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Quantum Anharmonic Phonon Thermodynamics from the Free Energy Cumulant Expansion

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Abstract

We present a computationally efficient workflow based on the free energy cumulant expansion to calculate vibrational thermodynamic properties with quantum effects and up to quartic anharmonicity. Helmholtz free energy, internal energy, entropy, and heat capacity are computed using renormalized self-consistent phonons, exact first- and second-order cumulants, and a rapidly convergent estimator for the reference potential energy. For classical Lennard-Jones (LJ) argon and Stillinger-Weber silicon, the free energies are within 0.25 meV/atom of thermodynamic integration (TI) at all temperatures with a comparable cost but simpler workflow. For quantum LJ neon, the cumulant expansion workflow is one-to-two orders of magnitude faster than TI because it does not require path-integral simulations. The predicted lattice constants and internal energies for LJ neon are within 0.004 Å and 0.05 meV/atom of the reference. The speed and accuracy of the cumulant expansion workflow make it ideal for high-throughput quantum anharmonic thermodynamics.

Introduction

Accurate finite-temperature calculations of vibrational thermodynamic properties require accounting for anharmonic effects, such as phonon–phonon scattering and frequency renormalization, and quantum nuclear effects, such as Bose–Einstein statistics and zero-point motion. Treating these effects together, however, is computationally demanding. Harmonic phonon theories provide a quantum description of vibrational thermodynamics, but they neglect the anharmonic contributions associated with interacting vibrational modes [1, 2]. In contrast, thermodynamic integration (TI) combined with path-integral molecular dynamics (PIMD) can capture anharmonic and quantum effects, but is computationally expensive [3]. Furthermore, TI directly computes only the free energy. Obtaining other thermodynamic properties such as entropy, internal energy, and heat capacity necessitates numerical differentiation and therefore additional simulations. These limitations motivate the development of computationally tractable methodologies that include quantum effects and anharmonicity (beyond frequency renormalization) while providing direct access to a broad set of thermodynamic properties.

We show herein how the free energy cumulant expansion [4–6] can be leveraged to develop such a method. Our approach combines renormalized self-consistent interatomic force constants (IFCs), exact evaluation of the first and second cumulants, and a rapidly convergent estimator for the reference potential energy. This workflow estimates the free energy, entropy, internal energy, and heat capacity without explicit molecular dynamics (MD) or PIMD during IFC fitting or thermodynamic property evaluation. The computational efficiency and direct access to free energy derivatives make the cumulant expansion method attractive for high-throughput materials characterization studies, where each calculation must be fast and should return not just a free energy estimate, but a wide range of thermodynamic properties. Furthermore, the low cost of the cumulant evaluation makes it practical to compute free energy over multiple volumes and temperatures, enabling equation-of-state fits from which zero-pressure lattice constants and thermal expansion coefficients can be extracted.

We consider systems with a fixed number of particles N , volume V , and temperature T . The thermodynamic potential minimized at equilibrium is the Helmholtz free energy $\mathcal{F}$, defined by

$$\mathcal{F} = \mathcal{U} - T\mathcal{S}, \quad (1)$$

where $\mathcal{U}$ is the internal energy and $\mathcal{S}$ is the entropy. Entropy, internal energy, and heat capacity, C_V , are defined as derivatives of the free energy [2]

$$\mathcal{S} = -\frac{\partial \mathcal{F}}{\partial T}, \quad \mathcal{U} = \frac{\partial(\beta \mathcal{F})}{\partial \beta}, \quad C_V = -T \frac{\partial^2 \mathcal{F}}{\partial T^2}, \quad (2)$$

where $\beta = (k_B T)^{-1}$ and k_B is the Boltzmann constant. We focus on the *vibrational* contribution to the free energy, given by

$$\mathcal{F}_{\text{vib}} = V_0 + \mathcal{F}_{\text{H}} + \mathcal{F}_{\text{Anh}}, \quad (3)$$

where V_0 is a reference potential energy, $\mathcal{F}_H$ is the harmonic part of the free energy, and $\mathcal{F}_{\text{Anh}}$ is the anharmonic part [7]. This representation neglects contributions from electronic and magnetic degrees of freedom. The harmonic part of the free energy is computed as a sum over the vibrational (i.e., phonon) modes [2]:

$$\mathcal{F}_H = \sum_{\mathbf{k}\lambda} \left[\frac{\hbar\omega_{\mathbf{k}\lambda}}{2} + \beta^{-1} \log(1 - e^{-\beta\hbar\omega_{\mathbf{k}\lambda}}) \right], \quad (4)$$

where $\hbar$ is the reduced Planck constant and $\omega_{\mathbf{k}\lambda}$ is the frequency of the phonon mode with wave vector $\mathbf{k}$ on branch λ . The definitions of V_0 and $\mathcal{F}_{\text{Anh}}$ depend on the level of theory used, as we will explore. Hereafter, all references to $\mathcal{F}$, $\mathcal{S}$, $\mathcal{U}$, and C_V refer to the vibrational component.

Under the harmonic approximation (HA), V_0 is the potential energy at mechanical equilibrium and $\mathcal{F}_{\text{Anh}} = 0$. The entropy, internal energy, and heat capacity can be obtained exactly by substituting Eq. (4) into Eq. (2). In the HA, V_0 is not temperature dependent and thus does not contribute to entropy, internal energy, or heat capacity. The HA captures zero-point motion and obeys quantum statistics, but cannot capture intrinsic anharmonic effects that become important at high temperature (i.e., phonon-phonon interactions) [7–9]. The accuracy of the HA can be improved by incorporating thermal expansion (i.e., the quasi-harmonic approximation) or more generally by using renormalized IFCs obtained from a method like the temperature dependent effective potential (TDEP) [7, 10]. In the TDEP formalism, the IFCs may be fit to classical MD or PIMD data, termed MD-TDEP, or through a self-consistent scheme called stochastic TDEP (sTDEP) [7, 11].

Using renormalized IFCs, V_0 is redefined to capture the average effect of anharmonicity [7]. For example, at the harmonic level of theory with sTDEP IFCs, $V_0 = \langle V - V_2 \rangle_H$ and with MD-TDEP IFCs, $V_0 = \langle V - V_2 \rangle$. Here, V is the true potential energy and V_2 is the harmonic part of the potential energy (including polar interactions), $\langle \cdot \rangle_H$ denotes an ensemble average where the Boltzmann weights employ the harmonic Hamiltonian, and $\langle \cdot \rangle$ denotes an ensemble average with the true Hamiltonian. The reference Hamiltonian must match the Hamiltonian used to fit the IFCs. Note that the first-order component of the potential energy, V_1 , is zero at equilibrium and does not contribute to V_0 . Substituting the above definitions of V_0 into Eq. (3) with $\mathcal{F}_{\text{Anh}} = 0$, we obtain what we call the sTDEP and MD-TDEP free energies [7]:

$$\mathcal{F}^{\text{sTDEP}} = \langle V - V_2 \rangle_H + \mathcal{F}_H \quad (5)$$

$$\mathcal{F}^{\text{MD-TDEP}} = \langle V - V_2 \rangle + \mathcal{F}_H. \quad (6)$$

The sTDEP IFCs and free energy are defined with respect to a harmonic reference (i.e., $\langle \cdot \rangle_H$). This definition means that MD or PIMD are not needed to compute $\mathcal{F}^{\text{sTDEP}}$. Instead, the harmonic ensemble can be sampled directly, as described in the Sampling Canonical Configurations section in the Methods. This sampling is possible because the phonon modes are orthogonal, making the normal-mode amplitudes independent realizations of Gaussian random variables whose variances are determined analytically

from the mode frequencies and temperature [11]. We employ sTDEP IFCs in this work so as to eliminate the computational expense of MD and PIMD simulations.

The TDEP free energies [Eqs. (5) and (6)] are renormalized harmonic free energies and capture the average effect of anharmonicity through V_0 . However, they do not explicitly account for fluctuations beyond the harmonic reference (i.e., $\mathcal{F}_{\text{Anh}} = 0$). These missing contributions can be obtained from TI between a reference Hamiltonian and the true Hamiltonian [7], but the required ensemble averages must be estimated along a coupling path. This sampling becomes expensive for quantum systems where PIMD is needed [3].

