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Thermodynamic properties of NaCl obtained by computer calculation

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Abstract

Some of the thermodynamic properties of the NaCl system have been calculated from first principles using computer simulation techniques. Pairwise-additive interaction potentials for the NaCl system were calculated using SCF-LCAO *ab initio* methods. These interaction potentials were used in conjunction with the Monte Carlo technique to calculate volumes, third law entropies, and enthalpies of NaCl at four temperatures and 1 bar. The calculated properties were mostly within five percent of their corresponding experimental values. The melting temperature was calculated to be 950 K (the experimental value is 1074 K) reflecting the difficulty inherent in predicting phase change information from first principles. The volume of crystalline NaCl as a function of pressure was also calculated using a free energy minimization technique. The calculated volumes compared well with experimental results to pressures of 120 kbar. In general the calculated thermodynamic properties did not increase rapidly enough with temperature; the interaction potential functions obtained from the *ab initio* calculations were too negative compared to Born–Huggins–Mayer effective pair potentials. This work demonstrates the possibility of determining thermodynamic data using computer simulation techniques, as well as some of the fundamental difficulties in applying Hartree–Fock pair potentials to predict the thermodynamic properties of condensed matter.

Introduction

Some recent attempts to understand the nature of various geochemical systems applied interaction potential functions in conjunction with computer simulation techniques to predict equilibrium properties. One particular approach employed interparticle potentials calculated with modified electron-gas theory or Hartree-Fock self-consistent-field theory. Combined with free-energy minimization techniques, binding energies, bond distances, and elastic properties of crystals have been calculated for alkali halide crystals (e.g., Cohen and Gordon, 1975; Zhadanov and Pdyakov, 1977; Mackrodt and Stewart, 1979) as well as various crystalline oxides—MgO, MnO, CaO, BeO, FeO, ZnO, Al_2O_3, SiO_2, and TiO_2 (e.g., Mackrodt and Stewart, 1979; Cohen and Gordon, 1976; Dienes et al., 1975; Tossell, 1980). Empirical potentials have also been used with energy minimization techniques to predict lattice energies for several silicate crystal structures (Catlow et al., 1982).

In addition, Monte Carlo (MC) and molecular dynamics (MD) techniques have been used to predict equilibrium and transport properties of various systems. These modeling efforts have started with potentials (usually of the Born–Huggins–Mayer form, see Tosi and Fumi, 1964; Woodcock, 1975 p. 4–12 for reviews of empirical potential functions) containing parameters which were determined by fits to properties of crystalline material at 298 K. MC and MD calculations employ the interaction potentials to predict the properties of the system as a function of the state variables. Both crystalline and liquid salt systems have been examined (e.g., Krogh-Moe et al., 1969; Woodcock and Singer, 1971; Larson et al., 1973; Adams and McDonald, 1974; Michielsen et al., 1975; Woodcock, 1975, p. 12–23) as well as silicate glasses (Woodcock et al., 1976; Soules, 1979; Soules and Busby, 1981; Angell et al., 1981; Angell et al., 1982, Hostetler, 1982).

In this work I present the results from a first principles simulation of the NaCl system. The interaction potential functions for the system have been determined using SCF-LCAO *ab initio* quantum calculations. These potential functions have been used in Monte Carlo computer simulations to calculate the enthalpy, entropy, and volume of both crystalline and molten NaCl as a function of temperature at one bar. The potential functions were also used with energy minimization methods to calculate the volume of crystalline NaCl as a function of pressure. These calculations provide a sensitive test of the accuracy of the computed interaction potential functions.

