NvT- and *NpT*-ensemble Monte Carlo Simulations of Ionized Matter. I. *NvT*-ensemble Study on Calcium Oxide Near Normal Melting Point

Akio YAMAMOTO and Hiromu MURATA

Department of Chemistry, Faculty of Science, Hiroshima University, Higashisenda-machi, Hiroshima 730

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With special attention to calcium oxide, values obtained by *NvT*-ensemble Monte Carlo calculations are reported for the internal energy, pressure, heat capacity, thermal pressure coefficient, Grüneisen's γ, and component radial distribution functions of ionized matter in the condensed phases. The calculations cover 14 vT points: seven points lying on one isochore at the X-ray density and eight on one isotherm at the normal melting point. Both thermodynamic quantities and structural properties in the vicinity of the melting point are indicative of the fluid-solid phase change. A brief comparison of the Monte Carlo results with the experimental data is also made.

Since the stimulating work by Metropolis *et al.*,[1] considerable work has been carried out on the application of Monte Carlo (MC) techniques to the calculation of the equilibrium properties of a wide variety of physical systems. The success of the method rests primarily on the fact that a model containing a relatively small number of particles is in general found to be sufficient to simulate the behavior of a macroscopic system. In addition, computer experiments on Coulomb systems[2] have in recent years provided much valuable information on the thermodynamic, structural, and transport properties of molten salts or plasmas. The purpose of the present paper is to describe the preliminary application of the isothermal-isochoric or *NvT* method to the study of neutral systems of classical charged particles before going into a detailed study of some intricate ionized matter; the present results are quite suggestive in exploring the question of whether the melting transition of a simple ionic system can be satisfactorily simulated by the simple interionic potential.

Calcium oxide has the simple rocksalt crystal structure[3] as do most alkali halides; it also has ionic crystals, but with the doubly charged ions. It appears that the computer simulations of the thermodynamic properties of the oxide and a detailed comparison of the results with both experiments and theories would lead to a better understanding of the material and perhaps aid in understanding the physical and chemical properties of the presumably better understood alkali halides.

Pair potentials derived from the cohesive energy of the solid[4] are used in the computations of the thermodynamic and structural properties in the condensed phases. Since the intermolecular potentials are well identified, the term-by-term contributions of the Coulomb and non-Coulomb energies to the total energy can be calculated explicitly. The values obtained by the MC method, such as pressure or Grüneisen's γ, involve no approximation other than that of the MC method:[5] the MC method is ideal for two- or three-digit accuracy, which is far more accurate than the results from approximate theories except in very special circumstances. Consequently, because we know the explicit form of the intermolecular potentials, it is in retrospect possible to select the theories from among the many suggested which successfully reproduce the machine results.

The principle of the method, furthermore, is equally applicable to other ensembles as well. We will describe in the next paper an application to ionic systems in the isothermal-isobaric or *NpT* ensemble.[6] The use of the *NpT*-MC method allows direct comparisons with experimental data, because the relevant experimental measurements have been usually made only at atmospheric pressure.

Monte Carlo Procedure

Of the many realistic potentials which could be chosen, we have picked an inverse power potential of the form

$$\phi_{ij}(r) = z_i z_j/r + R_{ij}/r^9 - A_{ij}/r^6,$$

where z_i is the ionic charge of the i-th kind of atom. The values of the coefficients, A_{ij} and R_{ij}, are calculated from the solid state properties of calcium oxide:[4]

A_{ij}	Ca	O	R_{ij}	Ca	O
Ca	35.5	63.6	Ca	7.55	32.5
O	63.6	135	O	32.5	113.5

in units of 10^{-60} erg·cm^6 and 10^{-82} erg·cm^9 respectively. No orientational dependence of the potential is specified, meaning that rotational and intramolecular vibrational modes of motion of molecules are supposed to be independent of density. Then the total energy, Φ, and the total virial, Ψ, of a configuration can be estimated as the sums of pair contributions.

