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Crystal stability of heavy-rare-gas solids on the melting line

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Contrary to static-energy predictions favoring a hexagonal-close-packed phase, heavy rare gases solidify into a face-centered-cubic phase over a large temperature range. Our recent perturbation theory and hard-sphere radial distribution functions are applied to give a conclusive calculation that agrees with experiment near the melting lines of heavy-rare-gas solids. The observed stability is due to thermal contributions to the Helmholtz free energy which far exceed the opposing static term. The Lennard-Jones potentials used here reproduce melting data of these solids to 1 GPa.

Rare gases are the simplest materials that occur in nature and their thermodynamic properties are well understood. However, there are a few exceptions, one of which is their crystal structures.[1,2] 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, whereas helium freezes mostly into a hexagonal-close-packed (hcp) phase (with a small temperature range where the freezing to a fcc phase was recently observed).[3] In contrast, theoretical calculations predict helium (at ≥ 15 K) in a fcc phase and heavier rare-gas solids in a hcp phase.[1,2] The behavior of helium is complex[4] because it is quantum mechanical and contains significant many-body contributions in its interaction potential. The present investigation is confined to heavy-rare-gas solids. Even in this case, the discrepancy between theory and experiment has remained as an *outstanding unresolved* question during the last decade.

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

$$A = E_0 + A(\text{harmonic}) + A(\text{anharmonic}). \tag{1}$$

A small difference in $[E_0(\text{fcc}) - E_0(\text{hcp})]/E_0(\text{fcc}) \approx -1 \times 10^{-4}$ favors the hcp phase and is due to the long-range attractive interactions.[1] Salsburg and Huckaby[5] showed that the harmonic approximation stabilizes the fcc phase for argon. Their careful calculation was limited to the 0-K density and depended sensitively on the second-nearest-neighbor approximation. Effects of density variation, higher-neighbor interactions, and anharmonic contributions on the crystal stability have not been analyzed yet.

The zero-point energy, E_z, favors the fcc phase (Ref. 1, p. 567), but its effect including anharmonic corrections is not only insufficient to overcome the static-energy difference, but unimportant at melting temperatures under consideration. Bell and Zucker computed the static energy difference, $\Delta E_0 = E_0(\text{fcc}) - E_0(\text{hcp})$, including long-range many-body forces. They (Ref. 6, pp. 157 and 164) conclude that the many-body forces diminish "the preference shown by the two-body force for the hcp structure, but these forces are too small..." to reverse the trend set by the two-body force and they are "almost certainly not sufficient to account for the fcc structure." Likewise, Niebel and Venables (Ref. 1, p. 564) conclude that "nonadditive long-range forces ... certainly do not stabilize fcc decisively." More significantly, our results below show that, at melting temperatures of heavy rare gases, thermal contributions, $\Delta A(\text{thermal})$, to the Helmholtz free energy become far more important than ΔE_0.

A theory which can distinguish small differences (within 0.1%) in the Helmholtz free energy of the two phases is required to resolve this issue. We have recently developed a fast and accurate perturbation theory (PT) of fluids and solids.[7,8] The motivation of the present work is to demonstrate how the power of a modern statistical mechanical theory can be applied to resolve the question about the crystal stability. We are not aware of any similar conclusive study on rare gases. In this letter, we show that the PT indeed predicts fcc phase stability for heavy-rare-gas solids.

Perhaps the most striking difference of PT from a quasiharmonic lattice dynamics (LD) method is that PT considers a short-range stiff (hence, anharmonic) repulsion as playing a major role in determining crystalline properties. It is essentially an adaptation of van der Waals' model of fluids to solids. Its most notable advantage over the LD is that it *fully* accounts for harmonic and anharmonic contributions without approximation. Comparisons[9,10] with experiment and computer simulations have proven that the PT gives reliable results, including the melting transition where large anharmonic effects makes the LD less useful.

The PT divides a pair potential, $V(r)$, into the reference, $V_0(r)$, and perturbation, $W(r)$, potentials, i.e.:

$$V(r) = V_0(r) + W(r), \tag{2}$$

$$\begin{aligned} &V_0(r) = V(r) - F(r), \quad \text{if } r \leq \lambda\,; \\ &V_0(r) = 0, \quad \text{if } r > \lambda, \end{aligned} \tag{3}$$

$$W(r) = F(r), \quad \text{if } r \leq \lambda\,;$$
$$W(r) = V(r), \quad \text{if } r > \lambda. \qquad (4)$$

