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Exchange-correlation energy and the phase diagram of Si

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Previous first-principles calculations of the melting properties of Si, based on the local-density approximation (LDA) for electronic exchange-correlation energy, underpredict the melting temperature by ~20 %. We present new first-principles results indicating that a large part of this problem is due to noncancellation of exchange-correlation errors between the semiconducting solid and the metallic liquid. It is shown that other sources of error, particularly those due to system size and Brillouin-zone sampling, can be made negligible. The same LDA errors cause an underprediction of the pressure of the diamond-Si → beta-tin-Si transition. The generalized-gradient approximation considerably improves both features of the Si phase diagram.

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The long-standing ambition of calculating phase diagrams from first-principles quantum mechanics has become a reality in the last 10 years.[1–4] A key stimulus to the recent developments was the paper of Sugino and Car (SC) on the melting of Si,[5] which showed how the technique of thermodynamic[6] integration combined with first-principles molecular dynamics[7] (FPMD) based on density functional theory (DFT) can be used to calculated the free energy of solids and liquids, and hence melting curves, with no experimental input apart from fundamental constants. But, although their paper was influential, their results on Si were not very satisfactory, since their predicted melting temperature ($T_{\mathrm{m}}=1350$ K) was ~20% below the experimental value (1685 K).[8] Our aim here is to search for the cause of this discrepancy, which we argue comes largely from noncancellation of DFT errors between solid and liquid, and specifically from errors of the local-density approximation (LDA) used by SC. This has implications for the reliability of other first-principles work on phase diagrams.

The basic approximation in any DFT calculation is the algorithm for exchange-correlation energy E_{xc}. If one can eliminate all sources of error in calculating total energies and doing the statistical mechanics, then failure to reproduce experimental melting properties must be due to errors in E_{xc}. But it is often claimed that these other sources of error cannot be made small enough; in particular, it is claimed that first-principles calculations cannot yet be performed on large enough systems to render size errors negligible.[4] We recall[1] that a noncanceling error δG per atom in the Gibbs free energy implies an error $\delta T_m = \delta G / \Delta S_m$ in the melting temperature, where ΔS_m is the entropy of melting per atom. For Si, $\Delta S_m \approx 3.5\ k_{\mathrm{B}}$/atom, so to obtain T_m correct to 100 K, δG errors must be reduced to ≈ 30 meV/atom.

The calculation of free energies to high enough precision was one of the major issues addressed by SC, who made strenuous efforts to ensure that their non-E_{xc} errors were negligible; our results indicate that they were largely successful. Turning to E_{xc} errors, the crucial question is the extent to which they cancel between the coexisting phases. Since diamond-structure Si (d-Si) is a fourfold coordinated semiconductor and liquid Si (l-Si) is an approximately sixfold coordinated metal,[9] electron screening should be very different in the two phases, so that noncancellation of E_{xc} errors becomes an issue. Here, we are helped by the fact that the pressure-stabilized β-tin structure (β-tin-Si) resembles the liquid in being metallic and sixfold coordinated. This suggests a close relation between the effect of E_{xc} errors on the melting temperature and on the $d-\mathrm{Si} \rightarrow \beta$-tin-Si transition pressure, and an analysis of this relation will help confirm that errors in the LDA E_{xc} account for the underprediction of T_{m}.

Our calculations employ ultrasoft pseudopotentials[10] and plane-wave basis sets. Most of our calculations are based on the LDA for E_{xc} used by SC, but we also present results using the generalized-gradient approximation (GGA).[11] The calculations were done with the VASP code.[12] The plane-wave cutoff was 150 eV, which gives a convergence of 6 meV/atom in the difference of total (free) energies between liquid and solid, and the pseudopotential core radii were 1.31 Å. Our strategy for computing the free energies of solid and liquid differs from that of SC, and resembles that used in our recent work on Fe (Ref. 1) and Al (Ref. 3). The Helmholtz free energy F of the solid can be written as $F=F_{\mathrm{perf}}+F_{\mathrm{vib}}$, with F_{perf} the free energy of the perfect non-vibrating crystal (it is a *free* energy, because we allow for thermal electronic excitations[13]), and F_{vib} the contribution from lattice vibrations. The latter is written as $F_{\mathrm{vib}}=F_{\mathrm{harm}}+F_{\mathrm{anharm}}$. The harmonic free energy per atom F_{harm} in the classical limit (melting occurs well above the Debye temperature) is $F_{\mathrm{harm}} = 3k_{\mathrm{B}}T\ln(\hbar\overline{\omega}/k_{\mathrm{B}}T)$, where the geometric-mean frequency $\overline{\omega}$ is given by