All the results reported in this paper were obtained with a system of $N=64$ particles. With periodic boundary conditions,[7] an infinite system was set up by replicas of the basic parent cube of side L translated by a positive or negative multiple of L along its edge. Unlike non-ionic systems, the estimation of the potential energy is complicated here by the presence of long-range Coulomb forces. No methodological difficulties are, however, encountered when the Coulomb energy is evaluated by the Ewald method.[8] Since there happen to be ions around $r=0.5L$, short-range interactions between particles separated by a distance less than $r_c=0.6L$ were included explicitly and the remaining interactions were combined into the integrals[7]

$$\Phi_c = 2\pi N/v \int_{r_c}^{\infty} r^2 \Phi \mathrm{d}r$$

and

$$\Psi_c = 2\pi N/v \int_{r_c}^{\infty} r^3 \{\mathrm{d}\Phi/\mathrm{d}r\} \mathrm{d}r,$$

by assuming that the particle density is uniform: here

$v=L^3$ denotes the MC-cell volume.

Configurations are generated by the method of Metropolis,[1,7] and hence they are accepted or rejected according to a criterion which ensures that a given configuration occurs with a probability proportional to the Boltzmann factor for that configuration. The rate of convergence of the overall averages as a function of the displacement parameter has not been studied systematically. In application of the NvT method a rule-of-thumb[7] used empirically by workers in this field is to assign to the parameter a value such that approximately one-half of the MC moves generate successful new configurations: the present data were accumulated by the use of such a rule. The pseudo-random numbers used here were obtained by the multiplicative congruential method:[9] the generator operates "modulo 2^{32}."

The basic MC data include ensemble averages (indicated by angular brackets) of

1. the potential energy $\langle\Phi\rangle$,
2. the virial $\langle\Psi\rangle=\langle\overset{N}{\underset{1}{\sum}}{}_{(k)}r_k(\mathrm{d}\Phi/\mathrm{d}r_k)\rangle$,
3. the variance and covariance $\langle\Phi^2\rangle-\langle\Phi\rangle^2$ and $\langle\Phi\Psi\rangle-\langle\Phi\rangle\langle\Psi\rangle$,

and 4. the component pair radial distribution functions obtained by compiling pair distance histograms with intervals of 0.05 Å at randomly sampled MC steps.

When a computation for a vT point started from the NaCl-type lattice configuration, the first 30000—50000 steps were rejected on account of large fluctuations. The numbers of configurations used to estimate the ensemble averages were rather small (approximately $M=70000$ for each point), and the procedure adopted to calculate the effects of distant particles has since been found to introduce small but systematic errors.

According to the coarsed-grain statistics,[5] the probable error in the MC data is given by

$$\Delta X = 0.6745[\overset{m}{\underset{1}{\sum}}{}_{(i)}(\langle X_i\rangle-\langle X\rangle)^2/m(m-1)]^{1/2},$$

where ΔX is the estimated probable error in the overall MC average, $\langle X\rangle$, calculated from m subaverages, $\langle X_i\rangle$, over successive groups of M/m configurations: $M/m=5000$ in this work. Of the subaverages, $\langle X_i\rangle$, those which deviate seriously from the overall average, $\langle X\rangle$, were omitted by the visual inspection of the control charts.

The calculations were performed on a HITAC 8700 electronic computer at the Computing Center of Hiroshima University.

Results

Thermodynamic Quantity. The present calculations cover 14 vT points: seven points lying on one isochore at the X-ray density,[3] $\rho=3.346$ g/cm^3, and eight on one isotherm at the normal melting point, $t_m=2572$ °C.[10] The temperature range extends from the room temperature to just below the normal boiling point, $t_b=2850$ °C, while the volume ratio is in the range between 0.90 and 1.10. The numerical results of the computer experiments described in this paper are summarized in Table 1.