Details of the division of $V(r)$ and specific expressions for $F(r)$ and λ in Eqs. (2) to (4) are given in Refs. 8 and 9. 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 (Ref. 11) is sufficient to yield accurate results at high temperature; i.e.,

$$A = A_0 + A_1 + A_{qm}, \qquad (5)$$

$$A_1 = \frac{\rho}{2}\int W(r) g_{\text{HS}}(r/d) d\mathbf{r}, \qquad (6)$$

$$A_{qm}(h^2) = \frac{h^2\rho}{24\pi mkT}\int \nabla^2 V(r) g_{\text{HS}}(r/d) d\mathbf{r}. \qquad (7)$$

In Eq. (5) 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 $-0.24Nk$,[12] while S_0(hcp) with the c/a ratio of $(8/3)^{\frac{1}{2}}$ (which agrees closely with the ratio for helium) is evaluated from information on the entropy difference, $\Delta S_0 = S_0(\text{fcc}) - S_0(\text{hcp})$ $(= 0.002Nk)$, at the close-packed density.[13] $W(r)$ and $\nabla^2 V(r)$ in Eqs. (6) and (7) depend only on a single relative scalar coordinate r. Hence, their Boltzmann averages $\langle W(r)\rangle$ and $\langle \nabla^2 V(r)\rangle$ only require a scalar pair distribution function, $g(r/d)$, for solids and fluids.

The second-order quantum correction A_{qm} (h^4) for neon near the triple point is only 1/40 of A_{qm} (h^2), which in turn is one tenth of A_0.[14] It implies that the inclusion of A_{qm} (h^2) in Eq. (5) is probably sufficient for the present calculations.

Equation (5) requires a knowledge of the hard-sphere diameter d and the hard-sphere radial distribution function $g_{\text{HS}}(r/d)$. Our calculations employ the Weeks-Chandler-Andersen formula[15] for d. For the fluid $g_{\text{HS}}(r/d)$, a reliable analytic fit[16] is available. For the solid $g_{\text{HS}}(r/d)$, we use accurate expressions which we recently developed for this purpose.[10]

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

$$V(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6], \qquad (8)$$

where parameters ϵ and σ for the heavy-rare-gas solids are summarized in Table I. These parameters[17] are reliable in the range of pressure and temperature where experimental melting data are available, i.e., from the triple point to at least 1 GPa.

TABLE I. Lennard-Jones parameters employed in the present work.

	ϵ/k (K)	σ (Å)	Ref.
Neon	36.76	2.786	17(a)
Argon	119.8	3.405	17(b)
Krypton	166.7	3.68	17(c)
Xenon	225.3	4.07	17(c)

The melting and freezing volumes represent a pair of points where the solid and fluid A vs volume plots show a common tangent, which is related to the melting pressure, P_m, by $P_m = -(\partial A/\partial V)_T$. Figure 1 compares the resulting melting lines with the corresponding experimental data.[18] (The LJ potential used here will become too stiff at higher pressures.[19]) Agreement between the two demonstrates that the PT should be reliable along the melting line up to 1 GPa. In contrast, the quasiharmonic lattice approximation predicts no melting, since isotherms for A(harmonic) lie below A(fluid) within den-

