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Low-order anharmonic contributions to the internal energy of the one-component plasma

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We present precise calculations of the second-order cubic and first-order quartic anharmonic contributions to the internal energy of the one-component plasma (OCP), which are then used with available computer-simulation data to estimate the size of higher-order anharmonic effects. We show that in both the zero-temperature and high-temperature limits the OCP is very harmonic. At zero temperature, we find that the two lowest-order anharmonic contributions are the largest anharmonic contributions, and of the two the second-order cubic contribution is nearly three times the first-order quartic. At high temperatures, we find that the second-order cubic contribution is about twice that of the first-order quartic, but their combined contribution to the internal energy is small compared with our estimate of the next-order anharmonic terms.

I. INTRODUCTION

The one-component plasma (OCP), a system of interacting point charges, embedded in a rigid, uniform background of neutralizing charge, is a useful model for a strongly interacting system having a phase transition. Almost all work on the OCP has been in the zero- or high-temperature limits. The zero-temperature limit describes the ground state which is a function of only one parameter, the density of the system. In the high-temperature limit Planck's constant disappears from all formulas and the system is therefore in a classical (as opposed to quantum-mechanical) regime. All physical properties also depend on only one parameter Γ, which is roughly the ratio of the potential and kinetic energies. Both the high- and low-temperature limits are much more tractable than the general case of arbitrary density and temperature. In this paper we limit our attention to these two limiting cases.

In addition to a considerable number of analytic studies,[1] the zero- and high-temperature properties of the model have been extensively investigated by computer simulations.[2-12] Besides providing useful benchmarks for analytic studies, they have also demonstrated a fluid to bcc solid transition. The analytic studies have been most useful in providing a quantitative understanding of the fluid phase rather than that of the solid phase. For the latter it is essential to understand how anharmonic effects contribute to the model's free energy. Since the importance of such effects is expected to grow as the density and temperature approach their melting values, several investigators have calculated infinite-order subsets of the anharmonic contributions by using self-consistent harmonic theory (SCH).[13-16] Unfortunately, as discussed by Albers and Gubernatis,[16] these corrections for the high-temperature properties, when compared to the computer-simulation data, are of the wrong size and sign.

The cause of this disagreement is found in the estimates of Carr *et al.*[17] for the second-order cubic and first-order quartic anharmonic contributions to the ground-state energy, the two lowest-order anharmonic contributions. The second-order cubic contribution is of greater size and opposite sign than the first-order quartic contribution. Since self-consistent harmonic theory ignores the cubic contribution while keeping the quartic one, the disagreement at high temperatures would be resolved if the second-order cubic contribution is the dominant term in the anharmonic expansion for the free energy. Using self-consistent phonon theory, Kugler[13] and Glyde and Keech[15] have also discussed the importance of the second-order term to the ground state.

In this note we present precise calculations of the second-order cubic and first-order quartic anharmonic contributions to the internal energy. We computed the internal energy instead of the free energy to facilitate comparisons with the Monte Carlo simulation. We then used our calculations and simulation data to estimate the size of the remaining higher-order anharmonic effects. We show that the zero- and high-temperature limits are both quite harmonic, that at zero temperature the lowest-order anharmonic contributions describe well the internal energy even at densities and temperatures approaching their values at melting, and that in the high-temperature limit at least the two lowest-order contributions are needed.

II. PERTURBATION CALCULATIONS

To lowest order in anharmonic effects, the free energy F of a crystal is[18-22]

$$F = F_0 + F_h + F_3 + F_4 \ , \qquad (1)$$

where F_0 is the static lattice contribution, F_h the harmonic contribution, F_3 the second-order cubic, and F_4 the first-order quartic contribution. Specifically,

$$F_3 = -6 \sum_{1,2,3} | V(1,2,3) |^2 W(1,2,3) \ ,$$

with

$$W(1,2,3) = \frac{(n_1+1)(n_2+n_3+1) - n_2 n_3}{\omega_1+\omega_2+\omega_3} - \frac{n_1(n_2+n_3+1) n_2 n_3}{\omega_1+\omega_2-\omega_3}$$

where $\hbar = 1$, n is the Bose function, and $V(1,2,3)$ is the Fourier transform of the third-order force-constant matrix as defined by Shukla and Cowley,[22] and