Thermodynamic quantities were calculated from the appropriate ensemble averages; some important relations for the NvT-ensemble are recalled here for the sake of easy reference.

The *total energy*, U, of the system is obtained from the mean potential energy by

$$U/NkT = \langle\Phi\rangle/NkT + 3/2,$$

where N is the number of particles in the MC cell and where k is the Boltzmann constant. In Table 1, the potential energy is further divided into the Coulomb and non-Coulomb contributions, the relative contributions being more dependent on the volume change than on the temperature. The *Madelung constant*, M, of the equilibrium configurations is also given in Table 1.

The mean virial determines the *pressure* according to[7]

$$pv/NkT = 1 - \langle\Psi\rangle/3NkT.$$

TABLE 1. NUMERICAL RESULTS FOR THE THERMODYNAMIC QUANTITIES

°C	v a)	State	BE b)	NC c)	M d)	Δ	p e)	Δ	C_v/Nk	Δ	$v\beta/Nk$	Δ	γ f)	Δ
35	16.8	solid	879.19	8.62	3.4962	0.0003	−59.46	0.23	2.69	0.06	4.16	0.20	1.55	0.06
1400	16.8	solid	864.18	9.24	3.4922	0.0003	8.6	0.5	2.56	0.06	3.34	0.16	1.32	0.06
2322	16.8	solid	854.13	9.62	3.4858	0.0004	50.8	0.8	2.623	0.045	3.98	0.16	1.529	0.044
2472	16.8	solid	851.73	9.79	3.4871	0.0007	61.2	1.2	2.46	0.05	3.81	0.16	1.548	0.040
2572	15.2	solid	848.38	12.88	3.4822	0.0010	355.2	1.8	2.39	0.06	3.38	0.24	1.39	0.06
2572	16.0	solid	850.93	11.18	3.4830	0.0009	185.3	0.8	2.68	0.05	3.78	0.16	1.420	0.037
2572	16.0	liquid					(343)							
2572	16.8	solid	850.89	9.80	3.4856	0.0010	63.6	1.1	2.66	0.07	3.98	0.16	1.496	0.044
2572	16.8	liquid					(188)							
2572	17.6	solid	848.19	8.66	3.4937	0.0007	−15.2	1.3	2.42	0.07	3.45	0.22	1.45	0.06
2572	18.0	liquid					(45)							
2572	18.4	solid	845.45	7.85	3.5033	0.0012	−80.5	1.1	2.308	0.036	3.53	0.09	1.533	0.037
2672	16.8	solid	849.87	9.80	3.4854	0.0003	68.4	1.4	2.46	0.06	3.20	0.13	1.294	0.037
2772	16.8	solid	848.55	9.81	3.4844	0.0008	73.9	1.0	2.50	0.06	3.49	0.14	1.391	0.041

a) Molar volume in cm^3/mol. b) Binding energy in kcal/mol. c) % contribution of non-Coulomb energy to Coulomb energy in magnitude. d) Madelung constant referred to lattice parameter. e) Pressure in kbar. f) Grüneisen's γ. The symbol Δ represents probable errors of the preceding columns.

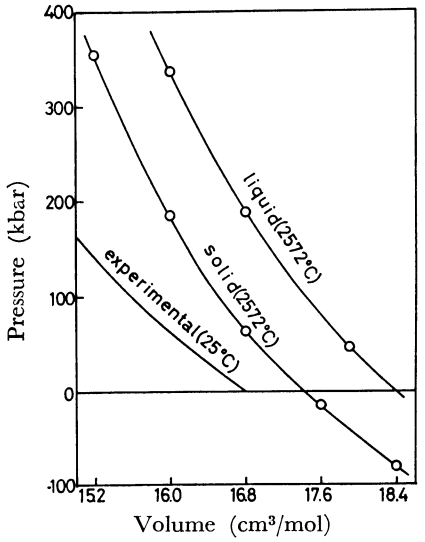

Fig. 1. The p, v-isotherms at the normal melting point.

