Critical examination of N dependence in the Monte Carlo calculations for a classical one-component plasma

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On the basis of Monte Carlo (MC) data from newly performed simulations for classical one-component plasma (OCP) as well as those from earlier work, we examine critically the validity of the center-of-mass correction through comparative studies on how the computed values of the excess internal energies depend on the number N of the MC particles. It is thereby concluded that the correction cannot be justified for the fluid OCP; an alternative internal-energy formula is derived.

In 1982, Slatter, Doolen, and DeWitt (SDD)[1] calculated the internal energy of the classical one-component plasma (OCP) using a Monte Carlo (MC) technique for 128, 250, 432, 686, and 1024 particles at various Γ for $1<\Gamma<300$, and thereby investigated the effect of a differing number of particles (denoted as N) on the thermodynamics. The parameter, $\Gamma=(\mathrm{Ze})^2/ak_BT$, characterizes the strength of Coulomb coupling for such an OCP,[2] with electric charge Ze, the ion-sphere radius $a=(3/4\pi n)^{1/3}$, number density n, and temperature T.

The excess internal energy of the OCP may be formulated as

$$\frac{U_{\mathrm{ex}}}{Nk_BT}=\frac{n}{2k_BT}\int d\mathbf{r}\frac{(\mathrm{Ze})^2}{r}[g(r)-1]\ , \tag{1}$$

where $g(r)$ is the radial distribution function. Equation (1) calculated directly from the MC average shall be denoted as U_{MC}/Nk_BT.

SDD obtained the excess internal energy with the "center-of-mass correction," so that

$$\frac{U}{Nk_BT}=\frac{U_0}{Nk_BT}+\left[\frac{U_{\mathrm{MC}}}{Nk_BT}-\frac{U_0}{Nk_BT}\right]\frac{N}{N-1}\ , \tag{2}$$

where

$$U_0/Nk_BT=a_{\mathrm{bcc}}\Gamma \tag{3}$$

is the Madelung energy of the bcc Coulombic lattice with $a_{\mathrm{bcc}}=-0.895\,929$. With these corrections, SDD derived accurate fitting formulas for the MC data, both in the fluid phase ($1\le\Gamma\le170$) and in the bcc crystalline phase ($170<\Gamma<300$), which contained N-dependent terms as

$$\left[\frac{U}{Nk_BT}\right]_{\mathrm{fluid}}=a\Gamma+b\Gamma^{1/4}+c\Gamma^{-1/4}+d+e\frac{\Gamma}{N}\ , \tag{4}$$

$$\left[\frac{U}{Nk_BT}\right]_{\mathrm{bcc}}=a_{\mathrm{bcc}}\Gamma+1.5+h\Gamma^{-2}+m\frac{\Gamma}{N}\ . \tag{5}$$

Here $a=-0.897\,744$, $b=0.950\,43$, $c=0.189\,56$, $d=-0.814\,87$, $e=0.009\,656$, $h=3225$, and $m=-0.000\,658\,7$. Comparing between the Helmholtz free energies in the fluid phase and in the crystalline phase, which were obtained through coupling-constant integrations[2] of Eqs. (4) and (5) in the $N\to\infty$ limit, they found the Γ value of the fluid-solid transition to be $\Gamma_m=178\pm1$.

The importance of the center-of-mass correction (2) was noted originally in the paper by Hoover *et al.*[3] Subsequently, in his OCP calculations, Hansen[4] remarked explicitly that because the center of mass of the system was not fixed in the MC calculations, the fraction of the internal energy due to the thermal motion of the particles, i.e., the difference between the excess internal energy and its purely static value U_0 must be multiplied by the factor $N/(N-1)$; hence Eq. (2) results.

The center-of-mass correction as stated above is rather easy to accept physically for a crystalline system, and can in fact be verified *a posteriori* with Eq. (5). The purely static value of the excess internal energy, i.e., that part of U independent of T is indeed given by U_0 in Eq. (5); the major part of the thermal energy, i.e., the harmonic contribution $1.5Nk_BT$ is simply proportional to N.

The center-of-mass correction is not so easy to accept physically in the case of a fluid system; however, neither can it be verified *a posteriori* with Eq. (4). For one thing, its static part $a\Gamma$ is different from U_0/Nk_BT, and the difference widens as Γ increases. The thermal parts retain weak but non-negligible N dependence in $b\Gamma^{1/4}$ and $c\Gamma^{-1/4}$, for another. The fact that the coefficient e of the N^{-1} correction term in Eq. (4) is greater by an order of magnitude than the corresponding coefficient m in Eq. (5) may even be interpreted as an evidence implying that Eq. (4) may contain a spurious N^{-1} dependence induced by a presumably unjustifiable use of Eq. (2) for a fluid state.

