Equation of state for solid neon from quantum theory

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(Received 25 June 2009; published 11 August 2009)

The equation of state $P(V,T)$ for solid neon is obtained from a quantum theoretical treatment using two- and three-body forces, and an anharmonic treatment for lattice vibrations and temperature effects within the Einstein approximation. Our results are in excellent agreement with experiment for the pressure and temperature range of up to 200 GPa and 900 K. The calculated equation of state is fitted to an analytical expression for the pressure-volume dependence $P(V)$ of the two- and three-body terms and the Einstein frequency $\omega_E(V)$ with high accuracy for a pressure range up to 500 GPa.

DOI: 10.1103/PhysRevB.80.064106 PACS number(s): 64.30.Jk, 61.66.Bi, 62.50.−p, 63.20.D−

I. INTRODUCTION

Neon is a noble gas, has closed electron shells, and it crystallizes only in a face-centered cubic structure. Because of its simplicity, neon seems to be an ideal test system for both wave-function and density-functional-based theoretical methods.[1] It is however a nontrivial task to accurately obtain the equation of state (EOS) for any solid including neon at any given temperature and volume up to high pressures.[2–5] The usual procedure to obtain precise equations of state is to fit results from accurate computer simulations using first-principles quantum theoretical methods or to experimental measurements. While accurate experimental measurements for neon are available for pressures and temperatures up to 200 GPa and 1000 K, respectively,[5–10] the simulation of the corresponding isotherms involve a fit to empirical expressions such as the Birch-Murnaghan[11] or Vinet[12] EOSs for experimental data,[13,14] which are not capable to reproduce the whole pressure-volume range.

On the theoretical side, equations of state for the hard-sphere model of solids have been derived for face-centered cubic and hexagonal closed-packed lattices.[15–18] Even though the polarizability of neon is quite small [2.67 a.u. (Ref. 19)], it cannot be treated within the hard-sphere model especially at higher pressures, as the quantum theoretical treatment of solid neon involves the correct description of dispersive type of interactions (van der Waals), overlap and repulsive effects and effects resulting from the lattice dynamics.[20,21] As density-functional theory is currently not capable to account for both dispersive type of interactions in the long range and overlap effects in the short range to sufficiently high accuracy,[22,23] the quantum theoretical treatment of rare-gas solids is restricted to wave-function-based theories. Recent developments include the method of increments (IC) within coupled-cluster (CC) theory developed by Stoll and Paulus,[24,25] which was successfully applied to rare-gas solids (at zero pressure and temperature) by Rosćiszewski *et al.*[26,27] However, the method of increments would be computationally too demanding to produce the equation of state up to high pressures and temperatures.

Here we present a quantum theoretical treatment within a many-body decomposition of the total interaction energy, which includes the accurate treatment of two- and three-body forces, to obtain the equation of state for solid neon. Our results are within the experimental uncertainty for the available pressure-temperature range.

II. THEORY

We obtain the pressure $P(V,T)$ as a function of volume V and temperature T from $P(V,T)=-dF(V,T)/dV$, with F being the Helmholtz free energy,

$$F(V,T) = E_2(V) + E_3(V) + E_{\mathrm{HZPV}}(V) + E_{\mathrm{AZPV}}(V) + k_B T \sum_i \ln\{1 - \exp[-\hbar\omega_i(V)/k_B T]\}. \quad (1)$$

The Tang-Toennis expression for the two-body interaction energy $E_2(V)$ between two neon atoms is used, which was recently obtained from a complete basis set limit study using relativistic coupled-cluster theory by Hellmann *et al.*[28] For the three-body term $E_3(V)$ we performed CC calculations including single and double substitutions plus noniterative triples, CCSD(T), using an augmented correlation consistent quintuple-zeta basis set (aug-cc-pV5Z) for Ne_3 (D_{3h}),[29] and subsequently adjusted our data to an extended triple-dipole Axilrod-Teller (EAT) potential, which takes care of both attractive overlap effects in the short-range region and repulsive effects in the long-range of the Ne_3 three-body term,

$$E_3^{\mathrm{EAT}}(i,j,k) = f_\theta[c_0 r_g^{-9} + (c_1 + c_2 r_g^2 + c_3 r_g^4)e^{-c_4 r_s}]$$

$$\text{with } f_\theta = (1 + 3\cos\theta_i \cos\theta_j \cos\theta_k),$$

$$r_g = (r_{ij} r_{jk} r_{ik})^{1/3}, \quad \text{and} \quad r_s = r_{ij} + r_{jk} + r_{ik} \quad (2)$$