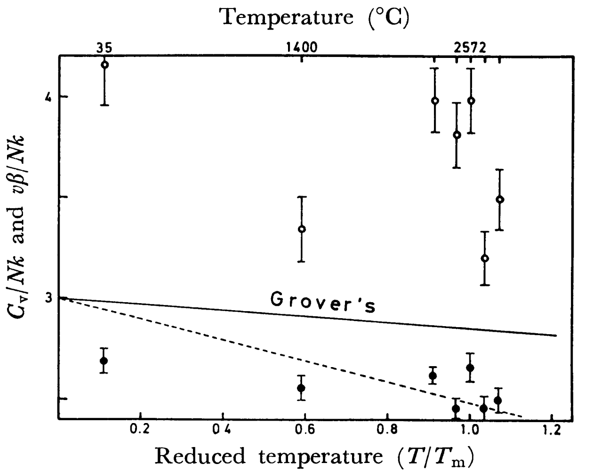

Fig. 2. Isochoric specific heat, C_v/Nk, and thermal pressure coefficient, $v\beta/Nk$, at the X-ray density.
○ $v\beta/Nk$, ● C_v/Nk.
Error bars and T_m represent the probable errors and the normal melting temperature respectively.

The p, v-isotherms at the normal melting point are shown in Fig. 1; no fluctuations indicative of a phase change were observed. The probable errors in the pressure are within 1 kbar. The preliminary data for the liquid branch are also included in Fig. 1. As has been pointed out by Woodcock and Singer,[11] the isotherms obtained from liquid runs are always higher than the solid-branch curve. The molar volume at zero pressure is estimated by interpolation to be approximately 17.4 cm³/mol at the melting point. As is summarized in Table 1, the calculated pressure at constant volume increases roughly linearly with temperature, and at the X-ray density the zero pressure is found to be attained around 1400 °C. The computed change of volume on fusion is 1.0—1.2 cm³/mol at the normal pressure.

The *specific heat* at constant volume, C_v, is determined by fluctuations about the mean as[12]

$$C_v/Nk = 3/2 + N(\langle\Phi^2\rangle - \langle\Phi\rangle^2)/(NkT)^2.$$

As can be seen from Table 1, the specific heat decreases with increasing temperature along isochores and changes little along isotherms. The specific heat on the X-ray density isochores (Fig. 2) shows a tendency to increase near the melting transition.

The *thermal pressure coefficient*, $\beta = (\partial p/\partial T)_v$, can be calculated from the covariance of the potential energy and the virial:[13]

$$v\beta/Nk = 1 + N\langle(\Phi - \langle\Phi\rangle)(\Psi - \langle\Psi\rangle)\rangle/(NkT)^2.$$

Since the coefficient, β, is evaluated as a covariance of two fluctuating quantities, the results are subject to large statistical errors. The calculated values listed in Table 1 show that β decreases with increasing volume along isotherms and that the rate of decrease also decreases in magnitude. The coefficient decreases slowly with increasing temperature along isochores; on fusion β decreases by about 20%. The sudden drop of the coefficient in the vicinity of the normal melting point, both along isotherms and isochores, is certainly indicative of the solid-fluid phase change.

The *Grüneisen's* γ, defined as $\gamma = v(\partial p/\partial T)_v/C_v$, is an extremely useful quantity in high-pressure physics. This parameter, given in the last two columns of Table 1, allows the extraction of a maximum of information from a minimum of data, which is a special virtue for experimental conditions where data are often difficult to obtain.

