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# Stability of the Face-Centered-Cubic Phase of Heavy Rare Gas Solids

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Our recent perturbation theory is applied to show that heavy rare gases solidify into a face-centered-cubic phase over a large temperature range near the melting lines. We have investigated the static, harmonic, and anharmonic contributions to the excess Helmholtz free energy and the stability to the face-centered-cubic phase. The observed stability is due to thermal contributions in the Helmholtz free energy.

X-ray diffraction experiments have shown that solid neon, argon, krypton, and xenon are in a face-centered-cubic (fcc) phase up to their melting lines, while helium freezes into a hexagonal close-packed (hcp) phase (with a small temperature range where the freezing to a fcc phase was recently observed).[1] In contrast, available theoretical calculations predict helium (at > 15 K) in a fcc phase and heavier rare gas solids in a hcp phase.[2,3] Helium behaves differently from the rest because of its highly quantum mechanical nature and significant many-body contributions in its interaction potential. We will confine the present investigation to heavy rare gas solids whose crystal structure has remained unexplained for the last two decades.

The crystal stability is governed by the Helmholtz free energy, A, which consists of the static, harmonic, and anharmonic contributions:

$$A = E_0 + A\,(\mathrm{harmonic}) + A\,(\mathrm{anharmonic})\ , \qquad (1)$$

where $E_0$ is the static lattice sum, and $A$ (harmonic) and $A$(anharmonic) are harmonic and anharmonic contributions to $A$, respectively. Since the fcc and hcp crystals have the same first and second neighbor lattice positions, $E_0$'s for the two lattices differ by interaction energies of higher neighbors.

The static energy for a physically reasonable pair potential almost always favors the hcp phases over the fcc phase. It is due to a small difference, $E/NkT = (E_{fcc} - E_{hcp})/E_{fcc} = -1\times10^{-4}$ in the long-range attractive interaction, but it contradicts the experimental observation. To overcome the difficulty, Alder and Paulson added a small bump to a pair potential near the third neighbor lattice position.[4] Strictly speaking, such an artificial bump has no theoretical basis. Salsburg and Huckaby showed that the harmonic approximation stabilizes the fcc phase for argon.[5] However, their careful calculation was limited to the 0K-density and depended sensitively on the second-nearest-neighbor approximation. Effects of density variation, higher-neighbor interactions, and anharmonic contributions to the crystal stability have not been included in their work.

Several investigators have examined three- and higher-body potentials as a possible cause for the crystal stability. Bell and Zucker computed the static energy difference including long-range many-body forces.[6] They concluded that the many-body forces are not sufficient to account for the stability of the fcc structure, although the hcp structure preference by the two-body forces is diminished. Niebel and Venables arrived at a similar conclusion (Ref. [2], p. 564).

A theory which can distinguish a small difference (within 0.1%) in the Helmholtz free energy of the two phases is required to resolve the crystal structure problem mentioned above. We have recently developed a perturbation theory (PT) of fluids and solids[7,8] and the hard-sphere radial distribution functions[9] for the fcc and hcp phases. The PT differs from the conventional quasi-harmonic lattice dynamics (LD) method in that the PT uses a short-range harsh (hence, very anharmonic) potential as a reference potential in contrast to the LD which considers only the harmonic lattice vibrations. We have previously shown that the PT gives reliable results at low solid densities and high temperatures (*e.g.*, near melting line) where large anharmonic contributions to thermodynamic quantities make the LD less useful. The motivation of the present work is to find out whether the PT can be applied to explain the crystal stability of rare gas solids and also to evaluate their melting properties. In this work, we show that the PT indeed predicts the observed fcc phase stability for heavy rare gas solids.