$$\ln(\overline{\omega}) = N_{\mathbf{k}s}^{-1} \sum_{\mathbf{k}s} \ln(\omega_{\mathbf{k}s}), \tag{1}$$

with the sum going over wave vectors $\mathbf{k}$ and branches s in the Brillouin zone, $N_{\mathbf{k}s}$ being the number of terms in the sum. The phonon frequencies $\omega_{\mathbf{k}s}$ calculated using the small-displacement method[14] are compared in Fig. 1 with experimental values. The extremely close agreement is what would be expected from previous work.[15]

The anharmonic term F_{anharm} turns out to be small (~15 meV/atom near the melting temperature), and is accurately given by the second-order expansion:

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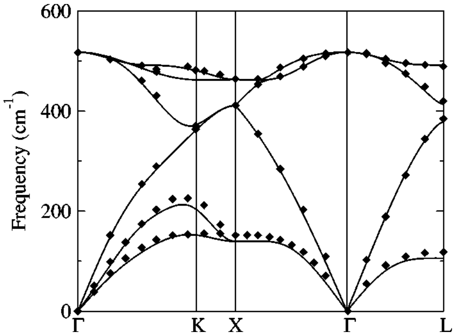

FIG. 1. Calculated zero-pressure LDA phonon dispersion ($V_0 = 19.64$ Å ^{3}/atom, solid lines) compared with experimental data (diamonds, obtained from Ref. 15).

$$F_{\mathrm{anharm}} \simeq \langle U_{\mathrm{anharm}} \rangle_{\mathrm{harm}} - \langle U^2_{\mathrm{anharm}} \rangle_{\mathrm{harm}} / 2 k_{\mathrm{B}} T, \tag{2}$$

where U_{anharm} is the anharmonic part of the first-principles total energy, and the thermal averages $\langle \cdot \rangle_{\mathrm{harm}}$ are evaluated in the canonical ensemble of the first-principles harmonic system. We verified the accuracy of Eq. (2) by comparing it with the exact expression: $F_{\mathrm{anharm}} = -k_{\mathrm{B}} T \ln \langle \exp(-U_{\mathrm{anharm}}/k_{\mathrm{B}}T) \rangle_{\mathrm{harm}}$.

Our calculations of F_{perf} were performed on the primitive two-atom unit cell, at volumes ranging from 16 to 22 Å^3/atom with k-point sampling dense enough to give a precision of ~ 0.1 meV/atom. Results were fitted to the Birch-Murnaghan[16] form, which reproduces the data to within ~ 0.1 meV/atom. For F_{harm}, we calculated the force-constant matrix using 54-atom cells, with spot-checks on cells of up to 250 atoms indicating convergence to within ~ 2 meV/atom. Our results for $\ln(\overline{\omega})$ were fit to a second-order polynomial $\ln(\overline{\omega}) = a + bV + cV^2$, with a fitting error in F_{harm} of ~ 1 meV/atom. The thermal averages needed for F_{anharm} were done on a 54-atom cell at volumes of $V = 18$ and 20 Å ^{3}/atom and temperatures of 1000, 1500, and 2000 K. The results are accurately reproduced by the form $F_{\mathrm{anharm}} = aT^2$, and the value $a = 7 \times 10^{-9}$ eV K^{-2} gives the required accuracy for both volumes.

The free energy of the liquid is calculated using thermodynamic integration (TI), with a modification of the Stillinger-Weber[17] (SW) empirical total-energy model used as reference system. The difference of Helmholtz free energy $\Delta F \equiv F_{\mathrm{AI}} - F_{\mathrm{ref}}$ between the *ab initio* and reference systems is obtained using the standard formula:[6]

$$\Delta F = \int_0^1 d\lambda \langle U_{\mathrm{AI}} - U_{\mathrm{ref}} \rangle_\lambda, \tag{3}$$

with U_{AI} and U_{ref} the *ab initio* and reference total-energy functions, and $\langle \cdot \rangle_\lambda$ the thermal average evaluated in the ensemble of the system whose total-energy function is $U_\lambda \equiv (1-\lambda) U_{\mathrm{ref}} + \lambda U_{\mathrm{AI}}$. In practice, the λ integral is performed either by evaluating $\langle U - U_{\mathrm{ref}} \rangle_\lambda$ at a set of λ values and using Simpson's rule, or by using "adiabatic switching," in which λ is slowly and varied between the two limits.[18]