For many solids, it is often assumed that quantum effects can be treated separately from the intrinsic anharmonicity. This assumption enables hybrid workflows in which the thermodynamic properties are computed from a harmonic or renormalized harmonic model at low temperature, while anharmonic corrections are obtained from classical sampling at higher temperature. Such mixed lattice-dynamics/MD strategies have been successful in a range of solids [12–14]. The validity of this separation, however, is difficult to assess *a priori*. In systems with light atoms, soft modes, or pronounced zero-point motion, quantum–anharmonic coupling can be non-negligible, and the accuracy of a hybrid treatment must be validated against a higher-fidelity reference [15].

To capture quantum effects and anharmonicity without explicit PIMD trajectories, we leverage the free energy cumulant expansion truncated beyond second order,

$$\mathcal{F} \approx V_0 + \mathcal{F}_H + \mathcal{F}_1 + \mathcal{F}_2, \quad (7)$$

where $\mathcal{F}_1$ is the first cumulant term and $\mathcal{F}_2$ is the second cumulant term, described in the Free Energy Cumulant Expansion section in the Methods. When the potential energy is represented by a Taylor effective potential (i.e., a Taylor series with IFCs fit from force-displacement data) truncated beyond fourth order, $\mathcal{F}_1$ is determined by quartic anharmonicity and $\mathcal{F}_2$ is determined by cubic anharmonicity [4]. The second-order cumulant expansion can therefore be viewed as an extension of the sTDEP free energy to include cubic and quartic anharmonicity.

The cumulant expansion can be used to directly estimate free energy, entropy, internal energy, and heat capacity without numerical differentiation. Historically, however, its use has been limited because evaluating $\mathcal{F}_1$ and $\mathcal{F}_2$ was computationally prohibitive. Consequently, prior work often relied on severe truncations and asymptotic simplifications (such as the high-temperature limit) to obtain tractable expressions [4–6]. While modern codes often employ cubic and quartic IFCs to compute anharmonic phonon lifetimes and thermal transport properties [16–19], their use for thermodynamic properties remains limited. Thermodynamic predictions in modern anharmonic lattice-dynamics frameworks often incorporate higher-order IFCs indirectly through renormalized phonon frequencies [20, 21], rather than by directly computing their contributions to the anharmonic free energy. Thus, the central challenge is not in obtaining higher-order IFCs, but in evaluating the resulting free energy terms ($\mathcal{F}_1$ and $\mathcal{F}_2$) efficiently. To address this challenge, we compute $\mathcal{F}_1$ and $\mathcal{F}_2$ as sums over the irreducible Brillouin zone, which can be trivially parallelized.

Table 1 Comparison of common methods for calculating vibrational thermodynamic properties. “Quantum effects” indicates inclusion of zero-point motion and quantum statistics (i.e., Bose–Einstein). “Renormalized IFCs” indicates that the harmonic reference is built from finite-temperature IFCs. “Trajectory-Free” indicates that the method does not require MD or PIMD sampling. “Direct access” indicates that $\mathcal{S}$, $\mathcal{U}$, and C_V are obtained directly from analytical free energy expressions (i.e., without numerical differentiation). The $\mathcal{F}^{\text{sTDEP}}$ column refers to Eq. (5).

	HA	$\mathcal{F}^{\text{sTDEP}}$	TI (MD)	TI (PIMD)	Cumulant
Quantum effects	✓	✓		✓	✓
Renormalized IFCs		✓	✓	✓	✓
Trajectory-Free	✓	✓			✓
Direct access to $\mathcal{S}$, $\mathcal{U}$, and C_V	✓				✓
Cubic/quartic anharmonicity					✓
Full anharmonicity			✓	✓	

As summarized in Table 1, the free energy cumulant expansion occupies a distinct regime among common vibrational thermodynamics methods. For classical free energies alone, TI remains the natural benchmark because its statistical error can be reduced by additional sampling. The cumulant approach instead trades this sampling-based error control for a truncated expansion around a self-consistent harmonic reference. This tradeoff is valuable when the objective is not only a single free energy value, but also a direct calculation of entropy, internal energy, and heat capacity, particularly when quantum effects are important.

This work details the derivation, implementation, and validation of an efficient free energy cumulant expansion workflow. We use sTDEP IFCs to define the renormalized self-consistent harmonic reference, which improves the accuracy at each temperature, and does not require MD or PIMD. Using renormalized IFCs results in a temperature dependent V_0 , which makes analytic computation of its contribution to the other thermodynamic properties challenging. We address this complication by developing a sampling-based estimator for the temperature derivatives of V_0 , enabling direct evaluation of entropy, internal energy, and heat capacity, eliminating the need for numerical differentiation. We validate the workflow on classical Lennard–Jones (LJ) argon and Stillinger–Weber (SW) silicon, and also on LJ neon, for which both quantum and anharmonic effects are pronounced [15].

To make our approach accessible, the full workflow, including the calculation of sTDEP IFCs, is available in Python and Julia through the `CrystalCumulants.jl` package [22]. Furthermore, $\mathcal{F}_1$ and $\mathcal{F}_2$ and their derivatives are implemented in the TDEP package [10].

Results

Approximating Temperature Derivatives of V_0

For a Taylor effective potential truncated beyond fourth order with self-consistent IFCs, we define

$$V_0 \equiv \langle V - V_2 - V_3 - V_4 \rangle_{\text{H}}. \quad (8)$$

This expression for V_0 is the average of the anharmonic terms omitted from the Taylor effective potential. To estimate entropy, internal energy, and heat capacity, V_0 must be differentiated with respect to temperature. To estimate these derivatives, consider a quantity A that depends only on the atomic positions. The temperature derivative of $\langle A \rangle_{\text{H}}$ can be written as

$$\frac{\partial \langle A \rangle_{\text{H}}}{\partial T} = \frac{\text{cov}_{\text{H}}(A, \tilde{V}_2)}{k_{\text{B}} T^2}, \quad (9)$$

where $\tilde{V}_2$ is a mode-weighted harmonic energy:

$$\tilde{V}_2 = \frac{1}{2} \sum_{\mathbf{k}\lambda} \frac{4 n_{\mathbf{k}\lambda} (n_{\mathbf{k}\lambda} + 1)}{(2n_{\mathbf{k}\lambda} + 1)^2} \omega_{\mathbf{k}\lambda}^2 q_{\mathbf{k}\lambda}^2. \quad (10)$$

Here, $q_{\mathbf{k}\lambda}$ is the mass-normalized amplitude of the $\mathbf{k}\lambda$ phonon mode and $n_{\mathbf{k}\lambda} = (e^{\beta \hbar \omega_{\mathbf{k}\lambda}} - 1)^{-1}$ is the occupation number for the phonon mode $\mathbf{k}\lambda$ given by the Bose-Einstein distribution. In the classical limit, $\tilde{V}_2 = V_2$. Derivations of Eqs. (9) and (10) can be found in Sec. S1 of the Supplementary Information.

To compute the associated contribution to the entropy, define $A \equiv V - V_2 - V_3 - V_4$ and apply Eq. (9), so that

$$\mathcal{S}_0 = -\frac{\partial V_0}{\partial T} \approx -\frac{\text{cov}_{\text{H}}(V - V_2 - V_3 - V_4, \tilde{V}_2)}{k_{\text{B}} T^2}. \quad (11)$$

As a consequence of the self-consistent harmonic reference, V_2 , V_3 , and V_4 are themselves temperature dependent, rendering Eq. (11) an approximation. The error associated with this approximation, however, is mitigated by the envelope theorem [23]. The harmonic sTDEP IFCs minimize $\mathcal{F}^{\text{sTDEP}}$ and therefore do not contribute to the temperature derivative. A discussion and proof of this property are presented in Secs. S2 and S3 of the Supplementary Information.

