term in the HNC energy is so close to that for the MC fluid static energy. The static term from HNC is nearly identical to the ion-sphere result[8] (-0.9Γ) and is 0.4% below the bcc lattice value, whereas the static term in Eq. (6) is 0.15% above the bcc lattice value. The thermal energy from HNC is very different in analytic form from the MC form, $\Gamma^{1/2}$ vs $\Gamma^{1/4}$, and the HNC thermal-energy function is numerically larger than the MC thermal-energy function; this difference is about 50% at $\Gamma = 100$.

In the HNC approximation all bridge graphs are neglected, whereas the effects of the bridge graphs are necessarily present in the MC results. At present there is no clear theoretical model that can account for the $\Gamma^{1/4}$ form of the MC thermal energy.

The author wishes to thank J. P. Hansen, W. G. Hoover, F. H. Ree, and S. M. Stishov for numerous stimulating and critical discussions. The help of J. Levatin with the innumerable least-squares fits was invaluable.

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*Work performed under the auspices of the U. S. Energy Research and Development Administration under contract No. W-7405-Eng-48.

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