The PT divides a pair potential, $V(r)$, into the reference, $V_0(r)$, and perturbation, $W(r)$, potentials. Details of the separation scheme are given Refs. 8 and 10. The division of the potential is made optimum so that, when the configurational Helmholtz free energy ($A$) is expanded as a perturbation series, the inclusion of the reference ($A_0$) and first-order perturbation ($A_1$) contributions, together with the first-order quantum correction ($A_{qm}$) for atomic mass of $m$, is sufficient to yield accurate results at high temperature; i.e.,

$$A = A_0 + A_1 + A_{qm}. \qquad (2)$$

In Eq. (2) $A_0$ is the Helmholtz free energy of the hard-sphere reference system.[8] Its expression requires the entropy constant of hard-spheres, $S_0$, at the close-packed density. The value of $S_0$ (fcc) is $-0.24Nk$,[11] while $S_0$ (hcp) is evaluated from the difference, $\Delta S_0 = S_0(\text{fcc}) - S_0(\text{hcp}) = 0.002Nk$.[12] Expressions for $A_1$ and $A_{qm}$ are given Refs. 10 and 13.

Evaluation of $A_1$ [Eq. (17), Ref. 9] requires a knowledge of the hard-sphere diameter, d, and the hard-sphere radial distribution function, $g_{HS}(r/d)$. Our calculations employ the Weeks-Chandler-Andersen formula for d.[14] For the fluid $g_{HS}(r/d)$, a reliable analytic fit is available.[15] For the solid $g_{HS}(r/d)$, we use accurate expressions which we developed recently.[13]

The present work utilizes the Lennard-Jones (LJ) potential,

$$V(r) = 4\varepsilon\,[(\sigma/r)^{12} - (\sigma/r)^{6}]\ , \qquad (3)$$

where parameters $\varepsilon$ and $\sigma$ for heavy rare gas solids are summarized in Ref. 13. The LJ potential parameters should provide accurate thermodynamic properties in the range of pressure and temperature where experimental melting data are available, *i.e.*, from the triple point to at least 1 GPa.[13] For higher pressure data, we use the exponential-6 (exp-6) potential. Figure 1 shows that the LJ potential fits the low pressure data[10,13] and exp-6 potential fits the high pressure data.[10]

To investigate the crystal stability, it is instructive to consider a difference of the free energies between the fcc and hcp phases,

$$\Delta A = A\,(\text{fcc}) - A\,(\text{hcp})\ , \qquad (4)$$

for the total as well as each of the three contributions (*i.e.*, static, harmonic, and anharmonic) to $A$. For this purpose, we made separate LD calculations to evaluate $A$ (harmonic). Differences between the PT and LD data in turn provide the anharmonic contribution. We will denote these differences as $\Delta A$ (total), $\Delta A$ (static), $\Delta A$ (harmonic), and $\Delta A$ (anharmonic). Figure 2 shows $\Delta A$'s for neon with and without quantum correction along the melting line. As the quantum correction, $A_{qm}$ is negligible for argon, krypton, and xenon, their $\Delta A$'s fall onto the classical calculation. $\Delta A$ (static) is nearly constant and has a positive sign. However, it is about one fifth of the thermal contributions, $\Delta A$ (thermal) = $\Delta A$ (harmonic) + $\Delta A$ (anharmonic), both of which are negative. As a result, $\Delta A$ (total) is small ($<$ 0.1% of $A$) but negative, implying that these solids will crystallize into a fcc phase (instead of a hcp phase). It is in agreement with experiment described earlier. Note that, even if the magnitudes of $A$ (anharmonic) and $A$ (harmonic) are significantly different, $\Delta A$ (harmonic) and $\Delta A$ (anharmonic) are similar in size. It demonstrates importance of the anharmonic contribution to the crystalline stability. The quantum corrected $\Delta A$ (anharmonic), hence, $\Delta A$ (total), is lower than the classical value by a small amount (about $0.001NkT$). The enhanced stability of the fcc phase for neon is due to the quantum mechanical contribution to $\Delta A$ (anharmonic).