with r_{ij} being the distance between two neon atoms i and j in the fcc crystal, and θ_i the corresponding angle between the vectors $\vec{r}_{ij}$ and $\vec{r}_{ik}$. The adjusted parameters (in atomic units) are $c_0=12.9236$, $c_1=466.449$, $c_2=-168.680$, $c_3=4.32545$, and $c_4=1.23818$. The three-body EAT potential is shown in Fig. 1 in comparison with three other potentials published previously.[30–33] As Fig. 1 clearly demonstrates the EAT potential has the correct long-range behavior of the triple-dipole AT term.

The total two- and three-body term $E_3(V)$ is obtained by summing over all three-body interactions in the fcc crystal considering translational symmetry,[34]

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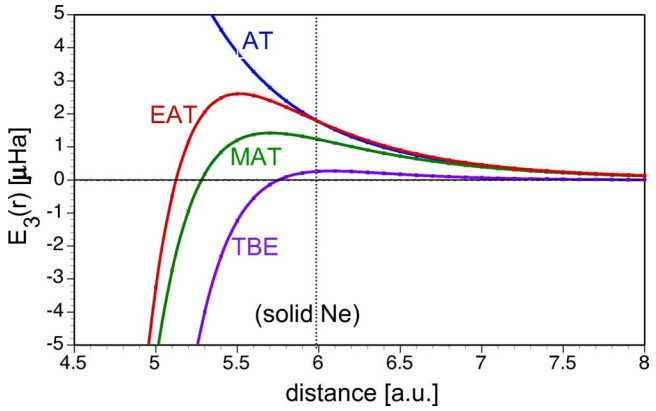

FIG. 1. (Color online) A comparison of different three-body potentials for the equilateral triangle of Ne_3 ($r_{12}=r_{13}=r_{23}$). AT: repulsive Axilrod-Teller term ($c_0=12.9236$); EAT: extended AT of Eq. (1) as used in this work; MAT: modified AT by Freiman and Tretyak (Ref. 30); TBE: three-body potential of Ermakova *et al.*(Ref. 31) The vertical line shows the nearest-neighbor distance in fcc neon.

$$E_2(V)+E_3(V)=\frac{1}{2}\sum_{i}^{N}E_2(r_{0i})+\frac{1}{3}\sum_{i<j}^{N}E_3(r_{0i},r_{0j},r_{ij}), \quad (3)$$

where r_{0i} is the distance between the inner most (central atom) and atom i in the fcc lattice for a specific lattice constant a and corresponding volume $V=a^3/4$. We took $N=50\,000$ atoms in our lattice summation for the two- and three-body forces, which is sufficient to converge the lattice constant out to five significant digits in our optimization procedure.

$E_{\mathrm{HZPV}}(V)$ in Eq. (1) is the harmonic (H) zero-point vibrational (ZPV) energy which takes care of the lattice dynamics. Here we adopt the simple Einstein (E) approximation by moving one neon atom in the static field of all other atoms in the fcc crystal, which gives the simple expression $E_{\mathrm{HZPV}}(V)=3\hbar\omega_E(V)/2$, where ω_E is the Einstein frequency obtained from two-body forces only. Anharmonicity effects, $E_{\mathrm{AZPV}}(V)$, were accounted for by using a perturbative approach (PT) within the Einstein approximation as outlined in Ref. 34. This greatly simplifies the last Boltzmann term in Eq. (1) leading to the expression for the thermal phonon pressure,

$$P_{th}=-3\{\exp[\hbar\omega_E(V)/k_BT]-1\}^{-1}\hbar d\omega_E(V)/dV. \quad (4)$$

Note that Eq. (4) is not valid near the melting point, as in the harmonic approximation ω_E approaches zero and the perturbative anharmonic treatment breaks down. This corresponds to a point where symmetry breaks and the fcc lattice becomes unstable. In our calculations this occurs at a volume of 17.8 $\mathrm{cm}^3/\mathrm{mol}$, which results in a density of 1.14 g/mol close to the experimental value of liquid neon [1.21 g/cm^3 at 27 K (Ref. 35)]. Moreover, at extremely high temperatures, pressure from electronic excitations has to be considered as well, which can be neglected here for the temperature range studied.