Radial Distribution Function. The angle-averaged component pair distribution functions, $g_{++}(r)$, $g_{--}(r)$, and $g_{+-}(r)$, are defined by[14]

$$g_{\alpha\beta}(r) = [\Delta n_{\alpha\beta}/\Delta r]/4\pi r^2,$$

where $\Delta n_{\alpha\beta}$ is the number of particles of kind β at a distance between r and $(r+\Delta r)$ from a reference particle of kind α; the mean radial distribution function is given by[15]

$$g_m(r) = [g_{+-}(r) + g_{-+}(r)]/4 + [g_{++}(r) + g_{--}(r)]/4.$$

These functions have been computed as appropriate averages over a total of about 300 randomly-sampled configurations at thermal equilibrium. All the curves are from a 64-particle system, so that beyond $r/L = 1/2$ they are directly influenced by the periodicity imposed upon the system; therefore, only the first and second peaks are illustrated in Fig. 3. Furthermore, since the radial distribution functions of like ions are found to be very similar, the averaged function, $g_1(r) = [g_{++}(r) + g_{--}(r)]/2$, is shown in Fig. 3 for the systems on X-ray density isochores. Let us remark that the unambiguous resolution of the component radial distribution functions by X-ray or neutron diffraction is in general difficult, if not impossible. The calculated curves shown in Fig. 3 make it clear that there is some penetration (a few percent) by like ions into the apparent first coordination shell. The appearance of the functions changes gradually with temperature; the well-separated steep peaks at lower temperatures become broad and flat with increasing temperature, and the peaks become connected with each other before 1400 °C. The positions of the first peak also shift slightly from the crystallographic peak position centered at $r = 2.405$ Å. In particular, the functions near the melting point exhibit some unexpected features which appear to antici-

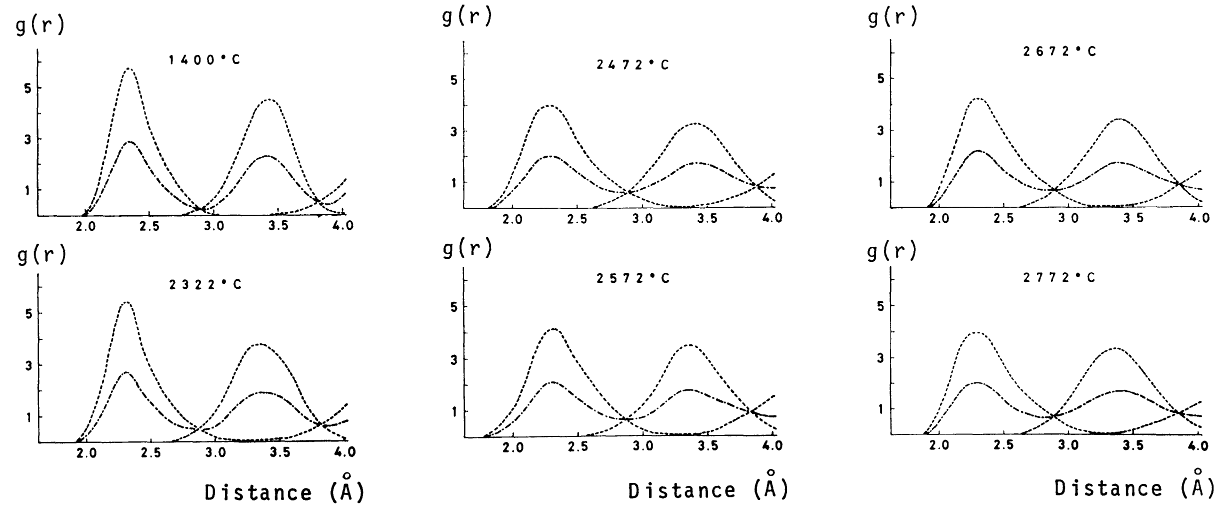

Fig. 3. Radial distribution functions on the X-ray density isochores.
(----) $g_l(r)$ or $g_u(r)$, (—·—) $g_m(r)$.
$g_l(r)=[g_{++}(r)+g_{--}(r)]/2$, $g_u(r)=[g_{+-}(r)+g_{-+}(r)]/2$, and $g_m(r)=[g_l(r)+g_u(r)]/2$.

pate the change on fusion: those below 2322 °C and above 2472 °C differ strikingly from one another.

