

Monte Carlo and perturbation-theory calculations for liquid metals

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Monte Carlo calculations of the thermodynamic properties of a pseudopotential metal fluid, approximating lithium, were carried out over a wide range of temperatures and densities. The calculations were compared with the predictions of variational perturbation theories employing the hard sphere, soft sphere, and the one component plasma (OCP) as reference systems. The OCP predictions are in better agreement with Monte Carlo pressures, but are comparable for energies. The OCP reference system has the lower Helmholtz free energy at all points studied.

INTRODUCTION

The first exact calculations for a dense plasma were made by Brush, Sahlin, and Teller¹ (BST) who, in 1966, carried out Monte Carlo calculations for the one-component plasma (OCP). In this system positive ions move about in a neutralizing negative background of constant density. This is physically realistic only when atoms are completely ionized at very high densities and low temperature. It is probably more useful if accepted as an idealized model of a plasma. More recently, Hansen² and Slattery *et al.*³ have exploited the faster available computers and improved numerical methods to extend the BST results to more data points and higher accuracy. In 1971 Hubbard and Slattery⁴ carried out Monte Carlo calculations for a plasma model in which the background electron gas was permitted to relax and screen the positive ions. Screening was computed by use of the Lindhard dielectric constant.⁵ This system, referred to as a screened Coulomb plasma (SCP), is physically correct at slightly less extreme densities than is the OCP. In an interesting application of thermodynamic perturbation theory, Galam and Hansen⁶ computed the properties of the SCP system by using the OCP results as a reference state. They treated the perturbation as the increase in potential energy due to the screening. Prior to this work, Ross and Seale⁷ also employed perturbation theory and had shown that the use of hard spheres as a reference system predicted SCP results in better agreement with Monte Carlo calculations than might be expected; although not as good as the subsequent results of Galam and Hansen using the OCP as a reference. Hard-sphere perturbation theory (HSPERT), in combination with pseudopotentials have, in recent years, been used extensively to compute the properties of liquid metals and alloys.⁸ In this paper we explore the possible

usefulness of a liquid metal theory employing the OCP system as the standard reference (OCPERT). OCPERT offers a softer reference system which might be more appropriate for simulating the longer-range, and softer, repelling forces found in metals. This possibility is implied by the results of Hansen and Galam.

In developing the original formulations of hard-sphere perturbation theory extensive comparisons were carried out against exact Monte Carlo and molecular-dynamics computer simulations for particles interacting pairwise via the argonlike Lennard-Jones potential.⁹ This potential has a stiff repulsion, intended to mimic the strong repulsions characteristic of closed-shell insulator molecules, and a weak attractive term to represent the induced-multipole interactions. The results of this research indicate that for fluids made up of insulator molecules, hard spheres are a satisfactory reference system. These theories have been applied to simple metals by using a pseudopotential, which is an effective pair potential, that has been derived from electron theory. Some justification for this step has been the resemblance between experimental liquid metal and the hard-sphere structure factors, for appropriately chosen hard-sphere diameters. In addition, thermodynamic and transport properties can be computed that are in reasonable agreement with experiment, if suitably adjusted empirical pseudopotentials are employed. However, it appears that no systematic computer studies, comparable to those carried out for the Lennard-Jones potential, have been reported for pseudopotential metals for testing approximate theories. Consequently, we have carried out Monte Carlo calculations for such a potential with parameters characteristic of lithium and have compared these results with the predictions of OCPERT and HSPERT. We also include calculations made with a modification of hard-sphere perturbation theory

that uses the inverse twelfth power, or soft-sphere repulsion, as the reference (SSPERT).¹⁰ We emphasize that no attempt has been made to simulate the properties of lithium *per se*. We have used a particular set of parameters taken from the literature¹¹ only as a guide for an appropriate model potential. We restrict ourselves to a study of the statistical mechanics and do not consider the separate question as to the validity of the pseudopotential concept itself.

MODEL CALCULATIONS

The model interaction Hamiltonian for the simple metal employed here is $H = H_{\text{eg}} + H_C + H_k$, where H_{eg} is the ground-state energy (per electron) for the electron background gas, H_C the Coulomb Hamiltonian, and H_k the ion kinetic energy:

$$H_{\text{eg}} = \frac{2.21Z}{r_s^2} - \frac{0.196Z}{r_s} + (-0.115 + 0.031 \ln r_s)Z, \quad (1)$$

$$H_C = \frac{N}{2V} \sum_k' \frac{4\pi(Ze)^2}{k^2} [S(k) - 1] + \frac{N}{2V} \sum_k' \frac{4\pi(Ze)^2}{k^2} f(k) \left(\frac{1}{\epsilon(k)} - 1 \right) S(k) + NE_0, \quad (2)$$