III. DISCUSSION

We tested our approach for the fcc lattice of the 20-Ne isotope where experimental data are available. The results are presented in Table I in comparison with recent calculations from other research groups.[27,40–42]

TABLE I. Optimized properties for fcc lattice of 20-Ne. Lattice constant a_0 in Å, cohesive energy E_{coh} in cm^{-1}, and bulk modulus B_0 in GPa. Experimental data (extrapolated to 0 K) from Refs. 36–39. See Eq. (1) for the definition of the individual interaction terms. IC: Method of increments (Ref. 25); L-MP2: Local second-order Møller-Plesset; PW91+vdW: The PW91 density functional plus van der Waals correction. HFWL: Hartree-Fock exchange plus Wilson-Levy correlation functional.

Method	a_0	E_{coh}	B_0
Expt.	4.4644	161.6 ± 0.7	1.102 ± 0.012
E_2	4.2794	229.2	2.037
$E_2+E_3^{\mathrm{AT}}$	4.2959	221.6	1.951
$E_2+E_3^{\mathrm{MAT}}$	4.2807	223.6	2.010
$E_2+E_3^{\mathrm{EAT}}$	4.2939	221.5	1.903
$E_2+E_3^{\mathrm{EAT}}+E_{\mathrm{HZPV}}^{E}$	4.4772	162.3	0.974
$E_2+E_3^{\mathrm{EAT}}+E_{\mathrm{HZPV}}^{\mathrm{PD}}$	4.4579	164.1	1.077
$E_2+E_3^{\mathrm{EAT}}+E_{\mathrm{HZPV}}^{E}+E_{\mathrm{AZPV}}^{\mathrm{PT}}$	4.4687	157.4	1.095
$E_2+E_3^{\mathrm{EAT}}+E_{\mathrm{HZPV}}^{\mathrm{PD}}+E_{\mathrm{AZPV}}^{\mathrm{PT}}$	4.4509	159.4	1.174
IC-CCSD(T)+$E_{\mathrm{HZPV}}^{\mathrm{PD}}$ [a]	4.468	164.8	1.09
LMP2[b]	4.35	165.5	0.61
PW91+vdW [c]	4.562		2.1
HFWL[d]	4.22	219.9	

[a]Reference 27.
[b]Reference 40.
[c]Reference 41.
[d]Reference 42.

Taking all terms into account as shown in Eq. (1) leads to results very close to experimental measurements. Only the more elaborate IC coupled-cluster calculations by Rościszewski *et al.*[27] are close to our values. It is also evident that for the lattice constant, cohesive energy, and bulk modulus ZPV effects need to be included. In fact, our results show that lattice vibrations lower the cohesive energy by 28% and the bulk modulus is basically halved. We mention, however, that for the bulk modulus the main change comes from the increase in the lattice constant due to zero-point vibrational contributions, as this property is very sensitive to slight changes in the lattice constant.

Included in our table are results from taking the phonon dispersion (PD) into account as described in detail in Ref. 43. They lead to relatively small changes compared to the Einstein approximation. Moreover, we tested the Einstein model at small constant volumes (high pressures of 500 GPa) which lead only to small changes in the calculated pressure. Table I also compares our three-body term with the standard Axilrod-Teller repulsive potential [in atomic units $c_0=12.02$, $c_i=0$ for $i\geq1$ (Ref. 32)] and to the empirically fitted modified AT (MAT) potential by Freiman and Tretyak[30] ($c_0=11.835$, $c_1=566.969$, $c_2=c_3=0$, and $c_4=1.1896$).[33]

The calculated isotherms from Eq. (1) are shown in Fig. 2 in comparison with experimental data. In order to make the different isotherms more visible, we also include graphs in the low-pressure region of up to 50 GPa. Our results are