Procedure

Interaction potential functions

The total potential energy of a system of N interacting particles is given by:

$$U = \frac{1}{2!}\sum_{\substack{i=1\\ i\neq j}}^{N}\sum_{j=1}^{N}\phi_{ij} + \frac{1}{3!}\sum_{\substack{i=1\\ i\neq j\neq k}}^{N}\sum_{j=1}^{N}\sum_{k=1}^{N}\phi_{ijk} + \cdots \qquad (1)$$

relative to a standard state of infinitely dispersed particles. Each index runs over all the particles, and the summands

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are the interaction potential functions representing the contribution to the potential energy from the particles indexed in the function. The interaction potentials (and the potential energy) are functions of the particle positions. In lieu of adequate theoretical knowledge of the effects of many-body interactions, defining a pairwise additive potential function which reproduces the potential energy of the system is convenient:

$$U = \left\langle \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \phi_{ij}^{eff} \right\rangle \tag{2}$$

where the angular brackets denote an ensemble average. The degree to which this effective pair potential fails to reproduce other properties of the system is a measure of the importance of many-body interactions. Stillinger (1964, p. 4–17) proposed theoretical arguements that polarization forces (which account for approximately one percent of the potential energy for the NaCl system) are the only important many-body interactions in molten salts.

The effective potentials used in this study have the form:

$$\phi_{ij}(r) = \frac{Z_i Z_j e^2}{r} + \frac{A_{ij}}{r^6} + \frac{B_{ij}}{r^7} + \frac{C_{ij}}{r^8} \tag{3}$$

where the Z_i are the formal ionic charges, e is the fundamental unit of electronic charge, and A_{ij}, B_{ij}, and C_{ij} are adjustable parameters. The potential is a function of the particle types and the distance between them, r. The first term represents the coulombic interaction between two ions and the latter terms represent a combination of the dispersion forces and repulsive forces. This particular form for the potential functions is similar to the Pauling (1928) form, and was chosen for convenient use with the (N,*P*,*T*) Monte Carlo technique (discussed below).

In order to determine the parameters in the effective pair-potential, a data set was generated consisting of the energies of a pair of particles as a function of separation. The energies of each particle pair were calculated using *ab initio* restricted Hartree-Fock self-consistent-field quantum techniques which involve computing all necessary one- and two-electron integrals. After initial assumptions are made (discussed below) no input data are needed to evaluate the energy of the system. The Gaussian-76 (Pople et al., 1978) program was used to calculate energies. The parameters were fit with the least squares technique using the equation:

$$\sum_i \sum_j \phi_{ij}(\mathbf{r}) = E_C - \sum_K E_K \tag{4}$$

where E_C is the energy of the cluster and E_k is the reference state energy of particle k.

Monte Carlo calculations

The Monte Carlo method is based on the theory of Markov processes and was first described by Metropolis et al. (1953). A modification of the basic method to allow calculation in the isobaric-isothermal (N,*P*,*T*) ensemble was described by Adams and McDonald (1974) and was used for this work. Starting from a given initial configuration a Markov chain of configurations is generated by displacing a randomly chosen particle by a random amount. The volume of the system is also randomly changed. The pseudo-Boltzmann weighting factor, W, from a state with potential energy *U* and volume *V* to a state *U'*, *V'* is calculated:

$$W = (U' - U) + P(V' - V) - NkT\ln(V'/V) \tag{5}$$

where k is Boltzmann's constant and N, P, and *T* are the number of particles, the pressure, and the temperature of the system. If W is negative for the transition the new configuration is accepted for inclusion in the ensemble average. Otherwise the configuration is accepted with probability which is $\exp(-W/kT)$. If the new configuration is rejected the old configuration is retained and included in the ensemble average. This algorithm ensures that each configuration shows up in the ensemble average with a frequency proportional to its weighting factor. The process is repeated for the number of configurations desired.

Two parameters govern the efficiency of the Monte Carlo sampling processes. These are the maximum amount any particle can be displaced, and the maximum change in volume for a transition. These parameters were chosen by trial and error such that the acceptance ratio was close to 0.5.