The corresponding contribution to the internal energy is then evaluated from

$$\mathcal{U}_0 = V_0 + T \mathcal{S}_0. \quad (12)$$

The contribution to the heat capacity follows by differentiating Eq. (11),

$$C_{V,0} = -T \frac{\partial^2 V_0}{\partial T^2} = T \frac{\partial \mathcal{S}_0}{\partial T}. \quad (13)$$

With $A \equiv V - V_2 - V_3 - V_4$ and $W \equiv \text{cov}_H(A, \tilde{V}_2)$,

$$C_{V,0} = \frac{2W}{k_B T^2} - \frac{1}{k_B T} \frac{\partial W}{\partial T}. \quad (14)$$

When differentiating W , the explicit temperature dependence of $\tilde{V}_2$ through the phonon occupation must also be retained. Holding the phonon frequencies and eigenvectors fixed,

$$\frac{\partial \tilde{V}_2}{\partial T} = \frac{1}{2T} \sum_{\mathbf{k}\lambda} \frac{4n_{\mathbf{k}\lambda}(n_{\mathbf{k}\lambda} + 1)}{(2n_{\mathbf{k}\lambda} + 1)^3} \frac{\hbar\omega_{\mathbf{k}\lambda}}{k_B T} \omega_{\mathbf{k}\lambda}^2 q_{\mathbf{k}\lambda}^2. \quad (15)$$

Expanding W and applying Eq. (9) to its expectation values then gives

$$C_{V,0} \approx \frac{2\text{cov}_H(A, \tilde{V}_2)}{k_B T^2} - \frac{1}{k_B^2 T^3} \left[\text{cov}_H(A\tilde{V}_2, \tilde{V}_2) - \langle \tilde{V}_2 \rangle_H \text{cov}_H(A, \tilde{V}_2) - \langle A \rangle_H \text{cov}_H(\tilde{V}_2, \tilde{V}_2) \right] - \frac{1}{k_B T} \text{cov}_H\left(A, \frac{\partial \tilde{V}_2}{\partial T}\right). \quad (16)$$

$C_{V,0}$ is likewise an approximation due to the temperature dependence of V_3 and V_4 . The associated error for $C_{V,0}$ is expected to be higher than that of $\mathcal{S}_0$ as heat capacity is a second derivative and consequently more chain-rule terms have been neglected. Details of the procedure used to generate samples for estimating $\langle \cdot \rangle_H$ and $\text{cov}_H(\cdot, \cdot)$ are given in the Sampling Canonical Configurations section of the Methods.

Calculation of the First and Second Cumulants

The first and second terms in the cumulant expansion, $\mathcal{F}_1$ and $\mathcal{F}_2$, can be numerically calculated when the Taylor series for V is truncated beyond fourth order (i.e., $V \approx V_0 + V_2 + V_3 + V_4$). The resulting expressions are:

$$\mathcal{F}_1 = \frac{\hbar^2}{8N} \sum_{\mathbf{k}\mathbf{k}'\lambda\lambda'} \frac{\Phi_{\lambda\lambda'\lambda'}^{\mathbf{k}, -\mathbf{k}, \mathbf{k}', -\mathbf{k}'}}{\omega\omega'} \left(n + \frac{1}{2}\right) \left(n' + \frac{1}{2}\right) \quad (17)$$

$$\begin{aligned} \mathcal{F}_2 = & -\frac{\hbar^2}{48N} \sum_{\substack{\mathbf{k}\mathbf{k}'\mathbf{k}'' \\ \lambda\lambda'\lambda''}} \frac{|\Phi_{\lambda\lambda'\lambda''}^{\mathbf{k}\mathbf{k}'\mathbf{k}''}|^2}{\omega\omega'\omega''} \left[\frac{(n+1)(n'+n''+1) + n'n''}{\omega + \omega' + \omega''} \right. \\ & \left. + 3 \frac{n''(n+n'+1) - nn'}{\omega + \omega' - \omega''} \right], \end{aligned} \quad (18)$$

where ω' and n' are shorthand for the frequency and mode occupation of the phonon mode indexed by $\mathbf{k}'\lambda'$. $\Phi_{\lambda\lambda'\lambda''}^{\mathbf{k}\mathbf{k}'\mathbf{k}''}$ is the $(\mathbf{k}\lambda, \mathbf{k}'\lambda', \mathbf{k}''\lambda'')$ element of the cubic mode-coupling tensor (defined in Ref. 9) and $\Phi_{\lambda\lambda'\lambda'}^{\mathbf{k}, -\mathbf{k}, \mathbf{k}', -\mathbf{k}'}$ is the analogous quartic element

of the quartic mode-coupling tensor (defined in Ref. 4 on p. 307). The derivation of $\mathcal{F}_1$, and $\mathcal{F}_2$ can be found in Sec. 5 (p. 320) and Appendix 23 (p. 434) of Ref. 4. The contributions for entropy and heat capacity are computed by analytical differentiation of $\mathcal{F}_1$ and $\mathcal{F}_2$ following Eq. (2). In these derivatives, only the phonon occupations are treated as temperature dependent. Due to the envelope theorem, the phonon frequencies do not contribute $\partial\omega/\partial T$ terms [23]. However, the mode-coupling terms $\Phi_{\lambda\lambda'\lambda''}^{\mathbf{k}\mathbf{k}'\mathbf{k}''}$ and $\Phi_{\lambda\lambda'\lambda'}^{\mathbf{k},-\mathbf{k},\mathbf{k}',-\mathbf{k}'}$ do have temperature derivatives that are neglected. The validity of this assumption is assessed in the next section. Internal energy is computed by rearranging Eq. (1) (i.e., $\mathcal{U}_1 = \mathcal{F}_1 + T\mathcal{S}_1$).

Classical Lennard–Jones Argon and Stillinger–Weber Silicon

To validate the cumulant expansion workflow, we calculated the free energy, entropy, internal energy, and heat capacity of LJ argon and SW silicon from the second-order cumulant expansion [Eq. (7)] with sTDEP IFCs. We chose these two materials because one (LJ argon) is strongly anharmonic and the other (SW silicon) is weakly anharmonic [9]. The classical thermodynamic properties of LJ argon and SW silicon from the cumulant expansion are plotted in Figs. 1(a)–1(d) as a function of temperature. Also plotted are ground truth values from MD simulations (described in the Molecular Dynamics section of the Methods) from Ref. 9. The temperature axis is normalized by the experimental melting temperatures, T_{melt} , of argon (83 K) and silicon (1690 K) [24, 25]. While these values are not the melting temperatures of LJ argon and SW silicon, they provide a convenient sense of scale for the temperature axis. The free energy and internal energy are normalized by their respective values at zero temperature, while the heat capacity and entropy are normalized by Nk_B . On this scale, the Dulong-Petit (i.e., classical and harmonic) heat capacity is 3.

For all four properties, the errors compared to the MD ground truth generally increase as temperature, and thus anharmonicity, increase. All free energy and internal energy calculations are within 0.25 meV/atom of the MD ground truth values for both materials. The entropy is accurate, with a maximum absolute error of $0.023k_B/\text{atom}$ for LJ argon and $0.014k_B/\text{atom}$ for SW silicon. The heat capacity shows the largest deviations of the four properties, although the errors are modest. The maximum error is $0.04 k_B/\text{atom}$ (1.1%) for LJ argon and $0.10 k_B/\text{atom}$ (3.2%) for SW silicon. The dominant error sources are neglected higher-order cumulants and neglected chain-rule terms when differentiating $\mathcal{F}_1$ and $\mathcal{F}_2$ [Eqs. (17) and (18)]. We do not attribute any error to truncation of the Taylor series beyond fourth order, as the fourth-order IFC models predict the forces with R^2 values of 0.986 for LJ argon and 0.999 for SW silicon.

The small errors justify not only the truncation of the cumulant expansion beyond second order, but also the approximations made to compute the temperature derivatives of V_0 , $\mathcal{F}_1$, and $\mathcal{F}_2$. We recently proposed a method to compute heat capacity from MD using a Taylor effective potential that achieved a 1.1% error for LJ argon at 80 K ($0.96 T_{\text{melt}}$) and a 0.70% error for SW silicon at 1300 K ($0.81T_{\text{melt}}$) [9]. At the same conditions, the cumulant expansion achieves a 1.1% error for LJ argon and a 1.8% error for SW silicon. While the cumulant expansion error is slightly larger, it is computationally less expensive because it does not require MD and has the additional advantage of supplying estimates for free energy, entropy, and internal energy.