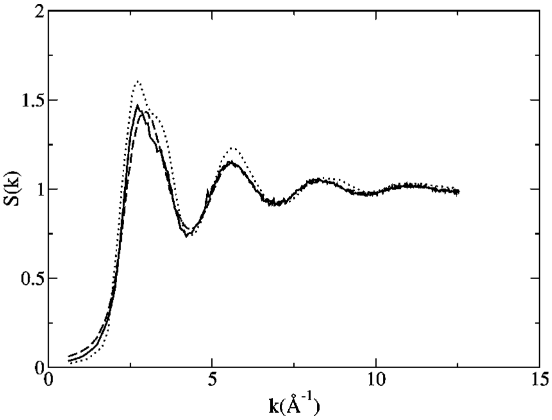

FIG. 2. Calculated LDA (solid line) and SW (dashed line) structure factors at $T = 1700$ K compared with experimental data at $T = 1713$ K (dotted line, Ref. 19).

The Stillinger-Weber form of reference total-energy function is a sum of two-body and three-body terms: $U_{\mathrm{ref}} = \frac{1}{2}\sum'_{i,j} v_2(r_{ij}) + \frac{1}{6}\sum'_{i,j,k} v_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k)$, with $\mathbf{r}_i$ the ions positions and $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$. The two-body potential has the form

$$v_2(r) = \epsilon A (B x^{-p} - 1) \exp[(x-a)^{-1}], \tag{4}$$

for $x < a$ and $v_2(x) = 0$ for $x > a$, with $x = r/\sigma$, where σ is a length characterizing the potential. The three-body potential has the form

$$\begin{aligned} v_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k) = \epsilon[&h(x_{ij}, x_{ik}, \theta_{jik}) + h(x_{ji}, x_{jk}, \theta_{ijk}) \\ &+ h(x_{ki}, x_{kj}, \theta_{ikj})], \end{aligned} \tag{5}$$

where $x_{ij} = r_{ij}/\sigma$ and θ_{jik} is the angle between the separation vectors $\mathbf{r}_j - \mathbf{r}_i$ and $\mathbf{r}_k - \mathbf{r}_i$. The dimensionless function $h(x, x', \theta)$ has the form

$$h(x, x', \theta) = \lambda \exp[\gamma (x-a)^{-1} + \gamma (x'-a)^{-1}] (\cos\theta + 1/3)^2. \tag{6}$$

As has often been stressed,[1] in a thermodynamic integration scheme like this, the final results for F_{AI} do not depend on the choice of reference system, but the *efficiency* of the calculations can be greatly improved by careful tuning of the reference system. As shown in Ref. 1 the most important criterion in chosing a reference system for free energy calculations is that the thermal equilibrium fluctuations of $U_{\mathrm{AI}} - U_{\mathrm{ref}}$ should be as small as possible. The original Stillinger-Weber model[17] total-energy model was developed nearly 20 years ago, without the benefit of *ab initio* calculations. We have therefore retained the functional form of their model, but adjusted their parameters to reduce as much as possible the mean square fluctuations of $U_{\mathrm{AI}} - U_{\mathrm{ref}}$. This optimization was performed using molecular dynamics simulations of liquid Si at the thermodynamic state $V = 18.16$ Å^3/atom and $T = 2000$ K. Only the parameters $\epsilon, \sigma, A, B, a, \lambda$ and γ were varied, the best fit being obtained with the values $\epsilon = 1.82$ eV, $\sigma = 3.48$ Å, $A = 7.52$, $B = 0.0882$, $a = 1.084$, $\lambda = 20.79$, $\gamma = 1.009$. With these parameters, the value of $[\langle [U_{\mathrm{AI}} - U_{\mathrm{ref}} - \langle U_{\mathrm{AI}} - U_{\mathrm{ref}} \rangle]^2 \rangle / N]^{1/2}$ is 0.084 eV. As further evidence of the quality of the reference model we compare in Fig. 2 the structure factor $S(k)$ of liquid Si at $V = 17.21$ Å^3/atom, $T = 1700$ K obtained with *ab initio* MD and with the reference model. The close agreement at all k vectors confirms that the reference model gives a good description of the liquid state. On the same figure, we show experimental data for $S(k)$.[19] The small differences between theory and experiments are similar to those found in previous studies of liquid Si.[20]