$$H_k = \sum_I \frac{P_I^2}{2M_I}, \quad (3)$$

where

$$r_s = \left(\frac{3}{4} \frac{V}{\pi N} \right)^{1/3}$$

and

$$f(k) = \left(1 - \frac{\Omega}{(1 + k^2 r_c^2)^2} \frac{k^2}{8\pi Z} \right)^2$$

and

$$E_0 = \frac{\Omega Z}{V}.$$

The primed sum means that the term $k=0$ is omitted. Z is the ion valence. $\epsilon(k)$ is the Lindhard dielectric constant, V is the volume, and N is the number of ions. P_I and M_I are the ion momentum and mass. E_0 appears as a result of omitting the $k=0$ term from the second sum. The derivation of

these equations from the basic physics is well known⁸ and need not concern us. The first term in Eq. (2) represents the direct interaction of ions in a uniform neutralizing background electron fluid. The second term accounts for the additional interaction, correct to second order, that results when the electron distribution surrounding an ion is distorted leading to a screened ion-ion interaction. $S(k)$ is the structure factor of the particular ion configuration. Ω ($= 23.0$) and r_c ($= 0.33$) are pseudopotential parameters. These parameters were determined for lithium by Wallace¹¹ and used by Jones¹² but with a dielectric constant that included correlation and exchange. We used the Lindhard (or Hartree) dielectric constant. These equations reduce to the screened Coulomb system when $\Omega=0$ and $f(k)=1$, and to the OCP when $\Omega=0$ and $\epsilon(k)=1$.

Monte Carlo calculations were carried out with a computer program essentially identical to one used previously for computing the properties of the screened Coulomb system.⁴ The only significant modification has been the introduction of the pseudopotential via the function $f(k)$. Reference 4 also includes the method by which the Coulomb internal energy U_C and Coulomb pressure P_C are computed. Calculations were carried out for 108 particles with equilibrium runs of 100 000 to 200 000 configurations. All runs were started from a random configuration and remained in the fluid. No attempt was made to determine the location of the freezing curve. This, however, should not affect our study. The results for $P_C V / N k_B T$ and $U_C / N k_B T$ are shown in column three of Tables I and II. Calculations were at the normal freezing point of lithium ($T = 452$ K, $V = 13.59$ cm³/mol), and up to 2000 K at volumes of 13.024 and 6.512 cm³/mol (approximately twofold compressed), respectively. In parentheses are the standard deviations of the runs. The dependence on the number of particles as estimated from experience with the OCP system³ are well within these uncertainties. These accuracies are sufficient to judge the goodness of the theories.

In applying thermodynamic perturbation theory, the Helmholtz free energy of the Coulomb sys-

TABLE I. Comparison of Monte Carlo $P_C V / N k_B T$ with perturbation theory.

T (K)	V (cm ³ /mol)	MC	OCPERT	HSPERT	SSPERT
452 (MP)	13.59	-12.24 ± 0.08	-12.35	-11.76	-11.98
500	13.02	-10.08 ± 0.08	-10.09	-9.65	-9.86
1000	13.02	-4.19 ± 0.05	-4.32	-3.80	-3.97
2000	13.02	-1.50 ± 0.03	-1.59	-1.18	-1.32
1000	6.51	8.65 ± 0.06	+8.51	9.19	9.05
2000	6.51	4.85 ± 0.03	+4.81	5.33	5.20

TABLE II. Comparison of Monte Carlo $U_C/Nk_B T$ with perturbation theory.

T (K)	V (cm ³ /mol)	MC	OCPERT	HSPERT	SSPERT
452	13.59	-137.46 ± 0.07	-137.67	-137.58	-137.75
500	13.02	-124.60 ± 0.07	-124.71	-124.71	-124.87
1000	13.02	-61.56 ± 0.04	-61.70	-61.51	-61.66
2000	13.02	-30.24 ± 0.03	-30.29	-30.13	-30.26
1000	6.51	-61.85 ± 0.06	-62.09	-61.77	-61.94
2000	6.51	-30.19 ± 0.03	-30.25	-30.02	-29.95

tem A_C is approximated by the use of the Gibbs-Bogolyubov inequality:

$$A_C \leq A_0 + \langle H_C - H_0 \rangle_0. \quad (4)$$

This states that the free energy of the actual system is bounded above by the free energy of the reference system (A_0) plus the difference in the potential energy between the actual system and the reference, averaged over all configurations of the reference.