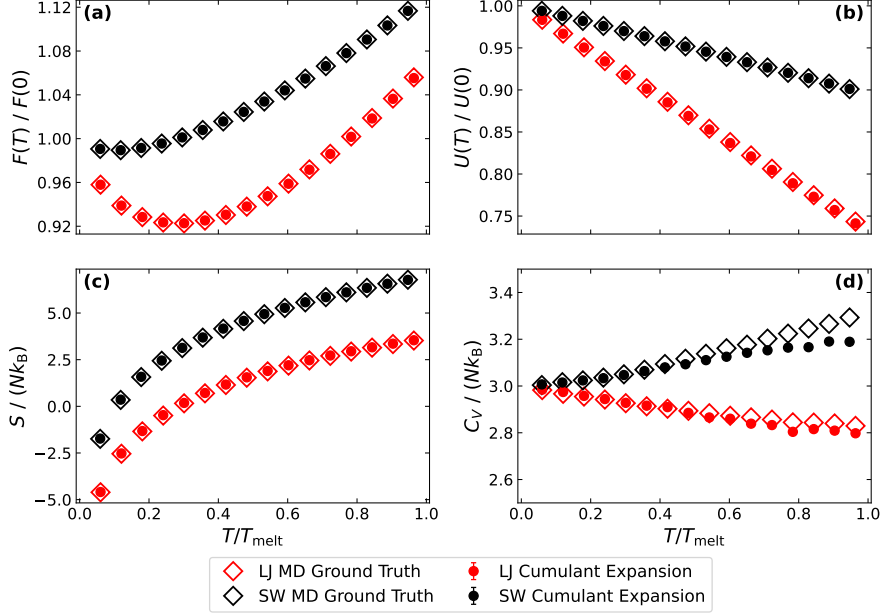


Fig. 1 Classical (a) free energy, (b) internal energy, (c) entropy, and (d) heat capacity of LJ argon and SW silicon predicted from the cumulant expansion [Eq. (7)] and ground truth values obtained from MD simulations done in Ref. 9 (see Methods). Free energy and internal energy are normalized by their values at 0 K while the entropy and heat capacity are normalized by Nk_B . The horizontal axis denotes the temperature normalized by the melting temperature. The error bars are smaller than the markers. The entropy plotted in (c) is the classical entropy, which can be negative because the phase space is continuous [26].

The free energy residuals relative to the MD ground truth values, which are based on TI, are plotted in Fig. 2. A breakdown of the first- and second-order cumulant contributions ($\mathcal{F}_1$, $\mathcal{F}_2$, and $\mathcal{F}_1 + \mathcal{F}_2$) is plotted in Figs. 3(a) and 3(b). Because phase stability is often determined by free energy differences of a few meV/atom, resolving free energies at the 1 meV/atom level is a useful practical target [27, 28]. In absolute units, the residuals are well below this threshold. For LJ argon, the residual is below 0.1 meV/atom at all temperatures. The SW silicon residual is below 0.1 meV/atom until 1300 K ($0.81T_{\text{melt}}$) and it increases to 0.21 meV/atom by 1600 K ($0.95T_{\text{melt}}$). The LJ argon residual is consistently smaller than the SW silicon residual. We attribute the larger error in SW silicon to strong size effects in the reference TI calculations that lead to larger uncertainty.

For both materials, $\mathcal{F}_1 + \mathcal{F}_2$ is small but non-negligible relative to the total free energy. For LJ argon, this sum is as substantial as -0.73 meV/atom (below the 1 meV/atom error heuristic), yet because the relevant temperatures are low, it corresponds to a sizable fraction of $k_B T$ (11%). This result suggests that the 1 meV/atom threshold is inappropriate for LJ argon. Because LJ argon is a much softer material than SW silicon, its energy scale is much closer to the thermal energy of the system than in SW silicon [9].

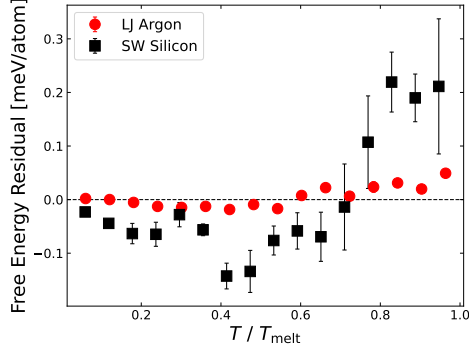


Fig. 2 Free energy residual for LJ argon and SW silicon. The residual is defined as the difference between the cumulant expansion result [Eq. (7)] and the TI result. The error bars are computed by combining the standard errors of the two datasets assuming statistical independence. The error bars for LJ argon are smaller than the markers.

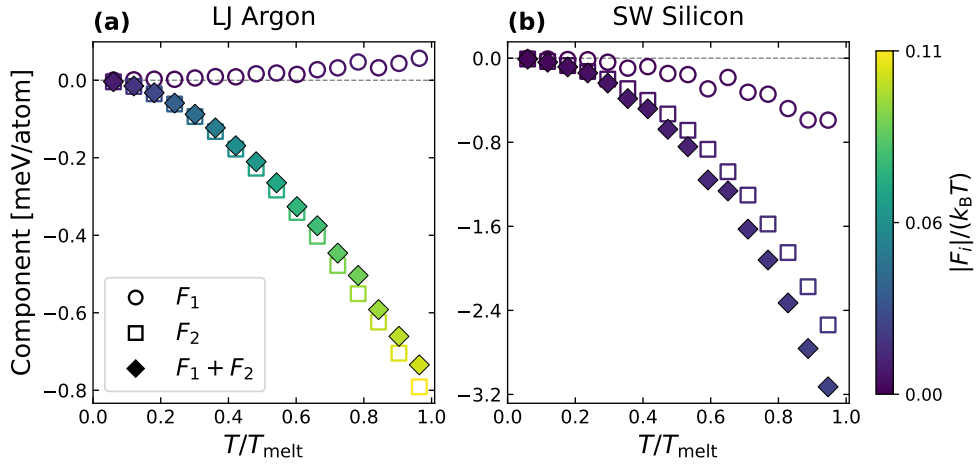


Fig. 3 Breakdown of the first- and second-cumulant contributions to the free energy for (a) LJ argon and (b) SW silicon. The color compares the size of each component i with the thermal energy $k_B T$. There are no error bars because $\mathcal{F}_1$ and $\mathcal{F}_2$ are evaluated deterministically.

Comparing $\mathcal{F}_1$ with $\mathcal{F}_2$ reveals that the anharmonic correction is typically dominated by the second cumulant, with $|\mathcal{F}_2| > |\mathcal{F}_1|$ over most of the temperature range for both materials. This result is not unreasonable because the order of the cumulants does not dictate their relative magnitudes. There is a small amount of point-to-point scatter visible in Figs. 3(a) and 3(b), which is most obvious in the first cumulant. This scatter is likely due to fitting noise, because each temperature uses an independently-fit IFC set generated from stochastic sampling. The impact of the wave vector grid is negligible on the scale of this scatter as both cumulants are well converged, as shown in Figs. S5-S7 of the Supplementary Information.

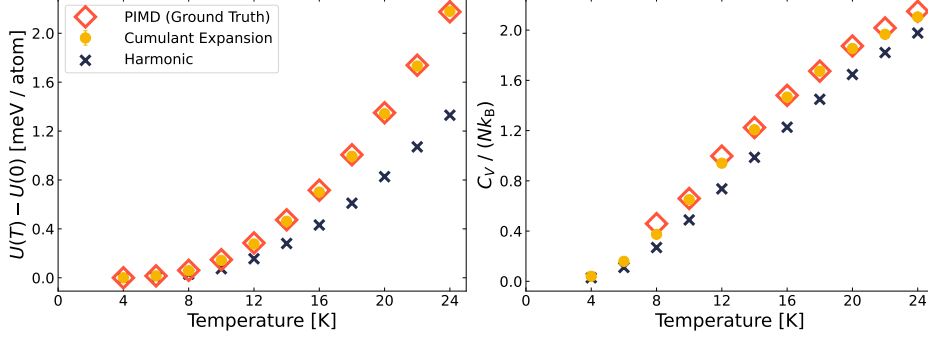


Fig. 4 (a) Internal energy and (b) heat capacity for LJ neon calculated from PIMD, the cumulant expansion [Eq. (7)], and the harmonic approximation with renormalized sTDEP IFCs. The internal energy at 0 K is subtracted from each dataset to facilitate comparison. The heat capacity is normalized by Nk_B

Quantum–Anharmonic Thermodynamics of Lennard-Jones Neon

To demonstrate the ability of the cumulant expansion to simultaneously capture anharmonic and quantum effects, we calculated the internal energy and heat capacity of LJ neon using the temperature-dependent lattice constants from Ref. 15. Due to its low atomic weight, neon is known to have both strong anharmonic and quantum effects at low temperatures [15]. The results are shown in Figs. 4(a) and 4(b), where they are compared with results from (i) calculations performed under the harmonic approximation with renormalized sTDEP IFCs and (ii) ground truth PIMD simulations (described in the PIMD section of the Methods). Heat capacity from PIMD is not reported at the two lowest temperatures studied (4 K and 6 K) as it was computationally intractable to converge.