In this paper we make an issue out of the points raised in the preceding paragraph and examine critically the validity of Eq. (2), through comparative studies of the N^{-1} dependence between the raw, uncorrected MC values U_{MC} and the reprocessed values U via Eq. (2). In so doing, we have performed a set of new MC calcula-

tions with quality comparable to SDD's; both the new and SDD's original data are used for the examinations of those N^{-1} dependences. We thereby find that in the fluid state the N^{-1} dependence is definitely *more enhanced* in U/Nk_BT than in U_{MC}/Nk_BT; it appears that Eq. (2) may have *generated* extra N^{-1} dependence, reflected in the magnitude of the coefficient e in Eq. (4). We thus conclude that the correction procedure (2) cannot be justified for the fluid OCP in light of those MC data currently available. On the other hand, we find that Eq. (2) acts significantly to *reduce* the N^{-1} dependence in the evaluations of the excess internal energies for a crystalline state; we here conclude that the correction procedure (2) is valid both conceptually and practically.

Table I lists the MC data which we have used for the examinations of N dependence. The numbers of configurations[1] in the MC calculations performed by the present authors (designated as P) are $(6-7)\times10^6$ and substantially smaller than those in some of SDD's calculations (designated as S). Correspondingly the standard deviations σ of the means of 10^5 configuration averages in P are somewhat larger than those in S; we have detected no systematic deviations in the values of U_{MC}, however, between those two sets of the MC calculations.

In Fig. 1 we treat the five cases of the MC runs at $\Gamma=80$ in P and plot the corrected (U/Nk_BT) and uncorrected (U_{MC}/Nk_BT) values (minus a constant value U_∞/Nk_BT) with error bars ($\pm\sigma$) as functions of N^{-1}, where U_∞/Nk_BT designates the value of Eq. (4) *without* the final correction term proportional to N^{-1}. We observe here that the uncorrected values (solid circles) remain almost constant, independent of N^{-1}, while the corrected values (solid squares) follow the dashed line corresponding to the final term $e\Gamma/N$ of Eq. (4). This may substantiate the aforementioned conjecture that bulk of the $e\Gamma/N$ term in Eq. (4) may have been generated by the use of (presumably unnecessary) correction procedure as expressed in Eq. (2).

Figures 2 and 3 show analogous comparisons at $\Gamma=160$ in P and in S, respectively. Although not so conspicuously as in Fig. 1, we clearly find in those figures as well that the N^{-1} dependence is more enhanced in U/Nk_BT than in U_{MC}/Nk_BT.

In Fig. 4 we examine N^{-1} dependence in the bcc lattice simulations at $\Gamma=200$ in S; here U_∞/Nk_BT desig-

TABLE I. Excess internal energies calculated in the MC simulations. (P refers to the present calculations; S, from Ref. 1.) The cases with $\Gamma=80$, 120, and 160 are fluid simulations; the cases with $\Gamma=200$, bcc lattice simulations.

Γ	U/Nk_BT	U_{MC}/Nk_BT	Error $\pm\sigma$	N	Configuration (millions)	
80	−69.717	−69.732	0.0022	128	7.7	P
80	−69.726	−69.734	0.0024	250	6.7	P
80	−69.728	−69.732	0.0023	432	5.7	P
80	−69.726	−69.729	0.0025	686	6.7	P
80	−69.730	−69.732	0.0023	1024	6.7	P
80	−69.715	−69.731	0.0022	128	9.0	S
80	−69.721	−69.729	0.0024	250	9.0	S
80	−69.725	−69.728	0.0011	686	30.8	S
120	−105.321	−105.338	0.0035	128	7.7	P
120	−105.334	−105.343	0.0031	250	6.7	P
120	−105.345	−105.350	0.0026	432	7.7	P
120	−105.348	−105.351	0.0031	686	6.7	P
120	−105.351	−105.353	0.0029	1024	6.7	P
120	−105.323	−105.340	0.0045	128	5.8	S
120	−105.342	−105.345	0.0015	686	31.8	S
120	−105.345	−105.347	0.0017	1024	23.0	S
160	−141.005	−141.023	0.0053	128	7.7	P
160	−141.018	−141.027	0.0042	250	6.7	P
160	−141.035	−141.040	0.0043	432	7.7	P
160	−141.028	−141.031	0.0031	686	7.7	P
160	−141.033	−141.035	0.0032	1024	7.7	P
160	−141.000	−141.018	0.0057	128	8.6	S
160	−141.031	−141.040	0.0070	250	4.6	S
160	−141.039	−141.044	0.0041	432	6.6	S
160	−141.036	−141.040	0.0015	686	38.6	S
160	−141.036	−141.038	0.0016	1024	27.2	S
200	−177.605	−177.618	0.0031	128	9.9	S
200	−177.603	−177.609	0.0019	250	22.0	S
200	−177.605	−177.609	0.0019	432	26.0	S
200	−177.603	−177.605	0.0014	686	23.0	S