$$F_4 = 3 \sum_{1,2,3} V(1,-1,2,-2)(2n_1+1)(2n_2+1) ,$$

where $V(1,2,3,4)$ is the Fourier transform of the fourth-order force-constant matrix. The numbers 1, 2, and 3 label eigenfrequency, wave number, and branches. At $T=0$ the free energy, of course, is equal to the internal energy U. To obtain the internal energy at high temperature, we replace the Bose factors in these expressions by kT/ω and then use the thermodynamic relation

$$U = -T^2 \frac{\partial}{\partial T}(F/T) .$$

For the OCP the static and harmonic contributions to the internal energy are well known. If we scale all lengths by the cube edge a and scale the harmonic frequencies by the plasma frequency ω_p

$$\omega_p^2 = \frac{4\pi n e^2}{m} ,$$

where n is the density of point charges, then U at $T=0$, in units of rydbergs, is

$$\frac{U}{N} = \frac{-1.791\,85}{r_s} + \frac{2.657\,24}{r_s^{3/2}} - \frac{u_3 - u_4}{r_s^2} , \qquad (2)$$

where r_s is the Wigner-Seitz radius, and the cubic and quartic anharmonic coefficients are defined by

$$u_3 = \frac{1}{24}\left[\frac{3}{4\pi}\right]^{2/3} \frac{1}{N^2} \sum_{1,2,3} \frac{|V(1,2,3)|^2}{\omega_1+\omega_2+\omega_3} \Delta(q_1+q_2+q_3) \qquad (3a)$$

and

$$u_4 = \frac{1}{16}\left[\frac{3}{4\pi}\right]^{2/3} \frac{1}{N^2} \sum_{1,2} V(1,-1,2,-2) . \qquad (3b)$$

At high temperatures ($T \rightarrow \infty$)

$$\frac{U}{NkT} = -0.895\,929\,256\Gamma + 3 + \frac{u_3 - u_4}{\Gamma} , \qquad (4)$$

where the dimensionless parameter Γ equals $e^2/r_s kT$, and

$$u_3 = \frac{1}{36}\left[\frac{3}{4n\pi}\right]^{2/3} \frac{1}{N^2} \times \sum_{1,2,3} \frac{|V(1,2,3)|^2}{\omega_1\omega_2\omega_3} \Delta(q_1+q_2+q_3) \qquad (5a)$$

and

$$u_4 = \frac{1}{24}\left[\frac{3}{4n\pi}\right]^{2/3} \frac{1}{N^2} \sum_{1,2} \frac{V(1,-1,2,-2)}{\omega_1\omega_2} . \qquad (5b)$$

In Eqs. (2) and (4) the first term is the static electrostatic energy contribution, where all the ions are located at lattice positions. The second terms of Eqs. (2) and (4) are the harmonic contributions. With the sign convention adopted in these equations, the cubic and quartic contributions will have opposite signs if the coefficient u_4 has the same sign as u_3, which must be positive.

III. RESULTS

To calculate u_3 and u_4, we first computed the eigenvalues and eigenfrequencies of the harmonic lattice using the Ewald-like methods described by Cohen and Keffer[23] to handle the nearly divergent lattice sums. We then used these eigenvalues and eigenvectors to compute $V(1,2,3)$ and $V(1,-1,2,-2)$. The more convergent lattice sums involved with these transforms were easily and efficiently handled on a Cray computer by directly summing over the first 748 lattice vectors of the bcc lattice. Convergence of the sums for a given wave number and branch was typically 1 part in 10^6.

The Brillouin-zone integrations [the wave-vector summations in (5)] were much more difficult to do. To do them we used two different uniform meshes. A uniform mesh allowed us to vectorize the most time-consuming parts of the calculation and to handle easily the Δ function in (5a). Since the Δ function forces $\mathbf{q}_3$ to be the sum of $\mathbf{q}_1$ and $\mathbf{q}_2$ (within a reciprocal-lattice vector), the number of $\mathbf{q}_3$ wave vectors that occur equals the product of the numbers for $\mathbf{q}_1$ and $\mathbf{q}_2$. By symmetry one can choose $\mathbf{q}_1$ in the irreducible part of the Brillouin zone; the wave vectors $\mathbf{q}_2$, however, must range over the full Brillouin zone. Hence, the number of $\mathbf{q}_3$ vectors quickly becomes enormous even for a moderate number of points in the irreducible part of the zone. We found it prohibitively expensive to calculate the attendant phonon eigenvectors and eigenfrequencies for so many points. The uniform