The widely used approximation of employing hard spheres as the reference HSPERT leads to the following expression for the free energy:

$$A_C = A_{HS} + E_M + E_{BS} + NE_0. \quad (5)$$

The first term is the free energy of a system of hard spheres¹³:

$$A_{HS} = \frac{4\eta - 3\eta^2}{(1 - \eta)^2} Nk_B T, \quad (6)$$

where $\eta = \pi N d^3 / 6V$ and d is their diameter. The second term is the Madelung energy and in the Percus-Yevick (PY) approximation for the hard sphere structure factor $S_{HS}^{PY}(k)$ it can be expressed analytically as¹⁴

$$E_M = \frac{N}{2V} \sum_{\mathbf{k}} [S_{HS}^{PY}(k) - 1] \frac{4\pi(Ze)^2}{k^2} \\ = -\frac{2Z^2\eta d^2}{V/N} \left(\frac{1 - \eta/5 + \eta^2/10}{(1 + 2\eta)} \right). \quad (7)$$

$S_{HS}^{PY}(k)$ is also a function of η . The third term often referred to as the band-structure energy, results from the screened ion interaction and becomes

$$E_{BS} = \frac{2Z^2N}{V} \int_0^\infty f(k) S_{HS}^{PY}(k) \left(\frac{1}{\epsilon(k)} - 1 \right) dk. \quad (8)$$

The best hard-sphere reference system is chosen as the one having the value of η that minimizes the free energy, the right-hand side of Eq. (4). The Coulomb contribution to the pressure and excess internal energy are computed numerically as

$$\frac{P_C}{N} = - \left. \frac{\partial A_C / N}{\partial V} \right|_T \quad (9)$$

and

$$\frac{U_C}{N} = \left. \frac{\partial \beta A_C / N}{\partial \beta} \right|_V, \quad (10)$$

where $\beta = 1/k_B T$ and k_B is Boltzmann's constant.

Equations (4)–(10) summarize hard-sphere theory as it is currently applied to liquid metals. Recently, we developed a modification of hard-sphere variational theory, that employed the free energy of the inverse twelfth power repulsive potential parameterized in terms of η , as the reference (SSPERT).¹⁰ The theory retains the Percus-Yevick distribution function (or structure factor) for simplicity and the convenience of using η as the variational parameter. SSPERT introduces a softer, more realistic reference system. Replacing A_{HS} in Eq. (4) by

$$A_{12} = A_{HS} - (\eta^4/2 + \eta^2 + \eta/2) Nk_B T$$

operationally converts HSPERT to SSPERT. The free energy is minimized and properties calculated as in HSPERT.

An analogous perturbation theory can be developed employing the OCP as a reference, OCPERT. Let us write the reference OCP Hamiltonian as

$$H_0 = \frac{N}{2V} \sum_{\mathbf{k}} \frac{4\pi(Z'e)^2}{k^2} [S(k) - 1] + H_{ee}, \quad (11)$$

where Z' , the effective ion charge, is the variable chosen to minimize the free energy. The free energy of this reference system, as determined from Monte Carlo results, may be written in the analytic form suggested by DeWitt¹⁵:

$$\frac{A_0}{N} = A\Gamma' + B\Gamma'^{1/4} + C \ln \Gamma' + D, \quad (12)$$

where $\Gamma' = (Z'e)^2 \beta / r_s$ and $A = -0.896434$, $B = 3.447408$, $C = -0.555130$, and $D = -2.995974$.

Introducing the dimensionless wave number $q = r_s k$, the Coulomb free energy may be written as

$$\frac{\beta A_C(\Gamma, r_s)}{N} \leq \frac{\beta A_0(\Gamma')}{N} + \frac{\Gamma}{\pi} \int_0^\infty f(q) S_0(q, \Gamma') \left(\frac{1}{\epsilon(q)} - 1 \right) dq + \left(\frac{\Gamma - \Gamma'}{\Gamma'} \right) \beta U_0(\Gamma') + \beta E_0. \quad (13)$$

A_0 and U_0 are the reference free energy and internal energy and $S_0(k, \Gamma')$ is the reference structure factor. The formulas for the Coulomb contribution to the excess internal energy and the pressure can be written as

$$\frac{\beta U_C(\Gamma, r_s)}{N} = \frac{\Gamma}{\Gamma'} \frac{\beta U_0(\Gamma')}{N} + \frac{\Gamma}{\pi} \int_0^\infty f(q) S_0(q, \Gamma') \left(\frac{1}{\epsilon(q)} - 1 \right) dq + E_0 \beta \quad (14)$$

and

$$\frac{\beta P_C(\Gamma, r_s)}{N} = \frac{\beta [U(\Gamma, r_s) - N E_0]}{3N} + \frac{\Gamma}{3\pi} \int_0^\infty f(q) S_0(q, \Gamma') r_s \frac{\partial \epsilon(q)}{\partial r_s} \frac{dq}{|\epsilon(k)^2|} - \frac{\Gamma}{3\pi} \int_0^\infty r_s \frac{\partial f(q)}{\partial r_s} S_0(q, \Gamma') \left(\frac{1}{\epsilon(q)} - 1 \right) dq + E_0 \beta. \quad (15)$$