The free energy F_{ref} of the reference model was calculated by thermodynamic integration starting from the Lennard-Jones system in the liquid state, for which accurate free energies have been published.[21] The calculations are done on systems of several hundred atoms and our tests on system size errors show that the results are converged to better than 1 meV/atom. In such thermodynamic integration, it is essential that the switching of the total energy function be reversible, and that the integration path should not cross any phase boundaries. To confirm reversibility, we use the technique of adiabatic switching, performing the switching in both directions (i.e., Lennard-Jones→Stillinger-Weber and vice versa), and check that there are no hysteresis effects. As further confirmation, we have used exactly the same technique to calculate the the free energy of l-Si, in the original Stillinger-Weber parameters and compared with the results of Broughton and Li,[22] which were obtained by completely different methods. At the two liquid states at $T=1691$ K and 2013 K and zero pressure, our free energy results agree with those to within 2 meV/atom.

TABLE I. Difference ΔF of Helmholtz free energy (eV/atom units, statistical errors in parentheses) at state $V=17$ Å ^{3}/atom, $T=1750$ K, between the *ab initio* and the modified Stillinger-Weber potential as function of size of simulated liquid system (number of atoms N) and number of Monkhorst-Pack **k** points (subscript on ΔF).

N	ΔF_1	ΔF_4	ΔF_8	ΔF_{32}	ΔF_{36}
64	-4.165(5)	-4.262(5)	-4.253(5)	-4.257(5)	-4.257(5)
128	-4.282(5)	-4.250(5)			
216	-4.281(5)	-4.262(5)			
512	-4.248(5)	-4.251(5)			

We made thorough tests of the convergence of ΔF with respect to system size and electronic **k**-point sampling by calculating it at the representative state $V=17$ Å ^{3}/atom and $T=1750$ K, using systems of up to 512 atoms and up to 36 Monkhorst-Pack[23] **k** points (see Table I). The tests were done as follows. The Γ-point results were obtained by explicit simulations on systems of all sizes, with ΔF calculated by thermodynamic integration [Eq. (3)]. In most cases, we used the five λ values 0.0, 0.25, 0.5, 0.75, and 1.0 together with Simpson's rule, and comparisons with other sets of λ values show that the residual error from the integration itself is less than 5 meV/atom. We then used thermodynamic integration, with the Γ-point system as the reference system, to obtain the results for other **k**-point samplings. For systems of $N \geqslant 128$ atoms, the fluctuations of the difference of energies calculated with Γ point and more **k** points are small enough to allow the second-order expansion to be used instead of explicit TI, but for $N=64$ this is not adequate and we used explicit TI. The results of Table I show that with 64 atoms and four **k** points the free-energy difference ΔF between *ab initio* and optimized Stillinger-Weber potentials is converged to better than 10 meV/atom, and we have used this system to obtain F_{AI} for the liquid at the set of state points $V=16$, 17, 18, 19, and 20 Å^3/atom and $T=1250$, 1500, and 1750 K. At each T, F_{AI} was fitted to a Birch-Murnaghan equation of state, the residual fitting error being no more than 2 meV/atom. Our fitted *ab initio* Helmholtz free energies of d-Si and l-Si allow us to obtain the Gibbs free energy $G \equiv F - V(\partial F/\partial V)_T$, and hence the melting curve. The zero-pressure results for T_{m} and the entropy and volume of fusion, ΔS and ΔV, are compared in Table II with those of SC and the experimental values. Our very close agreement with the SC value of T_{m} (difference of only 50 K) confirms that their size and **k**-point errors were indeed very small, and also confirms that LDA underpredicts T_{m} by $\sim 20\%$. We note that our ΔS and ΔV values are both somewhat greater than those of SC.

We now turn to the matter of noncanceling LDA errors between phases, exploiting the electronic and structural similarity between d-Si and β-tin-Si. At room temperature, the transition $d\text{-Si} \rightarrow \beta\text{-tin-Si}$ occurs at an experimental pressure in the range $10.3-12.5$ GPa (Ref. 27) (although also a low value of 8.8 GPa has been reported[28]). Earlier LDA calculations on the static zero-temperature crystals gave transition pressures in the range $7.8-8.4$ GPa,[29,30] and our own calculations yield the value 7.8 GPa. However, it is known that temperature strongly affects the transition pressure, which drops by $\sim 20\%$ as T goes from 0 K to room temperature,[31] so that the temperature-corrected LDA pressure is too low by at least 4 GPa. It is also known that GGA significantly improves the predicted transition pressure. With the Perdew-Wang GGA,[11] we find a transition pressure of 11.7 GPa (10.2 GPa when corrected to room temperature), which agrees closely with earlier GGA values.[30] We find that the main reason why LDA underpredicts the transition pressure is that it erroneously shifts the energy of d-Si upwards relative to β-tin-Si. The GGA goes a long way towards correcting this destabilization of d-Si. But a low melting temperature is also a sign of an erroneous destabilization of

TABLE II. Comparison of calculated and experimental melting properties of Si at ambient pressure: melting temperature T_m, volume change ΔV_m divided by volume of solid at melting temperature, entropy change ΔS_m per atom divided by Boltzmann's constant, and slope of melting curve dT_m/dP (units of K GPa^{-1}).