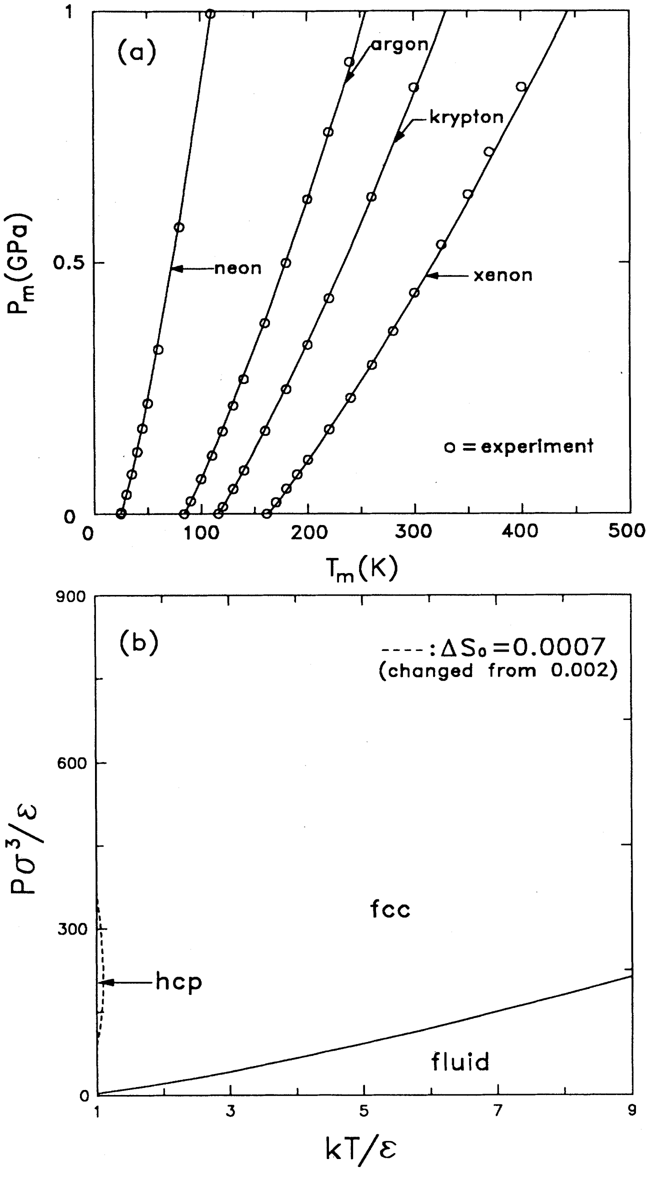

FIG. 1. (a) Melting lines of rare gases. Solid line is this work; circle is experiment Ref. 18; (b) the phase diagram of the LJ system. Dashed line is a fcc-hcp phase boundary produced by arbitrarily reducing the molecular dynamics value of $\Delta S_0 = 0.002Nk$ to $0.0007Nk$.

sity ranges where the LD frequencies are positive and the PT for fluid is reliable. It shows that the anharmonic term is crucial in determining the melting lines.

We compute A and its components in Eq. (1) separately. For this purpose, we made separate LD calculations[20] to evaluate A(harmonic). Differences between the PT and LD data in turn provide the anharmonic contribution,

$$A(\text{anharmonic}) = A(\text{PT}) - A(\text{harmonic}). \qquad (9)$$

At $(kT/\epsilon, \rho\sigma^3) = (1.5, 1.1)$, for example, Eq. (9) gives $A(\text{anharmonic}) = 0.19NkT$ which agrees exactly with Pollock's Monte Carlo calculation[21] of A(anharmonic).

Examination of differences between the fcc and hcp phases,

$$\Delta A = A(\text{fcc}) - A(\text{hcp}), \qquad (10)$$

for the total, static, harmonic, and anharmonic contributions, denoted by ΔA(total), ΔA(static), ΔA(harmonic), and ΔA(anharmonic), shed light on their relative importance in determining the crystal stability. Figure 2 shows ΔA's for neon, argon, krypton, and xenon along the melting lines. ΔA(static) is nearly constant and has a positive sign. However, it is about 16% to 20% less than the thermal contributions, $\Delta A(\text{thermal}) = \Delta A(\text{harmonic}) + \Delta A(\text{anharmonic})$, both of which are negative. As a result, ΔA(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, ΔA(harmonic) and ΔA(anharmonic) are similar in size. It demonstrates the importance of the anharmonic contribution to the crystalline stability.

The quantum correction, A_{qm}, is negligible for argon, krypton, and xenon along the melting lines. As a result, ΔA's vs kT/ϵ in Fig. 2 fall onto solid lines representing the classical calculation, which obeys the corresponding-states principle. For neon, ΔA(anharmonic), hence, ΔA(total), is lower than the classical result by a small amount ($\approx 0.001NkT$). The enhanced stability of the fcc phase for neon is due to quantum mechanical contributions in ΔA(anharmonic).

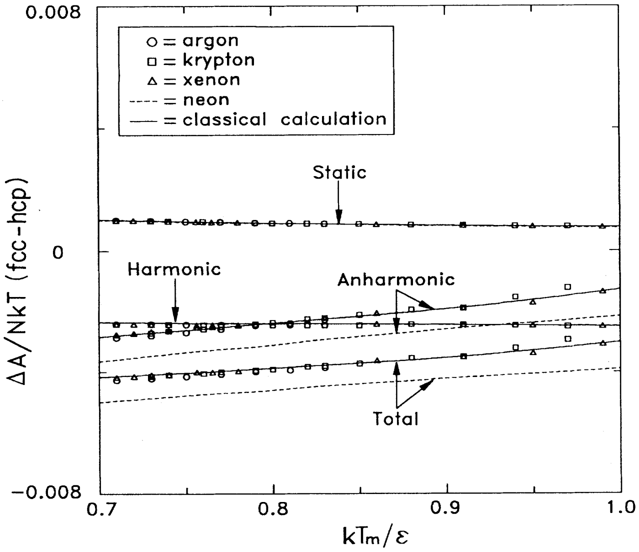

FIG. 2. Static, harmonic, and anharmonic contributions to $[A(\text{fcc}) - A(\text{hcp})]/NkT$ along the melting line of rare gases.