When compared to the PIMD results, the internal energy has a maximum error of 0.036 meV/atom at the highest temperature studied (24 K). The heat capacity error at 24 K is 0.044 k_B /atom (2.1%). The maximum heat capacity error occurs at 6 K, which we attribute to insufficient number of beads in the PIMD simulations. The choice of the bead number is discussed in Sec. S5. We attribute the heat capacity error, which generally increases with increasing temperature, to early truncation of the cumulant expansion and neglected chain rule terms. Even at these low temperatures, the harmonic approximation is clearly insufficient, as it underpredicts the internal energy by 0.85 meV/atom and the heat capacity by 0.17 k_B /atom (8.0%) at 24 K.

Lennard-Jones Neon Zero-Pressure Lattice Constants

The zero-pressure LJ neon lattice constant was computed as a function of temperature by minimizing free energy with respect to volume for the second-order cumulant expansion [Eq. (7)] and for the sTDEP free energy [Eq. (5)], as described in the Equation-of-State Fits section of the Methods. The results are plotted in Fig. 5 along with ground truth values calculated from a PIMD simulation in the NPT (i.e., constant number of particles, pressure P , and temperature) ensemble. When compared

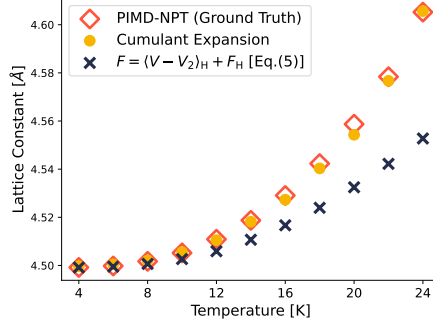


Fig. 5 Zero-pressure lattice constants of LJ Neon from PIMD-*NPT* compared to values fit from the Vinet equation of state applied to the second-order cumulant expansion free energy [Eq. (7)] and the sTDEP free energy [Eq. (5)].

to PIMD, the cumulant expansion has a maximum error of 0.004 Å (0.09%) whereas Eq. (5) has a maximum error of 0.052 Å (1.1%) at 24 K. Prior work showed that the sTDEP free energy was sufficient to capture the negative thermal expansion of silicon at low temperature [29]. For LJ neon, however, Eq. (5) consistently underpredicts the lattice constant. The error grows with temperature as the first and second cumulant terms, and anharmonicity, grow.

Computational Efficiency

We now compare the computational cost of the cumulant expansion workflow with the TI-MD (i.e., classical) and TI-PIMD (i.e., quantum) workflows for the LJ potential. The cumulant expansion enables the simultaneous evaluation of the free energy and its temperature derivatives, providing all thermodynamic properties from the same set of inputs. Thermodynamic integration provides the Helmholtz free energy, and a separate MD or PIMD simulation is needed to obtain the internal energy and heat capacity, which then supply the entropy via Eq. (1). All calculations reported herein use 40 cores (shared memory) on a single compute node with two Intel Xeon Gold 5218R CPUs and follow the procedure in the Computational Benchmarks section of the Methods.

As shown in Fig. 6, for classical LJ argon, the cumulant expansion workflow has a total run time of 449 s, which is 16% faster than the 520 s needed for the TI-MD workflow. The primary distinction at the classical level is not in the run time, but in the structure of the calculation. The cumulant expansion yields all thermodynamic properties in a single calculation and does not require equilibration, trajectory generation, checks for finite-size effects, or block averaging of observables to estimate error. Thus, even when the target is only the classical free energy and not other thermodynamic properties, the cumulant expansion workflow has a distinct advantage over TI-MD.

The advantage becomes much larger for quantum thermodynamics. Direct path-integral thermodynamic integration is roughly equivalent to N_{beads} classical MD steps (where N_{beads} is the number of beads used in PIMD). We therefore estimate the cost of TI-PIMD by linearly scaling the measured classical TI timings by the number of beads

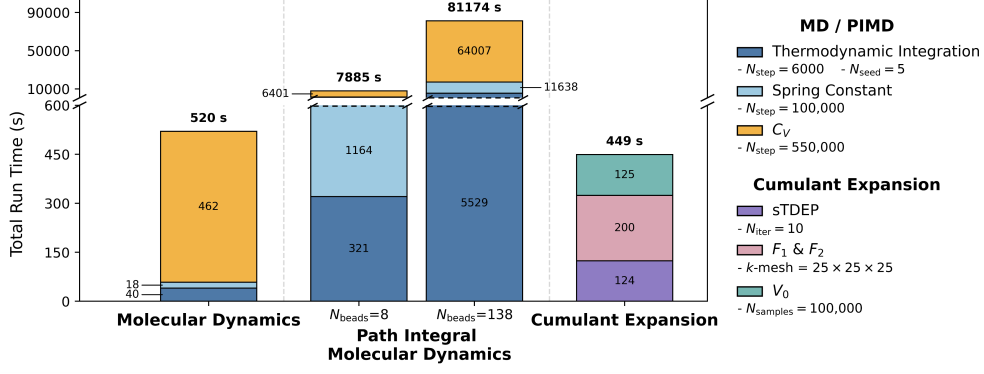


Fig. 6 Run time comparison of the TI-MD, TI-PIMD (estimated), and cumulant expansion workflows. The cumulant expansion timing includes the sTDEP IFCs, the estimation of V_0 and its associated error, and the first- and second-order cumulant terms. The cumulant expansion cost is independent of the use of classical or quantum statistics. The classical TI-MD timing combines thermodynamic integration for the free energy, a spring-constant calculation for the Einstein-crystal reference, and a separate MD calculation for the internal energy and heat capacity. The quantum TI-PIMD timing is a conservative estimate obtained by scaling the measured classical TI timings by the number of path-integral beads, N_{beads} .

used in the LJ neon calculations. This estimate is intentionally conservative. It assumes ideal linear scaling with N_{beads} and neglects additional overheads associated with path-integral sampling, equilibration, thermostating, and parallel communication. Thus, the estimate should be viewed as a lower bound on the practical cost of PIMD. The timing of the PIMD simulation for internal energy and heat capacity was directly measured.

The cumulant expansion workflow timing remains at 449 s for LJ neon because the cost is set by the IFCs and Brillouin-zone sums, which are independent of classical or quantum statistics. With the smallest (8) and largest (138) bead counts used in this work, the TI-PIMD workflow is $17\times$ (7885 s) – $180\times$ (81174 s) slower than the cumulant expansion workflow. This comparison highlights the main practical benefit, which is that quantum anharmonic thermodynamics can be obtained without explicit PIMD sampling.

Beyond run time alone, the cumulant expansion workflow affords a number of advantages. The TI-MD and TI-PIMD reference calculations require convergence studies (or justified choices) for the equilibration length, production length, block size, number of independent seeds, and supercell size. In contrast, for the cumulant expansion workflow, the supercell size only needs to be large enough to compute the IFCs. The supercell size does not affect the thermodynamic properties (Fig. S1). Numerical convergence is instead controlled by only two parameters: the number of Gaussian samples used to evaluate V_0 (Figs. S2-S4) and the wave vector mesh used to evaluate the cumulant terms (Figs. S5-S7). Because the Gaussian samples are independent, the statistical error in V_0 and its dependence on the number of samples can be estimated directly by bootstrapping from a single computation. The wave vector mesh

must also be converged (Figs. S5-S7). However, coarse and intermediate meshes are inexpensive, requiring only a few seconds of run time. The cumulant expansion therefore provides not only a lower-cost route to quantum anharmonic thermodynamics, but also a workflow requiring fewer *ad hoc* hyperparameters and sources of numerical error with greater transparency.

Discussion

To bridge the gap between quantum harmonic vibrational thermodynamics and the finite-temperature anharmonicity captured by TI, we developed a trajectory-free method based on the free energy cumulant expansion. This approach combines renormalized self-consistent phonons, explicit cubic and quartic anharmonic contributions to the free energy, entropy, internal energy and heat capacity [Eqs. (17) and (18)], and a trajectory-free estimator for the reference potential energy [Eqs. (9), (11), and (16)]. Such an integrated treatment is needed because phonon occupations are strongly affected by quantum statistics at low temperature, while anharmonic interactions increasingly reshape thermodynamic properties as temperature increases. Although TI-PIMD can capture both effects, it is generally too expensive for systematic studies. Furthermore, while cubic and quartic anharmonicity are now commonly included in calculations of lattice thermal conductivity [16–19] and frequency renormalization [20, 21], their use in thermodynamic property calculations has been limited.