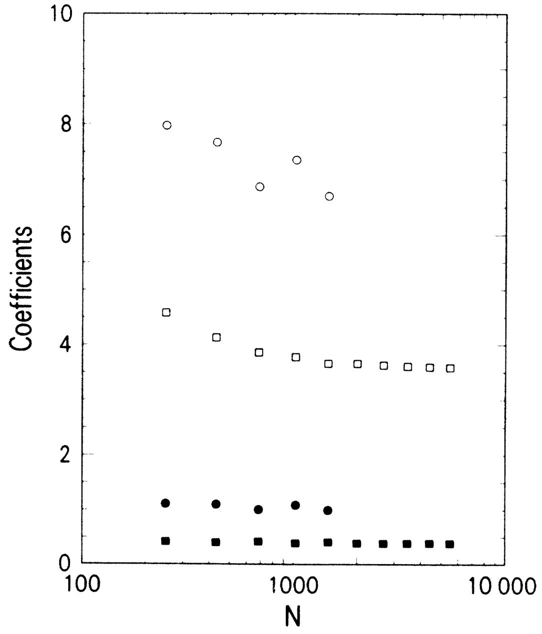

FIG. 1. Convergence of the coefficients u_3 and u_4 as a function of the number of points in a Wallace mesh in the first Brillouin zone. The circles represent u_3, and the squares, u_4; the open symbols are the high-temperature results; the solid symbols are the zero-temperature results.

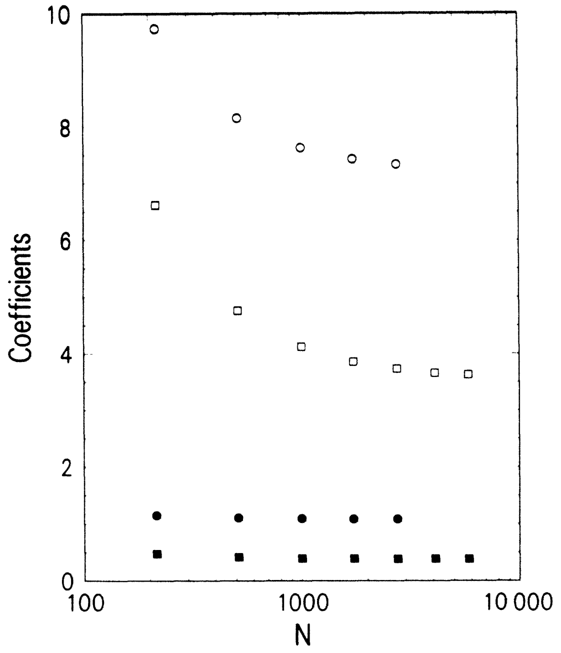

FIG. 2. Convergence of the coefficients u_3 and u_4 as a function of the number of points in a Born—von Kármán mesh in the first Brillouin zone. The circles represent u_3, and the squares, u_4; the open symbols are the high-temperature results; the solid symbols are the zero-temperature results.

mesh gets around this problem since the sum (or difference) of **q** points on a uniform mesh is also a member of the original uniform mesh, and hence only the small number of phonon frequencies and eigenvectors for this mesh need to be calculated.

Of the two different uniform meshes, one was that suggested by Wallace.[24] Although convergence was fastest for this mesh, it was also oscillatory, with the oscillation being most pronounced for the cubic contributions (Fig. 1). To determine the cubic contributions we used a Born—von Kármán mesh, that is, the wave vectors of a periodic lattice of N particles. For this mesh the convergence was uniform (Fig. 2). For the Wallace mesh the number of mesh points ranged from 249 to 5487, for the Born—von Kármán mesh from 215 to 5831.