	LDA	GGA	SC ^{a}	Experiment
T_{m}(K)	1300(50)	1492(50)	1350(100)	1685(2)^b
$\Delta V_m/V_s$	0.142	0.106	0.1	0.119^c, 0.095^d
ΔS_m	3.5	3.5	3.0	3.6^e,3.3^d
dT_m/dP	-58	-42	-50	-38^b

[a] Reference 5.
[b] Reference 8.
[c] Reference 24.
[d] Reference 25.
[e] Reference 26.

d-Si, and we hypothesize that the same underlying E_{xc} error is responsible for both underpredictions.

To test this, we have recalculated the melting properties using GGA. It is instructive to do this by evaluating the free energy difference between the LDA and GGA systems. We have therefore performed long simulations for solid and liquid at the zero-pressure volumes using the LDA, and calculated the GGA energies at a number of statistically independent configurations, for both the solid and the liquid. The calculations have been done on cells containing 64 atoms with four **k** points, and spot-checked with calculations on cells containing 512 atoms and Γ-point sampling. Firstly, we found that the energy differences between GGA and LDA are basically constant, i.e., do not depend on the configurations of the atoms, which confirms the idea that the shift should be the same as for the low temperature static lattices. This means that a second-order expansion formula analogous to Eq. (2) gives a very good approximation to the free energy difference between the GGA and the LDA systems.[32] Secondly, we found that the free energy of the liquid is raised by 58 meV/atom relative to that of d-Si. Given an LDA entropy change on melting of $3.5k_{\mathrm{B}}/\mathrm{atom}$, it is easy to work out a shift of melting temperature GGA-LDA of 192 K, bringing the GGA result to 1492 K, in closer agreement with the experimental datum. We also found that, at the volumes corresponding to the LDA zero pressure, the GGA pressures are about 3.5 GPa larger than the LDA ones, so the GGA zero-pressure volumes are larger. However, the bulk moduli for the solid and the liquid at the melting temperature are 78 and 34 GPa, respectively, so the liquid will expand more than the solid in the GGA. From this we can estimate a new volume change on melting of 9.4%, which is also in somewhat better agreement with the experiments. To calculate the entropy change on melting in the GGA approximation we have performed two additional simulations for solid and liquid at the GGA melting point. The entropy change on melting is then simply given by $\Delta S = \Delta E/T$, where ΔE is the difference of internal energies between solid and liquid. We find $\Delta S = 3.5k_{\mathrm{B}}/\mathrm{atom}$, which is essentially the same as the LDA value. In these simulations the volumes were adjusted so that both solid and liquid were at zero pressure (within 1 k_{Bar}), and this refinement resulted in a more accurate prediction of the volume change on melting of 10.6%. From the values of the volume and the entropy changes on melting, we can also extract the slope of the melting curve by means of the Clausius-Clapeyron relation, and we find $dT_m/dp = \Delta V/\Delta S = -42$ K/GPa, in very good agreement with the experiments.

The foregoing results demonstrate that noncancellation of exchange-correlation errors between solid and liquid is a major issue in a first-principles account of the melting properties of Si. Technical errors due to system size and **k**-point sampling are readily brought under tight control. The basic reason why this can be done is that system size affects only the small difference of free energy between the first-principles system and a carefully designed reference system. The noncancellation of exchange-correlation errors between the coexisting semiconductor and metal is also responsible for difficulties in predicting the pressure of the diamond-Si $\rightarrow$ β-tin-Si transition, and there is a semiquantitative relation between the error in this transition pressure and the error in melting temperature. For completeness, we point out that nonadiabatic effects (i.e., departures from the Born-Oppenheimer surface) might also conceivably shift the relative free energies of solid and liquid, and hence the melting point. Presumably such effects will be small, but to our knowledge, no quantitative estimate is available for the resulting correction to the free energies of high temperature solids and liquids. It would perhaps be useful to put bounds on the magnitude of these effects.

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