Discussion

Possible Error. The number dependence of a finite system can be theoretically studied in certain simple situations,[16] whereas similar studies in the "experimental" situations can only be done empirically by using a system with different sizes. So far, this sort of study[17] has yielded the information that differences between the equation-of-state data of the finite system and the corresponding thermodynamically infinite system are not larger than $1/N$, if the system under observation is in the one phase region. Accordingly, the differences are believed to be within two percent except near the phase-transition region: the discrepancies found were seemingly not larger than would be expected from the following MC fluctuations. Another type of error concerns the statistical errors, which can be derived by using the coarsed-grain techniques. The probable errors, listed in Table 1, display a moderately consistent pattern, amounting to approximately a few percent or less in C_v/Nk and $v\beta/Nk$.

Potential Form. The effects on the thermodynamic and structural properties which result from changes in the intermolecular potentials have been studied by many investigators.[18] From the theoretical considerations, the exponential form of the potentials is known to be a better representation of repulsive interactions between close atoms than is the inverse power form. Nevertheless, because of its mathematical simplicity and its apparent adequacy near the minimum of the interaction curve, the inverse power potential is still the most widely used potential of practical importance. Except in the very high density region, effects of deviations from the inverse power potential and from additivity of pair potentials are seen to be fairly small. For instance, the experimental p, v-isotherms at room temperature[19] suggest that CaO is largely ionic at pressures below 160 kbar, but that, as the interionic distance is reduced, new interactions come into play which are not appropriately considered in the pair potential. From an analysis of a considerable amount of shock data,[13] it is also known that Grüneisen's γ varies more rapidly with compression than that calculated by using the Lennard-Jones potential, and consequently infers that even the inverse-12th-power potential is inappropriate for highly compressed materials. At the highest compression, where only the repulsive forces are important, the value becomes $\gamma=[n/6+1/3]=1.88$: such a compressed condition cannot be attained in the present calculations. We have not yet been able to relate these apparent discrepancies to the parameters used in the pair potential. Moreover, the validity of the approximate theories can be best appreciated by comparing with the MC results rather than with the experimental data, since the potential form of the real systems is not fully specified. At present theoretical data does not exist which would enable us to make such a comparison.

The potential parameters used here were prepared so as to be compatible with the properties of the static lattices.[7] Any refinement of the potential parameters[20] was, however, impracticable on account of the heavy demand of computing time.

Polarizability. The effects of ionic polarization in ionic salts[21] are found to be small and negligible except for the excess properties of liquid mixtures.[22] For typical alkali halides, the net contributions to the total energy are estimated to be small (less than few percent in magnitude);[15] this suggests that the polarization is not a factor which significantly affects the structural and thermodynamic properties. Although the introduction of the polarization effects to the present rigid-ion potential appears to be straightforward,[15,23] we have chosen to leave these factors out entirely, in view of the fact that a satisfactory short-range interaction potential is in itself an incompletely understood quantity for the present material.

Thermodynamic Quantity. A preliminary comparison of the MC results with the experimental data

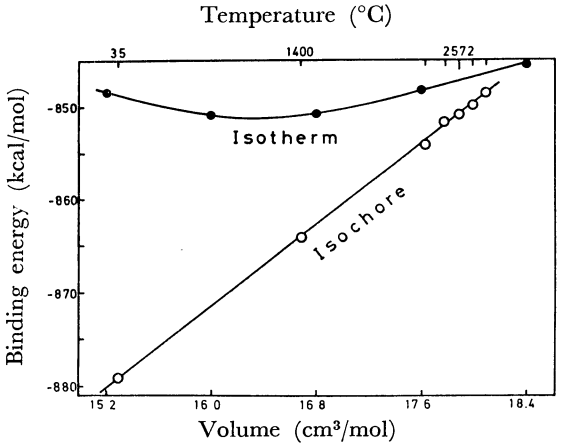

Fig. 4. Binding energy of calcium oxide.
○ Isochores at the X-ray density.
● Isotherms at the normal melting point.