The ensemble average of any configuration dependent property corresponds to the value of the property at the given *P* and *T*. In particular:

$$E = \langle U + 3/2NkT \rangle \tag{6}$$

$$H = \langle E + PV \rangle \tag{7}$$

$$V = \langle V \rangle \tag{8}$$

where *E* is the internal energy, *H* the enthalpy, and *V* the volume of the system. The third law entropy of the system was computed using (N,*V*,*T*) Monte Carlo runs at each calculated volume with the cell approximation method (Gosling and Singer, 1970):

$$S_i = \frac{\langle \phi - \phi_{min} \rangle}{2kT}\, 1.5\left\{1 + \ln\left(\frac{2\pi m_i kT}{h^2}\right)\right\} + \frac{1}{N}\ln C + \ln f_i \tag{9}$$

where $C = 1$ for solids, $N^N/N!$ for liquids, f_i is the free volume (Kirkwood, 1950), and ϕ_{min} is the minimum value of the potential in the free volume. The free volume is equal to a(V)*V* where a(V) is the acceptance ratio as a function of volume. The MC jump parameter is varied and the maximum calculated free volume is the MC estimate of the true free volume. Although the free volume can be estimated rather precisely using this method, the treatment of the minimum potential energy term is much less accurate. Gosling and Singer (1970) found that entropies computed in this manner were systematically lower than corresponding experimental values for liquid argon. In spite of this bias, we chose the free volume method for computing entropies in order to conserve computational resources; calculation of entropies using p dV integration along isotherms would have required about ten MC runs for each temperature.

To include the effects of the long-ranged coulomb potential and to minimize surface effects in the MC simulations periodic boundary conditions are enforced on the system. Two computational techniques were used in conjunction with the periodic boundary conditions. The minimum image convention allows each particle in the system to interact only with its N-1 nearest neighbors in the system; each neighbor is either a particle in the system or an image of the particle produced by the periodic boundary conditions. The Ewald technique (Ewald, 1921; Brush et al., 1966) was also used to evaluate the long range coulomb potential.

Free energy minimization

The free energy minimization method was used to calculate the volumes and free energies of crystalline phases as a function of pressure. The B1 and B2 phases of NaCl were studied at 0 K. (The phase change behavior for NaCl seems to be fairly insensitive to temperature, Cohen and Gordon, 1975) Using this simplifying assumption, the free energy is just:

$$G = U(V) + PV \tag{10}$$

Using the interaction potential model described above, at a given pressure the free energy depends on only one variable, the volume. Minimization of G with respect to the volume gives the free energy of the crystalline phase. The condition for the B1–B2 phase change is G(B1) = G(B2).

Results

The energies of Na^+–Na^+, Na^+–Cl^-, and Cl^-–Cl^- pairs were calculated as a function of separation distance using the Gaussian-76 (Pople et al., 1978) program. This *ab initio* method uses linear combinations of atomic orbitals (LCAO) to form the molecular orbitals. The number of atomic orbital functions, their mathematical form, and their adjustable parameters comprise a basis set for that atom. Larger basis sets are more flexible and possibly allow better description of the charge distribution in a molecular environment. Calculations were performed using several published basis sets (described briefly in Table 1).

Closed-shell ions were chosen as the reference state for the quantum calculations. The SCF equations assume each of the electrons in a system move in a coulombic field generated by the nuclei and the time averaged positions of the other electrons. In reality the electron motions are correlated. The correlation energy can be quite large. Using closed-shell ions as the reference state for calculations on a cation-anion cluster approximately conserves correlation error. When the energy of the reference state ions is subtracted from the ion pair energy, the correlation energy approximately cancels.

It should be kept in mind that all of the basis sets except for the (12,9) basis set used in this calculation were unbalanced (i.e. contained different numbers of basis functions per electron for Na and Cl). This lack of balance acts as a constraint on electron population distribution, which is determined in part by mathematical flexibility. The lack of balance is a potential source of error in determining Hartree-Fock energies.