Our estimates of the anharmonic contributions were obtained by extrapolating our data to an infinite N limit. We did this by fitting the three largest N results for each contribution to the form

TABLE I. Extrapolated values of the lowest-order anharmonic contributions. The dimensionless coefficients u_3 and u_4 are defined in (2) and (3).

	u_3	u_4
Zero temperature	1.087	0.384
High temperature	7.198	3.551

$$F(N)=f_\infty+a\exp(-b\ln N)\ ,$$

and then used the f_∞ as a determination of the estimate of the appropriate anharmonic contribution. For the cubic contributions we used the results based on the Born—von Kármán mesh, and for the quartic contributions, the Wallace mesh. Our results are shown in Table I.

From Table I one sees at zero and high temperatures that u_3 is several times larger than u_4, and both are positive. These facts help explain why SCH calculations compared poorly to the Monte Carlo simulations. We note the estimates of Carr *et al.*[17] ($u_3=1.14$ and $u_4=0.409$) and of Glyde and Keech[15] ($u_3=1.101$ and $u_4=0.37$) for the zero-temperature values of u_3 and u_4 are close to our values ($u_3=1.087$ and $u_4=0.384$), as is the estimate of Ceperly for u_3-u_4 (0.73).

At zero temperature the Ceperly[12] simulations on the solid phase were done for r_s ranging from 200 (an equilibrium state), through 67 (the estimated value for melting), to 50 (a metastable state). Over this range of r_s the magnitude of the lowest-order anharmonic contributions U_3+U_4 varies from 2% to 5% of the harmonic contribution U_h. At high temperatures the simulations of Slatterly *et al.*[11] were done for Γ ranging from 300 (an equilibrium state), through 166 (the estimated value for melting), to 150 (a metastable state). Over this range of Γ the ratio of U_3+U_4 to U_h varies from 0.05% to 0.1%. Consequently, both at zero and high temperatures the leading anharmonic contributions make only very small corrections to the internal energy and are small compared to the harmonic contribution.

Since we now have precise calculations for the electrostatic,[25,26] harmonic, and lowest-order anharmonic contributions, we can estimate the r_s and Γ dependence of the remaining anharmonic contributions by computing the difference between their sum (which we will call U_1) and the Monte Carlo results. In practice, this procedure is limited mainly by the numerical precision of the Monte Carlo results. As just discussed, the lowest-order anhar-

TABLE II. Summary of the zero-temperature results. U_{MC} is the internal energy per particle as determined by the Monte Carlo simulation of Ceperly (Ref. 12). U_1 is the internal energy per particle calculated exactly through the lowest-order anharmonic correction. U_2 is the internal energy per particle with the next-order anharmonic correction estimated from the $r_s=250$ results.

r_s	U_{MC}	U_1	U_{MC}-U_1	U_2	U_{MC}-U_2
30.0	−0.044 540	−0.044 338	−0.000 202	−0.044 545	−0.000 005
50.0	−0.028 660	−0.028 602	−0.000 058	−0.028 660	−0.000 000
100.0	−0.015 331	−0.015 332	0.000 001	−0.015 342	−0.000 011
200.0	−0.008 034	−0.008 037	0.000 003	−0.008 039	0.000 005

TABLE III. Summary of the high-temperature results. U_{MC} is the free energy per NkT as determined by the Monte Carlo simulations of Slatterly *et al.* (Ref. 11). U_1 is the internal energy per NkT calculated exactly through the lowest-order anharmonic correction. U_2 is the internal energy per NkT with the next-order anharmonic correction estimated from the $\Gamma=200$ results.

Γ	U_{MC}	U_1	$U_{\mathrm{MC}}-U_1$	U_2	$U_{\mathrm{MC}}-U_2$
160.0	−141.716	−141.826	0.110	−141.708	−0.008
170.0	−150.697	−150.787	0.090	−150.682	−0.015
180.0	−159.667	−159.747	0.080	−159.654	−0.013
200.0	−177.603	−177.668	0.065	−177.592	−0.011
220.0	−195.536	−195.588	0.052	−195.525	−0.011
240.0	−213.463	−213.508	0.045	−213.455	−0.008
300.0	−267.233	−267.267	0.034	−267.233	−0.000

monic contributions are already very small compared to the harmonic part, and, as can be seen from Tables II and III, the importance of remaining contributions depends on whether one is in the zero- or high-temperature limits. In any case, at the largest r_s and Γ shown the corrections are 10^{-6} times the total internal energy.