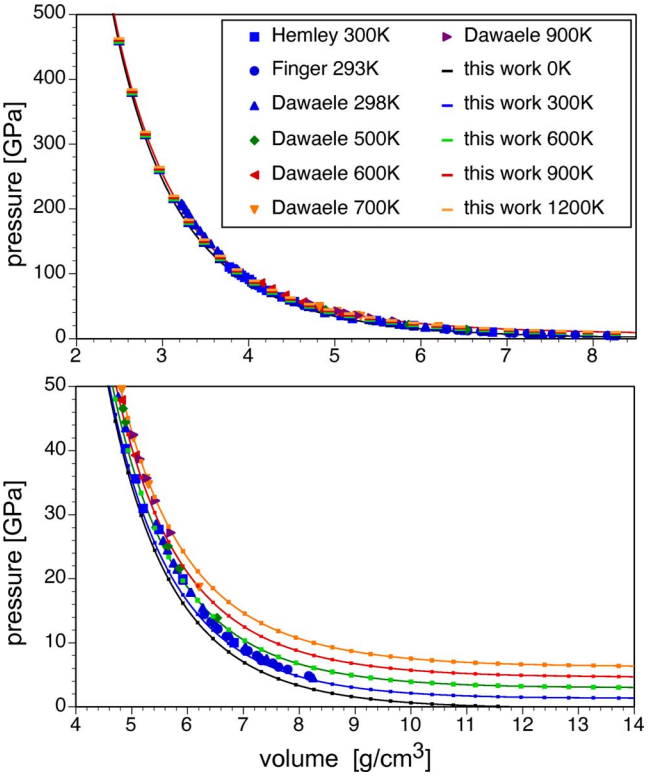

FIG. 2. (Color online) Calculated isotherms for solid neon up to 500 GPa (50 GPa for the bottom figure) and 1200 K. Experimental values obtained from different research groups are shown as well. In detail: 300 K measurements by Hemley *et al.*(Ref. 8); 293 K Finger *et al.*(Ref. 7); all other measurements at different temperatures by Dewaele *et al.* (Ref. 9).

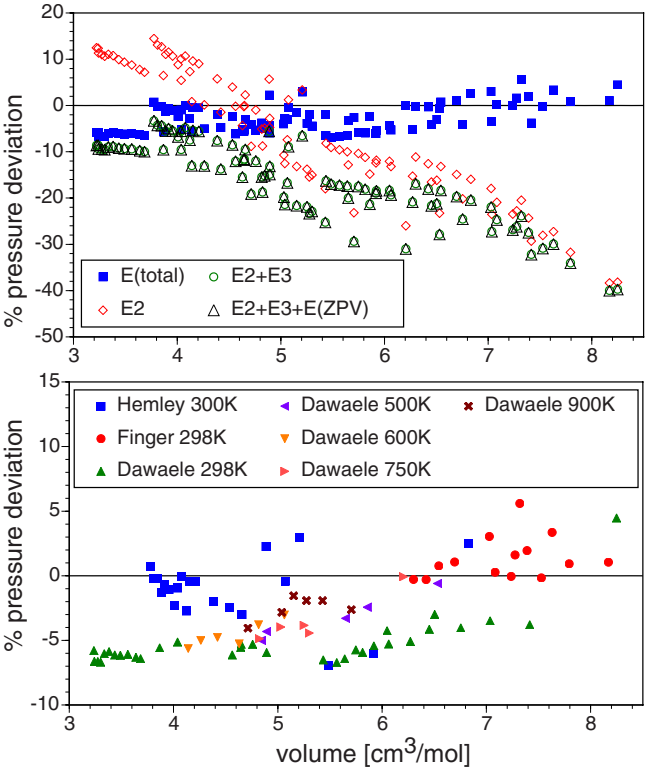

FIG. 3. (Color online) Percentage deviation from the experimental pressure values (Refs. 8 and 9) at given volume and temperature. Top: Deviations shown for individual terms used in Eq. (1). Bottom: Deviations shown for the complete sum terms in Eq. (1).

again in excellent agreement with experimental data. To make the agreement between our calculated results and the experimental data more apparent, we show in Fig. 3 the percentage deviations between theory and experiment (negative values imply that the calculated results are below experiment). We note that we are in better agreement with the data given by Hemley *et al.*[8] than with the newer measurements by Dewaele *et al.*,[9] which could be due to small deficiencies in our three-body potential or to systematic experimental errors.

In Fig. 3 we also show that three-body terms become most important in the low-volume (high-pressure) region [deviation from experiment using $E_2(V)$ only], while in the large-volume (low-pressure) region thermal contributions seem to dominate [deviation from experiment using $E_2(V)+E_3(V)+E_{\mathrm{ZPV}}(V)$]. Best agreement with experiment is only achieved if all contribution as shown in Eq. (1) are taken into account, with the exception of perhaps anharmonicity effects, which are rather small in the high-pressure regime. For example, at a lattice constant of $a=2.5$ Å ($V=2.352$ cm^3/mol) and a temperature of 300 K we calculate a total pressure of $P_{total}=560.7$ GPa. The individual contributions from Eq. (1) are: two-body $P_2=735.2$ GPa, three-body $P_3=-184.6$ GPa, harmonic ZPV correction $P_{\mathrm{HZPV}}=10.0$ GPa, anharmonic correction $P_{\mathrm{AZPV}}=-0.7$ MPa, and thermal correction $P_{th}=0.2$ GPa. In comparison, at $a=3.7$ Å ($V=7.626$ cm^3/mol) we have $P_{total}=6.49$ GPa, $P_2=4.54$ GPa, $P_3=-0.17$ GPa, $P_{\mathrm{HZPV}}=0.70$ GPa, $P_{\mathrm{AZPV}}=-1.8$ MPa, and $P_{th}=1.42$ GPa. Our results give also support to the fast convergence of the many-body expansion for neon even at high pressures.[44]