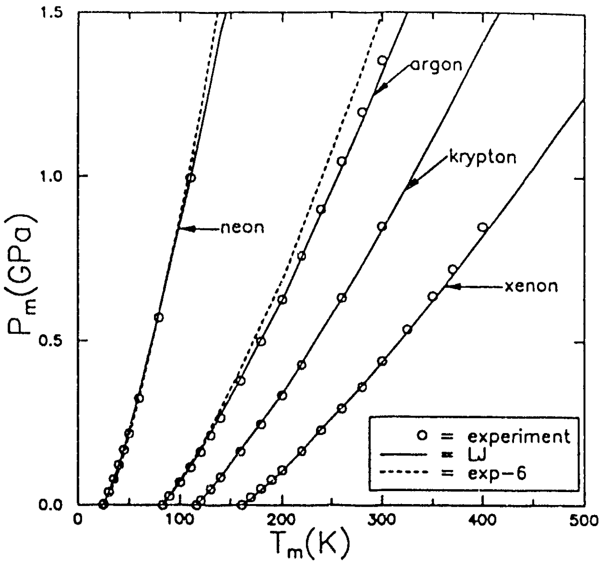

*Figure 1. Melting lines of neon, argon, krypton, and xenon. Solid line = Lennard-Jones potential; dashed line = exp-6 potential; circle = experimental data [Ref. 16].*

The magnitude of $\Delta A$ (total) decreases with temperature. A similar tendency is also seen in experimental data. It led Niebel and Venables[2] to suggest that the thermally excited lattice vibration will tend to destabilize the fcc crystal. Figure 2 shows that the anharmonic component, $\Delta A$ ( anharmonic), increases markedly with temperature and it, rather than $\Delta A$ ( harmonic), is largely responsible for destabilizing tendency.

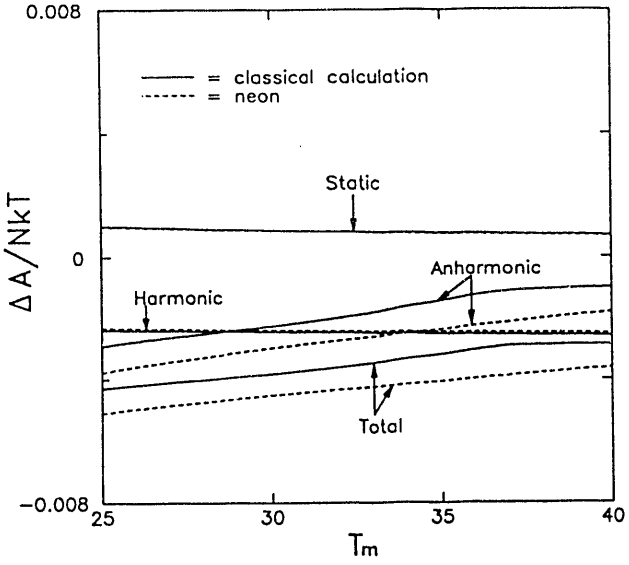

*Figure 2. Static, harmonic, anharmonic contributions to the Helmholtz free energy difference, [A ( fcc) - A ( hcp)]/NkT, along the melting lines of neon with quantum and classical calculations.*

In summary , the statistical mechanical results obtained in this work show that the crystal stability in the neighborhood of the melting lines of heavy rare-gas solids is due to the thermal contribution to $A$ rather than the static lattice energy sum. It is worthwhile to emphasize that the PT considers full harmonic and anharmonic contributions to $A$. The calculation only requires an effective pair potential that can reliably describe thermodynamic properties. Such an *"off the shelf"* potential (*e.g.*, as used in this work) can be found in the literature within a limited $( T , P )$ range of applicability.

The PT is based on the first-order perturbation correction, $A_1$, in the high-temperature perturbation expansion. Hence, its range of applicability is limited to temperatures above $kT/\varepsilon \approx 0.8$. It is expected to become less reliable at lower temperatures. However, our calculations for argon at 1 atm show that the PT correctly predicts the stability of the fcc phase at temperatures as low as 60 K (or $kT/\varepsilon = 0.5$).

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