In perturbation theory the next-order anharmonic contributions in the zero- and high-temperature limits have the forms a/r_s^2 and b/Γ^2. To attempt an estimate of the residual anharmonic contributions, $U_{\mathrm{MC}}-U_1$ in Tables II and III, we chose the largest r_s and Γ that seems to have a contribution above the error of the Monte Carlo simulations ($r_s=50$ and $\Gamma=300$) and assume that the next leading anharmonic contribution is dominant at these points. With this assumption we fit the data to find $a=-1.017$ and $b=3019$, and then add these contributions to U_1 to obtain U_2. In Tables II and III and Figs. 3 and 4 we compare new estimates of the anharmonic internal energy with the Monte Carlo simulations. As easily seen, within the numerical accuracy of the simulations, we find at $T=0$ no significant difference between the two, even above the melting transition and in the metastable regime where anharmonic effects should be most pronounced. At high temperatures we find at most a 10% difference.

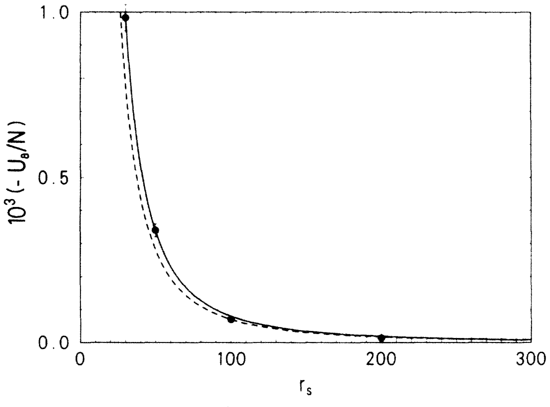

FIG. 3. The negative of the anharmonic contribution to the internal energy at zero temperature as a function of the Wigner-Seitz radius r_s. The circles are the Monte Carlo results of Ceperley *et al.*; the dashed line represents our calculation of the lowest-order anharmonic contribution; the solid line is the sum of our calculation of the lowest-order contribution and our estimate of the next-order contribution.

The remarkable agreement of the internal energy expression, even in the melting and metastable region, with the Monte Carlo data for the ground state suggest that the anharmonic perturbation is strongly convergent. In fact, if our assumption about fitting the second-order term is correct, the series by the third term has converged to the accuracy of the simulation. At high temperatures our estimate of the second-order anharmonic contributions suggest that if our assumption is correct, then small higher-order anharmonic corrections are still present. Most likely we should have assumed that at $\Gamma=300$ at least the second- and third-order corrections were present and fitted the unaccounted for anharmonicity to $a/\Gamma^2+b/\Gamma^3$; however, we feel it is more significant to suggest that the obvious smallness of the anharmonic contributions and small difference between our fit and the data indicates even at high temperatures the anharmonic perturbation series is converging to an accuracy comparable to the Monte Carlo results after a finite number of terms.

As another measure of anharmonicity we compared the first-order quartic term with the results[16] of self-consistent harmonic (SCH) theory, since the former is the leading term to the latter. In the zero-temperature limit we find that the total anharmonic contribution from SCH theory is 56% of u_4/r_s^2 at $r_s=30$, 62% at $r_s=50$, 71% at $r_s=100$, and virtually identical at $r_s=200$. In the high-

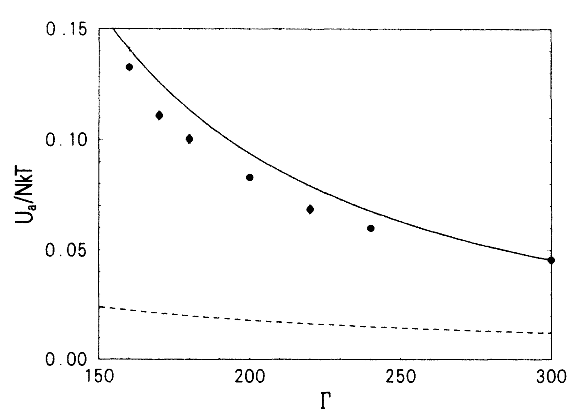

FIG. 4. The anharmonic contribution to the internal energy at high temperatures as a function of Γ. The dots are Monte Carlo results of Slatterly *et al.*; the dashed line represents our calculation of the lowest-order anharmonic contribution; the solid line is the sum of our lowest-order contribution and our estimate of the next-order contribution.

temperature limit, we find that u_4/Γ has a magnitude 51% of the anharmonic SCH result at $\Gamma=300$, 58% at $\Gamma=200$, and 78% at $\Gamma=100$. Thus the summation of all remaining even-order terms in perturbation theory (SCH) is of the same order of magnitude as the lowest-order even-order term.