We validated the workflow on classical LJ argon and SW silicon, showing that free energies and internal energies can be predicted within 0.25 meV/atom of ground truth values from TI, even near the melting temperature (Fig. 2), at a comparable computational cost. The workflow is also accurate for entropy, with maximum absolute errors of 0.023 k_B /atom for LJ argon and 0.014 k_B /atom for SW silicon. The largest deviations occur in the heat capacity, but they remain modest: the maximum errors are 0.04 k_B /atom (1.1%) for LJ argon and 0.10 k_B /atom (3.2%) for SW silicon. This level of agreement is only achieved when the expansion is carried out to include both the first and second cumulants, $\mathcal{F}_1$ and $\mathcal{F}_2$.

The workflow was then applied to LJ neon, a demanding test case where quantum and anharmonic effects are both essential to capture. Using a quantum harmonic reference together with the explicit anharmonic cumulant corrections, the workflow predicts the internal energy to within 0.036 meV/atom at 24 K [Fig. 4(a)] of a TI-PIMD reference. The heat capacity shows an error of 0.044 k_B /atom (2.1%) compared to that from PIMD at the same temperature [Fig. 4(b)], which is consistent with the stronger sensitivity of second derivatives of free energy to truncation error. Even so, the cumulant expansion improves upon the harmonic approximation, which underpredicts the internal energy by 0.85 meV/atom and the heat capacity by 0.17 k_B /atom (8.0%) at 24 K. We also showed that the anharmonic cumulant corrections are required to obtain accurate zero-pressure lattice constants (Fig. 5). The cumulant expansion produces a maximum lattice constant error of 0.004 Å (0.09%), whereas the sTDEP free energy yields a maximum error of 0.052 Å (1.1%) when compared to a PIMD reference. Notably, the cumulant expansion is estimated to be one-to-two orders of magnitude faster than the reference TI-PIMD calculations.

In summary, the free energy cumulant expansion workflow presents an efficient, trajectory-free route to quantum anharmonic thermodynamics given a crystal structure and self-consistent IFCs. The workflow accurately predicts free energy, entropy, internal energy and heat capacity across a wide range of conditions. Its low cost makes it practical to compute downstream properties that require repeated free energy evaluations, including thermal expansion, phase stability, and equilibrium lattice constants. Taken together, these results demonstrate that the cumulant expansion provides a computationally efficient framework for predicting the thermodynamic state of materials in a form suitable for high-throughput calculations.

Methods

Sampling Canonical Configurations

The harmonic canonical distribution of atomic displacements is a multivariate Gaussian with zero mean and a temperature-dependent covariance. In the normal-mode basis, each phonon mode is an independent Gaussian random variable with standard deviation

$$\sigma_{\mathbf{k}\lambda}^{\text{classical}} = \frac{\sqrt{k_{\text{B}}T}}{\omega_{\mathbf{k}\lambda}} \quad (19)$$

for classical statistics and

$$\sigma_{\mathbf{k}\lambda}^{\text{quantum}} = \sqrt{\frac{\hbar(2n_{\mathbf{k}\lambda} + 1)}{2\omega_{\mathbf{k}\lambda}}} \quad (20)$$

for quantum statistics [11, 30]. The Cartesian displacements for atom i may therefore be sampled as

$$\mathbf{u}_i = \frac{1}{\sqrt{m_i}} \sum_{\mathbf{k}\lambda} \mathbf{e}_{\mathbf{k}\lambda}^i \sigma_{\mathbf{k}\lambda} \zeta_{\mathbf{k}\lambda}, \quad (21)$$

where m_i is the mass of atom i , $\zeta_{\mathbf{k}\lambda} \sim \mathcal{N}(0, 1)$ is a standard normal random variable and $\mathbf{e}_{\mathbf{k}\lambda}^i$ is the 3×1 block of the phonon eigenvector for mode $\mathbf{k}\lambda$ corresponding to atom i . Critically, the $\zeta_{\mathbf{k}\lambda}$ should be *not* be re-sampled for every atom. All atoms, i , in the system must use the same set of random numbers within a configuration. This process is computationally trivial. The resulting configurations can be used to estimate statistics with respect to harmonic dynamics. For example, $\langle V - V_2 \rangle_{\text{H}}$ in the sTDEP harmonic free energy [Eq. (5)] or the covariance term in the calculation of $\partial V_0 / \partial T$ [Eq. (11)].

sTDEP Interatomic Force Constants

The sTDEP iterative algorithm to compute self-consistent finite-temperature IFCs using the TDEP code is summarized in Algorithm 1. The input variables are the number of iterations N_{iter} , the number of configurations to sample on the initial iteration N_{init} , the maximum number of samples for any iteration N_{max} , the sampling temperature, a boolean “mix” that sets if configurations from iteration $i - 1$ should be mixed with iteration i , and a guess for the maximum frequency ω_{max} . The maximum frequency

sets the displacement scale for the first iteration to generate the initial set of harmonic IFCs, $\Phi^{(0)}$. For LJ argon and LJ neon, $\omega_{\max} = 2.5$ THz, and for SW silicon, $\omega_{\max} = 18$ THz. For all materials, $N_{\text{iter}} = 10$, $N_{\text{init}} = 8$, $N_{\max} = 512$ and “mix” = True. The algorithm leverages the `extract_forceconstants` and `canonical_configurations` commands from the TDEP code [10] which are wrapped by our provided library [22].

Each iteration of the sTDEP algorithm only requires the second-order IFCs to begin the next iteration. The cubic and quartic IFCs are fit from the final set of configurations, after the second-order IFCs are converged. We assess convergence quantitatively through the harmonic free energy and qualitatively by plotting the phonon density of states. The sTDEP free energy is converged to within 0.1 meV/atom after six iterations.

Algorithm 1 Fitting sTDEP Interatomic Force Constants

1. Set the number of configurations at iteration i to be

$$N_{\text{conf}}^{(i)} = \min(N_{\text{init}}2^{i-1}, N_{\max}),$$

so that the ensemble size doubles until the cap $N_{\max}$ is reached.

2. Generate the initial configuration ensemble using `canonical_configurations` from TDEP with maximum frequency $\omega_{\max}$. This procedure defines the initial displacement scale before self-consistent IFCs are available.
 3. Compute forces and obtain the initial second-order IFCs $\Phi^{(0)}$ using `extract_forceconstants` from TDEP.
 4. For $i = 1, \dots, N_{\text{iter}} - 1$, repeat:
 - (a) generate $N_{\text{conf}}^{(i+1)}$ configurations using $\Phi^{(i-1)}$;
 - (b) if mix is enabled and $i > 1$, include all configurations from the previous iteration in the fitting set;
 - (c) compute forces and update the IFCs to $\Phi^{(i)}$;
 - (d) compute harmonic free energy and phonon density of states to assess convergence.
 5. Fit cubic and quartic IFCs to displacements generated by the final second-order IFCs.
-

Properties of the sTDEP IFCs and their equivalence to SSCHA IFCs are discussed in Secs. S2 and S3.

Harmonic Thermodynamic Properties

Like the harmonic free energy, $\mathcal{F}_H$ [Eq. (4)], other harmonic thermodynamic properties are computed as sums over the first Brillouin zone from [2]

$$\mathcal{S}_H = -\frac{\partial \mathcal{F}_H}{\partial T} = k_B \sum_{\mathbf{k}\lambda} \left[\frac{\beta \hbar \omega_{\mathbf{k}\lambda}}{e^{\beta \hbar \omega_{\mathbf{k}\lambda}} - 1} - \log(1 - e^{-\beta \hbar \omega_{\mathbf{k}\lambda}}) \right] \quad (22)$$

$$\mathcal{U}_H = \frac{\partial(\beta\mathcal{F}_H)}{\partial\beta} = \sum_{\mathbf{k}\lambda} \hbar\omega_{\mathbf{k}\lambda} \left(\frac{1}{e^{\beta\hbar\omega_{\mathbf{k}\lambda}} - 1} + \frac{1}{2} \right) \quad (23)$$

$$C_{V,H} = -T \frac{\partial^2 \mathcal{F}_H}{\partial T^2} = k_B \sum_{\mathbf{k}\lambda} \left(\frac{\beta\hbar\omega_{\mathbf{k}\lambda}}{2} \right)^2 \operatorname{cosech}^2 \left(\frac{\beta\hbar\omega_{\mathbf{k}\lambda}}{2} \right). \quad (24)$$

Despite the use of temperature-dependent phonons (i.e., sTDEP), the phonon frequencies, $\omega_{\mathbf{k}\lambda}$, do not contribute to the derivatives in Eq. (2) due to the envelope theorem [23]. This point is discussed in Secs. S2 and S3 of the Supplementary Information.