Table 1. Basis set size and balance

Basis Set	Number of Functions for Na	Number of Functions for Cl	Na Functions Per Electron	Cl Functions Per Electron
STO-3G[a]	18	18	1.8	1.0
STO-3GDZ[b]	24	36	2.4	2.0
(12,9)[c]	42	78	4.2	4.3
[6,4][d]	12	18	1.2	1.0
STO-3G[e]	30	30	3.0	1.7

[a] Three Gaussian fits to slater-type-orbitals (Pople et al., 1978)

[b] Double Zeta STO-3G (two basis functions per orbital) (Clementi, 1964)

[c] Twelve Gaussian functions with s type symmetry, 9 p functions (Veillard, 1968).

[d] Six Gaussian s type functions, 4 p functions; contracted from the (12,9) basis (Veillard, 1968).

[e] Polarization (d) functions added to the STO-3G basis (Pople et al., 1978)

In Table 2 energies for the Na^+–Cl^- pair separated at 3.0Å and for the reference states are compared for several basis sets. The energy obtained with the Born–Huggins–Mayer (BHM) model at this distance is 7.55×10^{-19} J (Adams and McDonald, 1974). Even for the large (12,9) basis set the agreement is rather poor. The STO-3G basis set was also used to calculate interaction energies as a function of distance for the Na^+–Cl^- ion pair. In Figure 1 the *ab initio* potential is plotted along with the coulomb energy and the BHM potential. The STO-3G potential is approximately twenty percent too negative at distances less than 3Å.

Negative deviations in computed potentials can be caused by counterpoise error. This error is a spurious lowering of the energy of a cluster relative to the reference energies. Counterpoise error is a mathematical artifact of the orbital approximation resulting from extra degrees of freedom in the cluster relative to the reference state (Carsky, 1980). In order to decrease the counterpoise error "ghost" atomic centers were added to the calculations of the reference state energy. These ghost centers carry the orbitals of the other nuclear center in the cluster but no nuclear or electronic charge. Thus the electrons in the reference state ion can interact with the orbitals of the other

Table 2. Calculated energies for Na^+–Cl^- ions separated by 3.0Å

Basis Set	E_{Na^+} (A.U.)	E_{Cl^-} (A.U.)	$E_{Na^+Cl^-}$ (A.U.)	ΔE (10^{-19} J)
STO-3G	-159.78462	-454.48042	-614.46194	-8.58
(12,9)	-161.67095	-459.56094	-621.41244	-7.87
[6,4]	-161.66011	-459.51591	-621.36484	-8.23
STO-3G*	-159.78462	-454.48042	-614.51582	-10.93

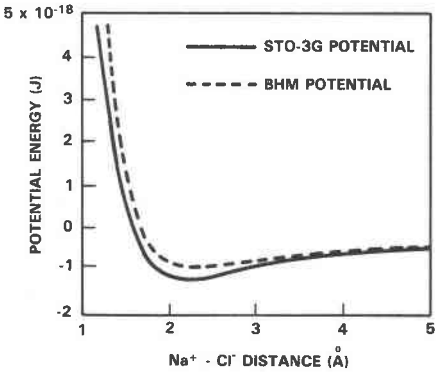

Fig. 1. Comparison of the *ab initio* STO-3G Na^+–Cl^- potential with the empirical Born–Huggins–Mayer potential (Adams and McDonald, 1974).

ion in the cluster, so the counterpoise correction is approximately the same in the reference state and the cluster. Table 3 contains the results for four basis sets for Na^+–Cl^- pair at 3Å as corrected for counterpoise error. Counterpoise error generally increases with both atomic number and negative charge (Carsky, 1980) and in these calculations most of the counterpoise correction does come from the $C1^-$-ghost term. Also note that the counterpoise error is inversely proportional to basis set size. A large portion of the negative deviations in the calculated Na^+–Cl^- potentials can be corrected in this way.