of the real systems is in order, since the available data for CaO are unfortunately too scanty to permit detailed comparison of calculated with measured quantities over a sufficiently wide vT range. First, the ***binding energy***, shown in Fig. 4, can give direct information about the temperature- and volume-dependence of the energy at any temperature of practical importance, while the corresponding energy estimated theoretically is exclusively concerned with the perfect crystal in the limit of 0 K. The binding energy of the static lattice is calculated to be 882.5 kcal/mol, which is the largest of the theoretical values reported so far: the thermochemical binding energy is 842 kcal/mol.[24,25] As is illustrated in Fig. 4, the binding energy at the finite temperature decreases linearly with increasing temperature, suggesting that the crystal lattice is destabilized by the thermal motion. On the other hand, the isothermal energy calculated varies only slowly with volume: the most stable molar volume at the normal melting point is energetically found to be around 16.5 cm³/mol. In the sixth column of Table 1 is given the *Madelung constant*, M,[9] of the equilibrium configurations, which, referred to the nearest-neighbor distance, can be said to present an effective number of nearest neighbors. The values listed are those referred to the lattice parameter, and hence they must be halved to obtain the nearest-neighbor values. The MC results indicate that the constant decreases roughly linearly with increasing temperature at constant volume: this points to an increasing cancellation of the potential as a result of an increase of thermal motion. On the contrary, the isothermal values of M vary gradually with volume: a value greater than that for the solid lattice ($M=3.4951$) shows a less complete cancellation of the negative and positive potential due to ion-pair formation. The presence of these pairs has often been pointed out in the molten salts;[26] the shape of the first peak of the radial distribution illustrates well this situation. The measurement of volume as a function of ***pressure*** can be accomplished in number of ways;[27] however, the data obtained from X-ray diffraction studies at room temperature are the only ones available at present. The experimental p, v-isotherms are included in Fig. 1, showing that the MC curves are similar in the dependence on the volume to the experimental facts. Next, the observed ***specific heat*** at constant pressure, C_p, can be modified by using the relation,[28]

$$C_V/Nk = C_p/Nk - \alpha^2 vT/\kappa(Nk),$$

to give the experimental specific heat, C_V: here α, κ, and v are the thermal volume expansivity, the compressibility, and the MC-cell volume respectively. The specific heat, C_V/Nk, at room temperature was thus calculated to be 2.3—2.7:[29–32] the MC results lie within the range of rather widely scattered experimental results. The MC calculations also indicate that the simulation fails entirely to account for the very rapid rise in specific heat that is observed near the critical temperature.[33] In the MC method the small value of N and the periodic boundary conditions are considered to suppress all large fluctuations, and the estimated specific heat is, therefore, very much too low in such a region. Aside from these restrictions, the pronounced maxima (Figs. 2 and 5) in the vicinity of the experimentally known melting point[26,34,35] are indicative of large fluctuations in the molecular arrangement. Despite these increases at near-critical temperatures, the calculated values of C_V/Nk decrease nearly linearly with increasing temperature: the data obey Grover's rule that $C_V/Nk=3(1-\delta\tau)$, where $\delta=0.15$ and τ is the temperature divided by the melting temperature, $T_m=2845$ K. The present value of δ is three times as large as that determined experimentally by Grover[36] for several metals, although the uncertainty in the computer-generated specific heat is quite large. The ***Grüneisen parameter***, γ, can be thermodynamically derived from the ratio of the thermal pressure coefficient to the specific heat. As for KCl, the parameter is found to be essentially constant in the temperature range from 0 to 750 °C.[37,38] Figure 6 shows that the isothermal values of γ are substantially constant, while the values on the isochores vary but slowly with tem-