Free Energy Cumulant Expansion

The free energy difference between the true and harmonic crystals can be expressed using a cumulant expansion of the anharmonic potential energy. This expansion is based on the cumulant generating function, C_X , of a random variable, X , defined as

$$C_X(t) = \log(\langle e^{tX} \rangle) = \sum_{n=1}^{\infty} \kappa_n(X) \frac{t^n}{n!}, \quad (25)$$

where $\kappa_n(X)$ is the n^{th} cumulant of the random variable X and t is an arbitrary variable [31]. Applying this definition to the anharmonic part of the potential energy allows the free energy to be written as a sum of cumulants evaluated with respect to a chosen reference ensemble.

The cumulant expansion may be derived using either the true or harmonic dynamics as the reference. We adopt the harmonic reference because atomic configurations that include zero-point motion can be generated efficiently by sampling a Gaussian distribution, as described in the Sampling Canonical Configurations section of the Methods. For brevity and clarity, we present the classical derivation of the cumulant expansion for free energy with respect to harmonic dynamics. A full derivation, which respects quantum mechanics, can be found in Sec. 5 of Ref. 4.

First, we write the partition function, $\mathcal{Z}$, as a reweighting of the harmonic partition function, $\mathcal{Z}_H$:

$$\begin{aligned} \mathcal{Z} &= \int e^{-\beta(\mathcal{H}_H + \Delta V)} d\Gamma \\ &= \mathcal{Z}_H \langle e^{-\beta\Delta V} \rangle_H, \end{aligned} \quad (26)$$

where $\Delta V = V - V_2$, $d\Gamma$ indicates that the integral is over all of phase space, and $\mathcal{H}_H$ is the harmonic part of the Hamiltonian. Importantly, we compute V_2 with renormalized IFCs. This choice maximizes the contribution from V_2 , thereby minimizing ΔV , which improves convergence and reduces size effects [7]. Next, we convert the partition function to a free energy via $\mathcal{F} = -\beta^{-1} \log(\mathcal{Z})$ and apply the cumulant expansion

from Eq. (25) with $t = -\beta$ and $X = \Delta V$:

$$\begin{aligned}
\mathcal{F} &= -\beta^{-1} \log(\mathcal{Z}_H) - \beta^{-1} \log(\langle \exp(-\beta \Delta V) \rangle_H) \\
&= \mathcal{F}_H - \beta^{-1} \sum_{n=1}^{\infty} \frac{(-\beta)^n}{n!} \kappa_n^H(\Delta V) \\
&= \mathcal{F}_H - \sum_{n=1}^{\infty} \frac{(-1)^n \beta^{n-1}}{n!} \kappa_n^H(\Delta V),
\end{aligned} \tag{27}$$

where κ_n^H is the n^{th} -order cumulant with respect to harmonic dynamics. For a classical harmonic reference, the first two cumulants in Eq. (27) are

$$\begin{aligned}
\kappa_1^H(X) &= \langle X \rangle_H, \\
\kappa_2^H(X) &= \langle X^2 \rangle_H - \langle X \rangle_H^2.
\end{aligned} \tag{28}$$

The quantum expression has the same cumulant structure, with the classical cumulants replaced by their quantum-mechanical counterparts [31].

Writing the true potential energy, V , as a Taylor effective potential [8, 9], we express ΔV as

$$\begin{aligned}
\Delta V &= V - V_2 \\
&= V_0 + V_3 + V_4 + \dots \\
&= V_0 + V_{\text{Anh}},
\end{aligned} \tag{29}$$

Substituting Eq. (29) into Eq. (27) and pulling out the constant term V_0 , we obtain the final expression for the free energy cumulant expansion:

$$\mathcal{F} = V_0 + \mathcal{F}_H - \sum_{n=1}^{\infty} \frac{(-1)^n \beta^{n-1}}{n!} \kappa_n^H(V_{\text{Anh}}). \tag{30}$$

We truncate the cumulant expansion after the second cumulant such that

$$\begin{aligned}
\mathcal{F} &\approx V_0 + \mathcal{F}_H + \kappa_1^H(V_{\text{Anh}}) - \frac{\beta}{2} \kappa_2^H(V_{\text{Anh}}) \\
&\equiv \mathcal{F}_H + \mathcal{F}_0 + \mathcal{F}_1 + \mathcal{F}_2.
\end{aligned} \tag{31}$$

For simplicity, we identify the first cumulant term as $\mathcal{F}_1$, and the second-order cumulant term as $\mathcal{F}_2$. Similar expansions can be written for entropy and heat capacity by taking the temperature derivatives in Eq. (2). Internal energy can also be calculated via a derivative, but we always calculate it from $\mathcal{U} = \mathcal{F} + T\mathcal{S}$ to guarantee self-consistency.

Table 2 Interatomic potential and structural parameters for the studied systems. SW silicon uses the `Si.sw` parameter file in LAMMPS [32].

Material	σ (Å)	ϵ (meV)	r_{cut} (Å)	a (Å)	N	T (K)
LJ Argon	3.400	10.423	8.50	5.2468	256	5–80
LJ Neon	2.782	3.2135	6.955	Variable	256	4–24
SW Silicon	–	–	–	5.43	216	100–1600

Cumulant Expansion Evaluation

All calculations use the second-order cumulant expansion [Eq. (31)] with sTDEP IFCs. The LJ length scale (σ), energy scale (ϵ), and cutoff radius (r_{cut}); and lattice constant (a) for all materials are included in Table 2 [15]. The SW silicon parameters are from the `Si.sw` file in LAMMPS [32, 33]. LJ argon and LJ neon are face-centered cubic supercells while SW silicon is a diamond structure. Supercell size does not affect the final predictions of the thermodynamic properties, as shown in Fig. S1 of the Supplementary Information. The LJ neon heat capacity and internal energy calculations use the lattice constants from Ref. 15. The zero-pressure lattice constants for LJ neon are also independently predicted by fitting a Vinet equation of state to the free energies of a set of 12 lattice constants corresponding to systems in tension and compression. This procedure is detailed in the Equation-of-State Fits section of the Methods.

The V_0 , S_0 , $\mathcal{U}_0$ and $C_{V,0}$ corrections are estimated from 100,000 samples. The phonon wave vector mesh to compute the cumulants (i.e., $\mathcal{F}_1$, $\mathcal{F}_2$, and their derivatives) was $25 \times 25 \times 25$ while that for the harmonic properties was $30 \times 30 \times 30$. Coarser grids could be used to obtain converged results in practice. The values here were chosen to mitigate error, not optimize runtime. The results of the convergence studies are presented in Figs. S2-S7 of the Supplementary Information.

Molecular Dynamics Ground Truth Simulations

The ground truth free energy for the classical systems (LJ argon and SW silicon) is calculated from LAMMPS through the `fix ti/spring` command [32, 34]. Unlike the cumulant expansion, where we use a temperature-dependent harmonic reference, LAMMPS uses an Einstein solid as the reference. The classical free energy results are the average of five MD simulations, with each simulation using the default parameters in Ref. 34: 1000 equilibration steps and 5000 switching steps where data are collected. The internal energy and heat capacity are computed from energy fluctuations and are averaged over 50 MD simulations, with simulation parameters taken from Ref. 9. Entropy is computed from $\mathcal{S} = (\mathcal{U} - \mathcal{F})/T$.

Path Integral Molecular Dynamics Ground Truth Simulations

To capture the ground truth data for LJ neon, we performed PIMD simulations using i-PI with LAMMPS as the force calculator [32, 35]. Following Ramírez and Herrero, we use a timestep of 3 fs [15]. We chose the number of beads, N_{beads} , according to $N_{\text{beads}} = 550/T$ for heat capacity and $200/T$ for internal energy. Justification for

this choice is provided in Sec. S5 of the Supplementary Information. All data are averaged over six PIMD simulations, with 100,000 equilibration steps followed by 500,000 production steps. The heat capacity is computed using the scaled-coordinate estimator [36].

While Ramírez and Herrero [15] report lattice constants for LJ neon, they used the static lattice approximation to calculate energies beyond nearest neighbors [2]. This choice reduced computational cost and led to a potentially coincidental agreement with experiments. Our LJ neon model, however, uses a hard cut-off (i.e., no contributions past the cutoff radius). We thus ran a PIMD simulation in the *NPT* ensemble at zero-pressure for each temperature to obtain reference lattice constants for the hard cut-off model. The simulations were initialized with the structures from Ref. 15. Each simulation was 3,000,000 steps with 100,000 steps of equilibration. We used a timestep of 0.75 fs. Block averaging is used to assess convergence and estimate error [15].