Given the results in Table 3 and the constraints on computer time, the STO-3G* basis was chosen for calculation of the detailed interparticle potential functions. The computed interaction energies for the three pairwise interactions at 28 interionic distances are listed in Table 4. These results were all corrected for counterpoise error using the method described above.

Expansion coefficients were fit to the data in Table 4 using equations (3) and (4). The expansion coefficients for each potential are presented in Table 5. A small constant was also needed to fit the data. The deviations from the Adams and McDonald (1974) BHM potentials are plotted in Figure 2. The total deviation is negative near the equilibrium geometry, becoming smaller with increasing separation (i.e. the Hartree-Fock potentials are too soft). The effects of the deviations on computed thermodynamic properties will be examined next.

Table 3. Calculated energies for Na^+–Cl^- ions separated by 3.0Å corrected for counterpose error

Basis Set	E_{Na^+} (A.U.)	E_{Cl^-} (A.U.)	$E_{Na^+Cl^-}$ (A.U.)	ΔE (10^{-19} J)
STO-3G	-159.78483	-454.49379	-614.46194	-7.99
STO-3GDZ	-160.52267	-456.47274	-617.17922	-8.01
[6,4]	-161.66014	-459.52043	-621.36484	-8.03
STO-3G*	-159.78599	-457.91274	-617.87287	-7.59

Table 4. Interaction potentials for the NaCl system

	ϕ (10^{-19}J)		
separation (A)	Na^+Cl^-	Na^+Na^+	Cl^-Cl^-
2.60	-8.278	-	-
2.75	-8.061	-	-
2.80	-7.974	-	-
2.85	-7.883	-	-
2.90	-7.788	-	-
2.95	-7.691	-	-
3.00	-7.592	-	-
3.25	-7.091	-	-
3.50	-6.616	-	-
3.70	-	6.232	-
3.75	-6.184	-	6.007
3.80	-	6.067	-
3.90	-	5.912	5.789
3.95	-	5.837	5.721
4.00	-5.796	5.764	5.655
4.05	-	5.694	5.590
4.10	-	5.625	5.527
4.15	-	5.556	5.467
4.20	-	5.490	5.405
4.30	-	5.363	-
4.40	-	5.241	-
4.50	-5.146	5.125	5.067
4.70	-	4.907	-
4.90	-	4.707	-
5.00	-4.626	4.613	4.584
5.75	-	4.011	4.002
6.30	-3.666	-	-
6.50	-3.553	-	-

The Monte Carlo calculations were performed for a system containing 64 ions (i.e., 32 of each type) in a cube with periodic boundary conditions. For runs below the experimentally determined melting point (1074 K) the starting configuration was a simple cubic lattice with edge length of 8.4Å. For the runs above 1074 K, a random initial configuration was prepared by heating the crystalline starting configuration at 2000 K for 10^5 configurations. The initial 10^5 configurations were also discarded from each of the high temperature runs. Three independent runs were made at each temperature of 2×10^5 configurations, and the results averaged. The maximum particle displacement and volume change parameters were chosen for each temperature so that the acceptance ratio was near 0.5. The pressure was one bar for all of the MC runs.

Thermodynamic properties calculated with the MC technique at 4 temperatures are listed in Table 6. Except for the

Table 5. Expansion coefficients for the interaction potential functions (short-range terms)

$$U(\text{short}) = \sum_i \sum_j \frac{a_{ij}}{r^6} + \frac{b_{ij}}{r^7} + \frac{c_{ij}}{r^8} + K$$

	Na^+Cl^-	Na^+Na^+	Cl^-Cl^-
a_{ij} (J Å^6)	-1.082×10^{-16} (3)	-2.766×10^{-18} (1)	2.144×10^{-16} (1)
b_{iij} (J Å^7)	4.520×10^{-16} (3)	0	-2.322×10^{-15} (1)
c_{ij} (J Å^8)	-3.205×10^{-16} (3)	2.248×10^{-17} (1)	5.125×10^{-15} (1)