Equations (13)–(15) are an extension of the Galam and Hansen⁶ derivation for the screened Coulomb system. Using these equations with tabulated OCP structure factors¹⁶ for 20 values of Γ spanning the entire OCP fluid, the free energy is minimized with respect to Γ' , and thermodynamic properties computed.

RESULTS AND DISCUSSION

The results of the calculations are shown in Tables I and II labeled OCPERT, HSPERT, and SSPERT and compared with the Monte Carlo (MC) results. Shown in Table III are the computed Helmholtz free energies A_C and the values of the variational parameters Γ' and η found to minimize this function.

The results in Table I show that OCPERT is clearly best for calculating pressure. For calculating energy all appear to be good. Table III shows OCPERT to have the lower Helmholtz free energies at all the points, indicating that it is the best reference system. Monte Carlo free energies are not readily computable.

In order to judge the practical significance of these results we computed the total pressure:

$$P = P_C + \frac{RT}{V} + P_{eg},$$

where

$$P_{eg} = - \frac{\partial H_{eg}}{\partial V}.$$

These results are listed in Table IV. It is of interest to note that, for three of the Monte Carlo points, the hard-sphere model predicts values of $\eta = 0.45$, commonly identified with the liquid structure near freezing.¹⁷ These are at $V = 13.59$ cm³/mol and $T = 452$ K (the normal freezing point), $V = 13.02$ cm³/mol, and $T = 500$ K and $V = 6.51$ and $T = 1000$ K. At all of these points HSPERT is in disagreement with Monte Carlo by from 1.3 to 2.5 kbar. Consequently attempts to compute quantitatively the pressure of metal liquids at these conditions from theoretical pseudopotentials using hard-sphere theory are unrealistic. While OCPERT is better, it differs by only -0.3 to $+0.8$ kbar; it also lacks sufficient accuracy to permit quantitative calculations at normal liquid conditions with theoretical potentials. Optimum agreement with data will continue to require the adjustment of parameters to fit experiment. In general, the OCPERT pressure and energies are too low, indicating the OCP potential is too soft. HSPERT and SSPERT pressures tend to be too high, which leads us to the conclusion that the best reference system is somewhere between, but

TABLE III. Computed Helmholtz free energies, $A_C/Nk_B T$ and variational parameters Γ' and η .

T (K)	V (cm ³ /mol)	OCPERT	HSPERT	SSPERT	Γ'	η
452	13.59	-134.08	-133.53	-133.98	130.5	0.455
500	13.02	-121.33	-120.75	-121.12	114.7	0.451
1000	13.02	-59.22	-58.75	-59.10	59.7	0.372
2000	13.02	-28.61	-28.25	-28.50	28.8	0.298
1000	6.51	-58.64	-57.77	-58.24	119.8	0.453
2000	6.51	-27.93	-27.25	-27.79	52.9	0.376

TABLE IV. Comparison of total pressures (kbar).

T (K)	V (cm ³ /mol)	MC	OCPERT	HSPERT	SSPERT
452	13.59	-0.4 ± 0.2	-0.7	+0.9	+0.3
500	13.02	5.6 ± 0.2	5.6	7.0	6.3
1000	13.02	14.2 ± 0.3	13.4	16.7	15.2
2000	13.02	28.2 ± 0.4	26.9	32.3	30.5
1000	6.51	307.0 ± 1.0	305	314	312
2000	6.51	333.0 ± 1.0	332	345	342

closer to, the OCP.

The conclusions in this paper are consistent with the earlier work of Galam and Hansen who observed a similar correspondence between these two reference systems for the screened Coulomb potential. It should be emphasized, although it has been generally ignored, that the results of hard-sphere variational perturbation theory are well known to be inaccurate, even for the Lennard-Jones potential, at temperatures below the critical. This is where almost all of liquid metal research takes place. However, the hard-sphere system does remain a useful phenomenological model. It is easier to use than the OCP, because of the analytic properties of the Percus-Yevick $S(k)$. In addition, because the pseudopotential must be determined from experiment it can be made to compensate for inadequacies in the statistical mechanics.

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