We can now address the important problem of finding an EOS for solid neon. As we use the Einstein approximation we express the total pressure in functions of $V, \omega_E(V)$ and T,

$$P[V,\omega_E(V),T] = P_{2+3}(V) + P_{\mathrm{ZPV}}[\omega_E(V)] + P_{th}[\omega_E(V),T]. \tag{5}$$

Hence we only require least-squares adjustments for the two functions $P_{2+3}(V)$ and $\omega_E(V)$, where $P_{2+3}(V)$ is the pressure containing the two-and three-body interaction terms derived from $E_2(V)$ and $E_3(V)$ in Eq. (1). With the two functions one easily determines from Eq. (5) the complete EOS. This, of course, cannot be done so easily if we take the full phonon dispersion into account.

From both the particle-in-a-box and the Fermi electron-gas model we expect that $P \sim V^{-5/3}$.[45] This term is, for example, included in the second-order Birch-Murnaghan[11] EOS. However, neither the Birch-Murnaghan nor the Vinet EOSs gave reasonable least-squares adjustments for the whole pressure range. We therefore use a simple exponential expression for both $P_{2+3}(V)$ and $\omega_E(V)$ which we found to perform best, i.e.,

$$f(V) = \sum_{n=0} a_n V^{-n} e^{b_n V}. \tag{6}$$

TABLE II. Adjusted coefficients for EOS [Eq. (6)] obtained from a least-squares fit procedure of $P_{2+3}(V)$ and the harmonic $\omega_E(V)$. V in cm^3/mol, $\omega_E(V)$ in K, $P_{2+3}(V)$ in GPa. Mean absolute error (MAE) and root-mean-squared error (RMSE) in GPa for $P_{2+3}(V)$ and in Kelvin for $\omega_E(V)$.

Coefficient	$P_{2+3}(V)$	$\omega_E(V)$
a_0	+5829.103	+312.1647
a_1	+2374.312	+4429.646
a_2	+30225.84	−1044.288
a_3	−127.2272	−19.94239
b_0	−1.421602	−0.6617924
b_1	−0.5428883	−0.1385099
b_2	−1.815097	−1.768841
b_3	+0.1176168	+0.4774531
MAE	0.016	0.146
RMSE	0.022	0.326

The adjusted parameters are listed in Table II. Anharmonicity effects are within the error of our least-squares fit procedure (see mean absolute error in Table I), and we therefore report the adjusted parameters for the harmonic Einstein frequency only. This formula is valid in the range of $0 \leq P \leq 500$ GPa and gives a lattice constant of $a_0=4.297$ Å in reasonable agreement with our $E_2+E_3^{\mathrm{EAT}}$ result shown in Table I. Even for the bulk modulus we obtain 1.794 GPa in good agreement with the value shown in Table I.

IV. CONCLUSION

In conclusion, we presented calculations for the EOS for solid neon up to high pressures and temperatures, which are in good agreement with experiment. Further improvements require a more complete treatment of the three-body force similar to the work by Røeggen[46] for helium, the four-body force, and the correct treatment of the phonon dispersion including anharmonicity effects. Close to the melting point dynamic effects need to be considered. We mention that we demonstrated recently that such an approach also leads to very accurate melting temperatures for neon and argon under normal conditions.[47,48] On the experimental side, the measurements presented by different research groups can deviate significantly (e.g., see the scatter of data in Fig. 3), and more accurate low- and high-pressure measurements for solid neon are required. We expect that the method applied will lead to similar good results for the EOS of the heavier rare-gas solids. Investigations into solid helium are currently underway.

ACKNOWLEDGMENTS

We thank the Royal Society of New Zealand (Marsden Grant No. 07-MAU-016) and Education NZ for financial support. Grants of computer time from Massey University are gratefully acknowledged. We thank R. Hellmann (Rostock) and E. Pahl (Auckland) for useful discussions.

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