In principle, the r_s^{-2} and Γ^{-2} contributions could be computed from the proper perturbation contributions; however, the cost of doing such a calculation accurately, particularly the triple Brillouin-zone integrations now needed, may be prohibitive. For example, our calculations of the two cubic contributions for $N=5381$ took over 3 h on a Cray-XMP computer. Although more efficient integrations schemes than the uniform mesh may exist, the slow convergence of the integrations was surprising and untraceable to any obvious singularity in the integrand. For example, we tried doing the same calculations for other inverse power-law potentials $[V(r)=(\sigma/r)^n,\ n>1]$ and found for $2\le n\le 6$ and a bcc lattice that convergence was even slower than for $n=1$. On the other hand, for a fcc lattice and $1\le n\le 12$, convergence was rapid. We left the cause of this peculiar behavior uninvestigated.

IV. CONCLUDING REMARKS

We presented calculations of the second-order cubic and first-order quartic anharmonic contributions to the internal energy of the one-component plasma. With these calculations and available computer-simulation data we estimated the size of higher-order anharmonic effects. For both the zero- and high-temperature limits, we showed that the system is quite harmonic; the lowest-order anharmonic contributions are at best a few percent of the harmonic contribution over the range of the simulations (including the melting and metastable regions). Quantitatively, at zero temperature we find

$$\frac{U}{N}=\frac{-1.791\,85}{r_s}+\frac{2.657\,24}{r_s^{3/2}}-\frac{0.703}{r_s^2}-\frac{1.017}{r_s^{5/2}}\,, \tag{6a}$$

while at high temperatures

$$\frac{U}{NkT}=-0.895\,929\,256\Gamma+3-\frac{3.647}{\Gamma}+\frac{3019}{\Gamma^2}\,. \tag{6b}$$

We note that at high temperatures Pollack and Hansen[4] have argued that the lowest-order anharmonic contributions are negligble, and hence they and others have fit their data to a form in which only the Γ^{-2} contributions represent the anharmonic effects. Although this procedure may produce a good fit to the data, our calculations now allow the proper importance of the anharmonic contributions to be established more quantitatively and thus allow a more correct interpretation of the simulation data.

The relative importance of the cubic over the quartic anharmonic term is most likely a consequence of the soft-core nature of interatomic, Coulomb potential. In metals and ionic crystals the cubic and quartic terms are found to be of approximately equal size.[27] In those systems the interatomic potential has a reasonably steep hard core. In the rare-gas crystals the quartic term is found to be approximately twice the size of the cubic term. There the interatomic potential has a very steeply rising hard core. Basically, the anharmonic perturbation theory converges less well for a steeply rising hard-core potential, and this makes the quartic term relatively more important than the cubic term.

In closing we remark that it is extremely unusual for harmonic contributions to dominate the equation of state so strongly, especially near melting. We believe that this situation also results from the long-ranged electrostatic forces present in the OCP model, which qualitatively as well as quantitatively distinguish the OCP from other two-body central force models. Some indication of the unique features caused by this long-range force, besides the need for Madelung techniques to handle the nearly divergent lattice sums, is the isotropic term $\omega_p^2\delta_{ij}/3$ in the harmonic dynamical matrix that is absent for all short-ranged interatomic potentials. It would be interesting to study an OCP with Thomas-Fermi screening, i.e., a system with a pairwise potential of

$$V(r)=e^2\exp(-r/\lambda)/r\ ,$$

as a function of the screening length λ to see if the harmonic terms become more dominant as the screening length goes to infinity. The long-range forces may induce a nonanalyticity in the equation-of-state properties. By this we mean that the $\lambda\rightarrow\infty$ limit of the Thomas-Fermi screened model could have qualitative as well as quantitative differences from the OCP. For example, the Thomas-Fermi screened model will always lack the $\omega_p^2\delta_{ij}/3$ term in the dynamical matrix, because no matter how large λ is, the screening length is still finite.

ACKNOWLEDGMENTS

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