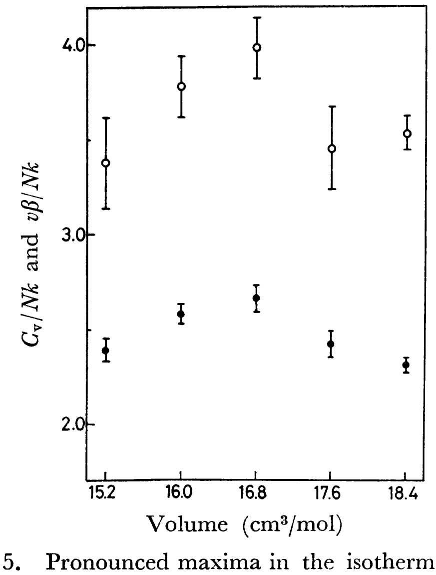

Fig. 5. Pronounced maxima in the isothermal specific heat(●), C_V/Nk, and the thermal pressure coefficient (○), $v\beta/Nk$, at the normal melting point. Error bars represent the probable errors.

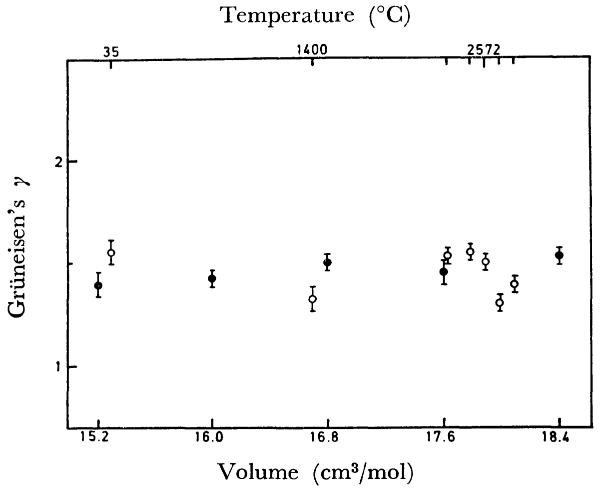

Fig. 6. Isothermal (●) and isochoric (○) Grüneisen parameters of calcium oxide.

perature. The constant-volume data can only be obtained by means of lattice dynamics: the value of 1.76 was assigned to it by Sirdesmukh and Rao.[39]

As the relevant experimental measurements have been made only at effectively constant pressure, we have found it more convenient to work in an isothermal-isobaric ensemble; furthermore, a strict test of the calculation model would involve a comparison of the results with ideal systems having some well-defined intermolecular potentials. Work along these lines is now in progress, and the detailed interpretation of the results and comparison with both experiments and theories will be discussed in a future publication.

Melting Transition. In systems of finite size, especially the small ones which can be treated on a computer, both the region over which metastable phases can occur, and the time for which they persist can be large. Precisely, these difficulties have complicated the search for the phase transitions in small systems. Even in the largest three dimensional systems investigated so far,[5] the particles are found to be either all in the fluid phase or all in the crystalline phase. Most runs were started from a perfect crystal, obviously unstable at low enough density and at high pressure: they would melt spontaneously. Thus the solid phase was extended from high density where it was at least metastable into the low density where it was seemingly unstable thermodynamically. Due to the irregular nature of a fluid structure it is not easy to invent an unbiased initial condition for a fluid run.[40] We plan a more detailed study of the liquid portion of the phase diagram in the near future, and the comparison of two disconnected branches overlapping in the density of the transition will yield some useful information on phase changes. As to the "computer-generated" solid branch, both large fluctuations of the total energy and the abrupt drop of the thermal pressure coefficient in the close vicinity of the experimentally known solid-fluid transition are certainly suggestive of the existence of the transition; the structural properties also indicate such a transition.

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