The magnitude of ΔA(total) decreases with temperature. A similar tendency is also seen in experimental data.[1] It led Niebel and Venables[1] to suggest that the thermally excited lattice vibration will tend to destabilize the fcc crystal. Figure 2 shows that the anharmonic component, ΔA(anharmonic), increases markedly with temperature and it, rather than ΔA(harmonic), is largely responsible for the destabilizing tendency.

To ascertain that the predicted fluid → fcc transition is inherent to the rare-gas solids (i.e., independent of the LJ potential employed in the analyses), we made similar calculations for argon with exponential-6 (exp −6) potentials,

$$V(r) = \epsilon/(\alpha - 6)\{6\exp[\alpha(1 - r/r^*)] - \alpha(r^*/r)^6\},$$

using a parameter set (ϵ, r^*, α) based on 0-K crystal properties[22] and another based on high-pressure shock-wave data up to 40 GPa.[23] The three calculations are similar; i.e., the hcp phase has a higher Gibbs free energy (and higher-melting pressure). Table II(a) compares melting data obtained with the exp −6 (Ref. 23) and the LJ potentials at 200 K. Thus, an important physics result, which we obtained up to 1 GPa, will likely remain unchanged to 40 GPa for argon, provided that a realistic effective pair potential is used. Namely, the fluid → fcc transition along the melting lines of heavy rare gases occurs through ΔA(thermal), which is much larger in size than the opposing static contribution.

The predicted fluid → fcc transition is also independent of an expression for the solid-phase $g_{\text{HS}}(r/d)$ used in the PT. To verify this, we used Jackson's, and Swol's analytic $g_{\text{HS}}(r/d)$ (Ref. 24) in place of the expressions used in our work. Table II(b) shows the melting data of argon for the two different analytic fits. Both expressions give similar transition data, predicting a lower Gibbs free energy and a lower melting pressure for the fcc phase.

In summary, the crystal stability in the neighborhood of the melting lines of heavy-rare-gas solids is due to the thermal contributions to the Helmholtz free energy rather than ΔE_0. We emphasize that the PT considers these

TABLE II. Sensitivity of melting properties of argon at 200 K: (a) pair potentials and (b) solid-phase $g_{\text{HS}}(r/d)$.

	V_m(cm^3/mol)		P_m(GPa)		G/NkT	
(a)	LJ	exp-6[a]	LJ	exp-6[a]	LJ	exp-6[a]
fcc	21.73	21.33	0.623	0.685	8.316	9.034
hcp	21.71	21.32	0.624	0.686	8.346	9.044
(b)	This work	JS[b]	This work	JS[b]	This work	JS[b]
fcc	21.73	21.81	0.623	0.627	8.316	8.372
hcp	21.71	21.85	0.624	0.638	8.346	8.533

[a] Ross (Ref. 23): $(\epsilon/k, r^*, \alpha) = (122\text{ K}, 3.85\text{ Å}, 13.2)$.

[b] Expressions for $g_{\text{HS}}(r/d)$ by Jackson and Swol (Ref. 24).

effects *fully* and *unambiguously*. 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 main limitation of the PT is that it is based on the first-order perturbation correction, A_1, in the high-temperature perturbation expansion.[15] Its range of applicability is limited to temperatures above $kT/\epsilon \approx 0.8$. Although it will become increasingly unreliable at lower temperatures, our calculations for argon at 1 atm show that the stability of the fcc phase persists at temperatures as low as 60 K (or $kT/\epsilon = 0.5$).

The stability of the fcc phase also extends to higher pressures above the melting pressure, e.g., at least to 100 GPa for argon. Even if the result should turn out to be in agreement with experiment, it might be fortuitous at these high pressures, since the LJ potential parameters were calibrated below 1 GPa. Our prediction on the stability for the fcc phase over the entire (T, P) range makes use of the molecular dynamics value $(0.002Nk)$ (Ref. 13) of ΔS_0. One can produce a small parabolic domain of the hcp stability, e.g., between $P\sigma^3/\epsilon = 91$ and 368 at $kT/\epsilon = 1$ in Fig. 1(b), by arbitrarily reducing ΔS_0 to $0.0007Nk$. It does not affect our results along the melting lines under discussion. In this regard, the fcc $\rightarrow$ intermediate phase $\rightarrow$ hcp transition occurs for xenon at pressures between 14 and 75 GPa.[25] The observed transition, however, is due to an increased hybridization between the valence band and upper-lying conduction band. A pair potential alone cannot describe such an electronically induced transition.[26]

Finally, it would be useful to extend the present formulation to helium, which has a complex phase diagram.[3] The small mass of helium atom produces a large quantum effect; its small attractive interaction parameter, ϵ, means highly anharmonic atomic vibrations, and its short-range interaction has significant many-body effects by the Pauli principle that forces electronic charge densities of a He atom and its neighbors to alter under high compression. We plan to report on our study of helium in the future.

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