$K = 1.521 \times 10^{-21}$ (J)

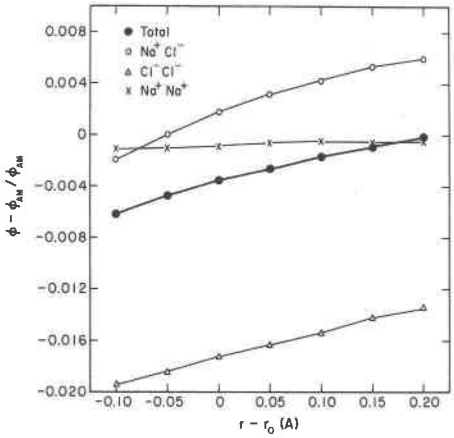

Fig. 2. Deviations of the counterpoise corrected STO-3G* potentials (this work) from the Born–Huggins–Mayer potential (Adams and McDonald, 1974).

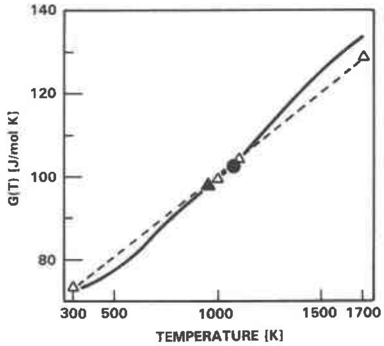

Fig. 3. Gibb's function $(-(G_T - H_{298})/T)$ as a function of temperature. Heavy line from Robie et al. (1978). Open triangles this work. Solid circle is experimental melting point of NaCl, solid triangle represents melting point derived this work.

enthalpy function, the values are within five percent of the available thermodynamic data. The enthalpies are about ten percent too low. The volumes found for all of the liquids were all lower than the volume at the melting point, which is 37.6 cm^3. The entropies were computed using (N,V,T) MC runs at the volume determined by the (N,P,T) result; the low volumes tending to produce low entropies. These results indicate that the potentials are too soft compared to the Adams and McDonald (1974) BHM potentials, which more accurately reproduce the enthalpy and volume at 1073 K. This result is consistent with the data in Figure 2 which show decreasing deviation with increasing distance.

A common thermodynamic technique uses interpolation on the Gibb's function to find the temperature at which two phases are in equilibrium. Linear interpolation for the low and high temperature data shows liquid and crystalline NaCl have equal free energies at 950 K. If the same procedure were used with the experimentally determined free energy data the equilibrium temperature would be 1040 K. (The actual melting temperature is 1073 K.) The free energy results are illustrated graphically in Figure 3. This figure points out the difficulty of accurately predicting phase relations using this method due to the similarity of slopes of the Gibb's function for the liquid and the solid. A better result might have been obtained by interpolating over a smaller temperature range.

Table 6. Monte Carlo results for the NaCl system at four temperatures

		298K[f]	1000K[f]	1100K[g]	1700K[g]
H(T)[a,b]	MC[d]	0	36.45 (50)	60.34 (50)	65.82 (40)
	EX[e]	0	39.88	67.93	67.78
S[a]	MC	72.29 (50)	135.73 (100)	164.46 (100)	194.42 (100)
	EX	72.12	139.37	171.89	201.30
G(T)[a,c]	MC	72.29	99.28	104.11	128.60
	EX	72.12	99.49	103.96	133.52
V(cm^3)	MC	27.12 (5)	28.69 (4)	30.36 (4)	35.13 (3)
	EX	27.02	-	-	-

[a] units of J/mol K
[b] $H(T) = (H_T - H_{298})/T$
[c] $G(T) = -(G_T - H_{298})/T$
[d] Monte Carlo results
[e] experimental results Adams and McDonald (1974), Robie
[f] simple cubic lattice start
[g] random start