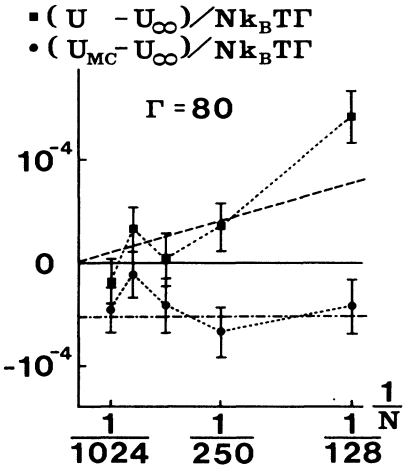

FIG. 1. Corrected (U/Nk_BT) and uncorrected (U_{MC}/Nk_BT) excess internal energies (minus a constant value U_∞/Nk_BT) vs N^{-1}, the inverse of the number of MC particles, at $\Gamma=80$ for the fluid simulations in the P cases (see the text). U_∞/Nk_BT is the value of Eq. (4) at $N\to\infty$; the dashed line represents $e\Gamma/N$, the last term of Eq. (4); the dot-dashed line corresponds to the value of Eq. (6).

nates the value of Eq. (5) *without* the final correction term proportional to N^{-1}. Contrary to the cases of the fluid simulations as exemplified in Figs. 1–3, we here observe a clear evidence for the validity of the correction procedure (2), in that the significant N^{-1} dependence contained in the uncorrected U_{MC}/Nk_BT data is erased almost completely in the corrected U/Nk_BT data. The center-of-mass correction is thus meaningful for the lattice simulations.

In light of the comparative studies as described above, and especially in view of the fact that the values of

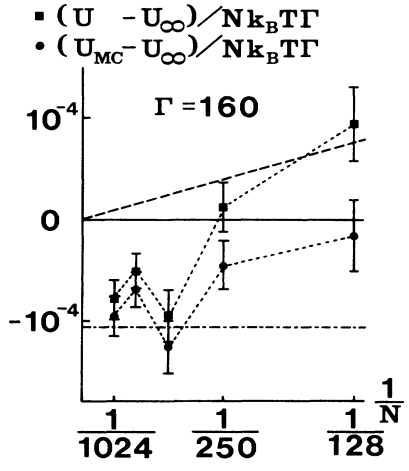

FIG. 2. The same as Fig. 1, but at $\Gamma=160$.

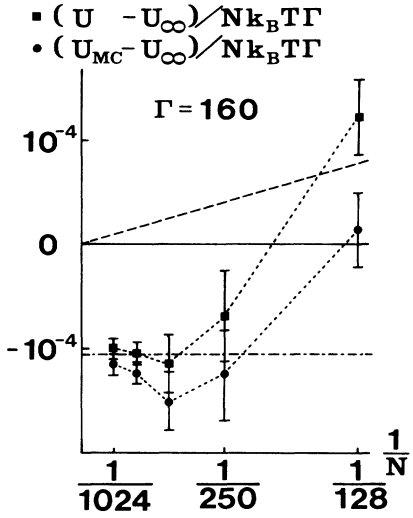

FIG. 3. The same as Fig. 1, but at $\Gamma=160$ in the S cases.

U_{MC}/Nk_BT stay almost constant within error bars for $N=432$, 686, and 1024 in the fluid simulations (cf. Figs. 1–3), we derive an alternative fitting formula for the excess internal energies of the fluid OCP, on the basis of the U_{MC} data at those three cases of N in the P and S simulations. Using the least-squares method, we find

$$\left[\frac{U_{MC}}{Nk_BT}\right]_{\text{fluid}} = -0.898\,004\Gamma + 0.967\,86\Gamma^{1/4} + 0.220\,703\Gamma^{-1/4} - 0.860\,97 \,. \quad (6)$$

In Figs. 1–3, the values of Eq. (6) are depicted by the dot-dashed lines. If we replace Eq. (4) by Eq. (6) and re-

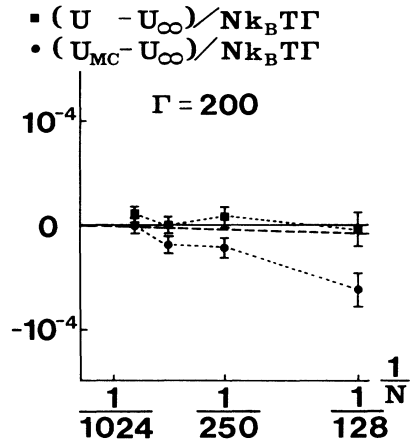

FIG. 4. The same as Fig. 1, but at $\Gamma=200$ for the bcc lattice simulations in the S cases. U_∞/Nk_BT is the value of Eq. (5) at $N\to\infty$; the dashed line represents $m\Gamma/N$, the last term of Eq. (5).

tain Eq. (5), we obtain a slightly different prediction $\Gamma_m = 180 \pm 1$ for the fluid-solid transition in the OCP.

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[2]See, e.g., S. Ichimaru, Rev. Mod. Phys. **54**, 1017 (1982).

[3]W. G. Hoover, M. Ross, K. W. Johnson, D. Henderson, J. A. Barker, and B. C. Brown, J. Chem. Phys. **52**, 4931 (1970).

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