Equation-of-State Fits

Zero-pressure lattice constants for LJ neon were predicted from equation-of-state fits at each temperature. For each temperature between 4 K and 24 K, the free energy per atom was computed via the cumulant expansion for 12 lattice constants. The 12 lattice constants were obtained by scaling the lattice constants in Ref. 15 over a range of $\pm 3\%$. The resulting free energy per atom was fit independently to the volume per atom at each temperature using the Vinet equation-of-state [37, 38]

$$\mathcal{F}(\eta) = \mathcal{F}_{\text{eq}} + \frac{2B_{\text{eq}}V_{\text{eq}}}{[B'_{\text{eq}} - 1]^2} \left[2 - (5 + 3B'_{\text{eq}}(\eta - 1) - 3\eta) e^{-\frac{3}{2}(B'_{\text{eq}} - 1)(\eta - 1)} \right], \quad (32)$$

where

$$\eta = \left(\frac{V}{V_{\text{eq}}} \right)^{1/3}. \quad (33)$$

The parameters $\mathcal{F}_{\text{eq}}$, V_{eq} , B_{eq} , and B'_{eq} are the equilibrium free energy, volume, bulk modulus, and pressure derivative of the bulk modulus. The parameters were fit independently at each temperature.

We fit the free energy per atom so that V_{eq} corresponds to the equilibrium volume per atom. We studied face-centered-cubic LJ neon, whose conventional cell contains four atoms. The conventional unit cell lattice constant was therefore obtained from

$$a(T) = [4V_{\text{eq}}(T)]^{1/3}. \quad (34)$$

Computational Benchmarks

The run time comparison presented in Fig. 6 was carried out to compare workflows that produce the same thermodynamic information. For the classical simulation benchmark, the free energy was obtained from TI and the internal energy and heat capacity were obtained from a separate MD simulation. The total classical run time is

$$t_{\text{classical}} = t_{\text{TI,MD}} + t_{\text{spring,MD}} + t_{C_V,\text{MD}}, \quad (35)$$

where $t_{\text{TI,MD}}$ is the thermodynamic-integration time, $t_{\text{spring,MD}}$ is the time required to estimate the Einstein-crystal spring constant, and $t_{C_V,\text{MD}}$ is the MD time used to estimate the heat capacity. The TI calculations follow Ref. 34, with the coupling parameter λ dynamically varied during the simulation. The classical TI production calculation used $N_{\text{step}} = 6000$ MD steps and $N_{\text{seed}} = 5$ independent seeds to estimate statistical uncertainty. The Einstein-crystal spring constant was estimated from a small MD simulation requiring 50,000 equilibration steps and 50,000 production steps. Heat capacity times are computed from 50,000 equilibration steps and 500,000 production steps. These values were chosen conservatively to favor the simulation-based workflow over the cumulant expansion workflow.

The quantum TI benchmark was estimated from the measured classical timings and actual PIMD simulations. We do not report $\mathcal{F}$ from TI with PIMD as it is computationally prohibitive and there are no readily available codes. Instead, the cost of TI in PIMD is estimated by scaling $t_{\text{TI,MD}}$ and $t_{\text{spring,MD}}$ by the number of beads used in our PIMD simulations, N_{beads} . We report values for the minimum and maximum values of N_{beads} used from

$$t_{\text{PIMD}}(N_{\text{beads}}) \approx N_{\text{beads}} (t_{\text{TI,MD}} + t_{\text{spring,MD}}) + t_{C_V,\text{PIMD}}. \quad (36)$$

This estimate assumes ideal linear scaling and does not include additional overhead from PIMD-specific sampling, equilibration, thermostating, or communication [35]. It is therefore a conservative estimate that favors the TI-PIMD workflow over the cumulant expansion workflow. For LJ neon, the bead count was chosen as $N_{\text{beads}} = 200/T$ for the internal energy calculations and $N_{\text{beads}} = 550/T$ for the heat capacity calculations. The choice of N_{beads} is justified in Sec. S5 of the Supplemental Information. The timing comparison reports the smallest and largest bead counts used in this work, corresponding to $N_{\text{beads}} = 8$ (24 K, internal energy) and $N_{\text{beads}} = 138$ (4 K, heat capacity). The cost of the heat capacity is computed from the average step-time of a PIMD simulation in *i-pi* multiplied by the number of steps used in classical MD [35]. This choice is intentionally conservative, in practice PIMD would require more steps.

The cumulant expansion timing includes the calculation of the sTDEP IFCs and the evaluation of all terms entering the second-order free energy cumulant expansion. The harmonic contribution is obtained from a Brillouin-zone integral and is negligible in the total wall time. The reference contribution V_0 is evaluated by Gaussian sampling of the sTDEP harmonic reference distribution. For each sample, the full potential energy and its harmonic, cubic, and quartic approximations are evaluated. We used $N_{\text{sample}} = 100,000$ Gaussian samples for all materials. In practice, the dominant contributions to this stage are the evaluations of V and V_4 .

The first- and second-order cumulant terms, $\mathcal{F}_1$ and $\mathcal{F}_2$ [Eqs. (17) and (18)], are evaluated on a $25 \times 25 \times 25$ Brillouin zone mesh. Symmetry reduces the outer wave vector sum from the full Brillouin zone to the irreducible Brillouin zone, while the remaining wave vector sums are performed over the full mesh. The mode-coupling tensors are not stored for all wave vector combinations. Instead, each required mode-coupling element is computed and immediately accumulated into the free energy sum. This on-the-fly accumulation avoids storing the full tensor over the entire wave vector mesh.

For $\mathcal{F}_1$, the resulting memory complexity is $\mathcal{O}(N_{\text{prim}}^4)$ and the computational complexity is $\mathcal{O}(N_{\mathbf{k}}^{\text{IBZ}} N_{\mathbf{k}}^{\text{full}} N_{\text{prim}}^6)$. Here N_{prim} is the number of atoms in the primitive cell, $N_{\mathbf{k}}^{\text{IBZ}}$ is the number of $\mathbf{k}$ -points in the irreducible Brillouin zone, and $N_{\mathbf{k}}$ is the number of points in the first Brillouin zone. For $\mathcal{F}_2$, the memory complexity is $\mathcal{O}(N_{\text{prim}}^3)$ and the computational complexity is also $\mathcal{O}(N_{\mathbf{k}}^{\text{IBZ}} N_{\mathbf{k}}^{\text{full}} N_{\text{prim}}^6)$. The practical cost therefore depends strongly on the symmetry of the crystal and the number of atoms in the primitive cell. Temperature derivatives of the free energy are accumulated at the same time as the free energy terms and do not require additional Brillouin-zone sums.

Different supercell sizes were used for the simulation and cumulant expansion workflows because the two approaches converge differently with system size. The TI calculations used large supercells to reduce finite-size errors associated with the Einstein-crystal reference [34]: 10 976 atoms for LJ argon and 13 824 atoms for SW silicon (the results of the convergence study are plotted in Fig. S9). In contrast, the cumulant expansion used 256 atoms for LJ argon/neon and 216 atoms for SW silicon. The small supercells are sufficient for the cumulant expansion because size effects only come through the phonon calculations (i.e., $\mathcal{F}_H$). To calculate the IFCs, we only need to choose a supercell that is larger than twice the cutoff radius.

Data Availability

Force constants, crystal structures and thermodynamic results are available in the GitHub repo for CrystalCumulants.jl: <https://github.com/ejmeitz/CrystalCumulants.jl/tree/main/paper>.

Code Availability

The full workflow, including calculation of the sTDEP IFCs, is available in Python and Julia through the CrystalCumulants.jl repo: <https://github.com/ejmeitz/CrystalCumulants.jl/tree/main>. Documentation can be found at <https://ejmeitz.github.io/CrystalCumulants.jl/dev/>. The cumulant terms are also separately available in the TDEP code in the `anharmonic.free.energy` command: <https://github.com/tdep-developers/tdep>.

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Author Contributions

E.M. implemented the final workflows, derived and implemented the constant correction, collected all data, and wrote the manuscript. A.C. implemented the exact

expressions for the first- and second-cumulant terms and revised the manuscript. A. J. H. M. and G.W. revised the manuscript and supervised research. All authors contributed to theoretical discussions and debugging.

Competing Interests

The authors declare no competing interests.

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