Using the free energy minimization technique, the volume of the B1 and B2 phases of crystalline NaCl were determined at 0 K as a function of pressure. These data are presented in Figure 4. The heavy solid line is the negative of the difference between the more stable phase and the volume of the B1 phase at zero pressure (V_{01}) divided by V_{01}. The upper row of dots are the same quantity for the B1 phase, and the lower row of dots are for the B2 phase. The phase transition was found to be at 160 kbar versus the experimental value of 300 kbar (Bassett et al., 1968). This result is quite similar to the value of 107 kbar determined by Cohen and Gordon (1975) using the ionic model. Both

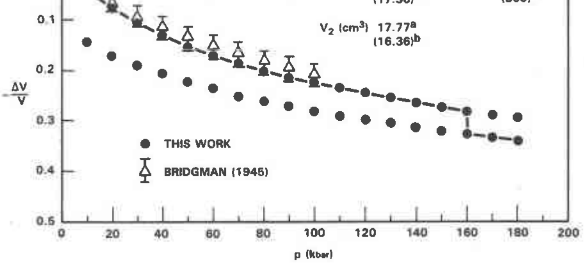

Fig. 4. Volume changes of the B1 and B2 phases of NaCl as a function of pressure. V_{01}—volume of B1 phase at zero pressure; V_1, V_2—volumes of B1 and B2 phases at the phase change pressure; $V_{12} = V_1 - V_2$; p_{12} – pressure of the phase transition. Upper dots and crosses for B1 phase, lower dots for B2 phase. Heavy line represents volume change for thermodynamically stable phase.

models provide a good prediction of the B1 phase up to around 100 kbar.

Discussion

Computation of accurate interaction potential functions using *ab initio* SCF-LCAO methods requires care in basis set selection. Errors in computed potentials can arise from a variety of sources: incomplete cancellation of correlation error, incomplete correction for counterpoise error, and lack of basis set balance. The basis sets used in this work were optimized for isolated neutral atoms, and no reoptimization for isolated ions or for ion-pairs was performed. Also, only ion-pair clusters were used to develop the effective pair potentials in this work. Another possible approach would employ solid state energy calculations to develop pseudopotentials from a geometry variation. Despite these limitations, the computed interaction potentials are quite close to empirically determined potentials (Adams and McDonald, 1974) and to potentials determined using an ionic model (Gordon and Kim, 1972).

Monte Carlo calculations provide a sensitive test of interaction potentials. The equilibrium properties computed in this study deviate from the experimental values because the potential functions are too negative. Furthermore, the amount by which the Hartree-Fock potentials deviate from an effective pair potential changes with interparticle separation (Fig. 2). The deviations in the enthalpy function are the largest, approximately ten percent. Ten percent of the enthalpy function represents a difference of 3 kJ in the enthalpy at 1000 K. The lattice energy of the B1 phase of NaCl was calculated to be -764 kJ. This agreement to within one-half percent (relative to the ion reference state) is consistent with the deviations in the potential functions from the BHM model (Fig. 2) and illustrates the difficulty in obtaining thermodynamic data from potential energy-based techniques. The thermodynamic quantities are derived from quite small differences between states containing large potential energies. (The potential energies themselves are computed as small differences between the Hartree–Fock energies of the cluster and reference state, see equation (4), Tables 2 and 3.) This difficulty is similarly manifested in computing phase relationships. For both the one atmosphere MC simulations and the 0 K energy minimizations, the predicted phase change points were not as accurate as the predicted free energies and volumes.

This work demonstrates the possibility of determining thermodynamic data (for a simple system) from first principles using computer simulation techniques. This work also points out some of the fundamental difficulties in applying Hartree–Fock pair potentials to condensed matter. Future work, refining the interaction potential functions, should lead to a great improvement in the accuracy of computed equilibrium properties, and an increased understanding of the interparticle interactions in the NaCl system.

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