Free energies of crystals computed using Einstein crystal with fixed center of mass and different spring constants

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Free energies of crystals computed using a center of mass constraint require a finite-size correction, as shown in previous work by Polson et al. Their reference system is an Einstein crystal with equal spring constants. In this paper we extend the work of Polson et al. to the case of *different* spring constants. The generalization is convenient for constraining the center of mass in crystals with atoms of different masses and it helps to optimize the free energy calculations. To test the theory we compare the free energies of LiI and NaCl crystals from calculations with *different* spring constants to those computed using equal spring constants. Using these center of mass finite size corrections, we compute the true free energies of these crystals for different system sizes to eliminate the intrinsic finite-size effects. These calculations help demonstrate the size of these finite-size corrections relative to other contributions to the absolute free energy of the crystals.

I. INTRODUCTION

Solid phase free energy computations[1–6] are widely used to predict fluid-solid equilibria,[7–11] solid-solid equilibria[12] and relative stability of polymorphs.[13,14] The Frenkel-Ladd method[3] computes the free energy difference between the solid under consideration and an Einstein crystal, a reference system whose free energy is analytically known. The method uses thermodynamic integration to transform between the Einstein crystal and real solid. To supress a weak divergence of the integrand used in computing the free energy, it is recommended to fix the center of mass (COM) of the system.[3,8,15,16] To compute the absolute free energy of the unconstrained crystal we need to correct for the effect of imposing this constraint in the calculations. The numerical value of the free energy correction per atom (or molecule) tends to zero as the system size tends to infinity, hence it is a finite-size correction. Polson et al.[15] derived an $\mathcal{O}(\ln N/N)$ term in transformation from constrained to unconstrained crystals as a finite-size correction. Their calculation is based on an Einstein crystal with fixed center of mass and *equal* spring constants. Note that an alternate method, the Einstein molecule method,[4,6,17,18] does not require a center of mass constraint or the associated corrections. However, this paper is aimed at completing the theory for the Einstein crystal method.

For crystals comprised of atoms with different atomic masses, different spring constants (in the Einstein crystal approach[3]) can help to maintain the center of mass[8] constraint (if the molecular dynamics package does not have built-in features to achieve the same) by choosing mass-scaled spring constants that equate the angular frequencies. See supplementary material for details. Alternatively, different spring constants can help to optimize the numerical integration to compute the free energy difference by choosing spring constants that reproduce the mean-squared displacement (MSD) of atoms in the real crystal [16] (referred to as MSD-based springs in this article).

In this paper, we extend the finite-size corrections of Polson et al.[15] to the case of *different* spring constants in an Einstein crystal. To test the results we compare the solid free energies of LiI and NaCl crystals from three calculations: i) mass-scaled springs that exert a null force on the system and help constrain the COM without the need of built-in functions to constrain the COM, ii) MSD-based springs that reproduce the mean-squared displacement (MSD) of atoms in the real crystal that help optimize the numerical integration, and iii) calculations with a set of equal springs. A fourth option, not explored here, is to artificially set all masses and spring constants to equal values, respectively, and then analytically recover the free energies for the real masses, e.g. using equations in Polson et al.[15] For the MSD-based and equal spring sets we make use of the built-in center of mass constraint features in the molecular dynamics code LAMMPS[19]. These calculations confirm that the two procedures (employing different and equal springs) are equivalent. They also demonstrate the accuracy gained by the use of spring constants that reproduce the MSD of atoms in the real crystal along with the relative magni-

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tudes of the finite-size corrections and other contributions to the absolute free energy of the crystal.

Note that in addition to the finite size correction due to the COM constraint in the calculations, the free energy of solids presents an intrinsic system size dependence as shown by Vega et al.[4] These finite size corrections need to be computed by repeating the free energy calculations for several system sizes and extrapolating to infinite size. This intrinsic finite size effect is also computed for the LiI and NaCl crystal systems to emphasize the difference between the two different types of finite size effects entering the solid free energy calculations., i.e., the one stemming due to the COM constraint in the Einstein crystal method and the other, the intrinsic finite size effect related to the cutoff in the phonon spectrum introduced by the finite lattice size.[20]

II. THEORY

The free energy (F) of a real crystal (C) is computed using the following path:

$$F_{EC} \rightarrow F_{EC}^{CM} \rightarrow F_C^{CM} \rightarrow F_C$$

where CM indicates a center of mass constraint and EC refers to an Einstein crystal.
Therefore,

$$F_C = F_{EC} + (F_{EC}^{CM} - F_{EC}) + (F_C^{CM} - F_{EC}^{CM}) + (F_C - F_C^{CM}) \tag{1}$$

where the absolute free energy of the Einstein crystal can be obtained from its analytically computable partition function:

$$\beta F_{EC} = -\ln\left(Q_{EC}\right) \tag{2}$$

and the free energy differences are

$$\beta(F_{EC}^{CM} - F_{EC}) = -\ln\left(\frac{Q_{EC}^{CM}}{Q_{EC}}\right) \tag{3a}$$

$$\beta(F_C^{CM} - F_{EC}^{CM}) = \beta \int_{\lambda=0}^{\lambda=1} \left\langle \frac{dU}{d\lambda} \right\rangle_{\lambda}^{CM} d\lambda \tag{3b}$$

$$\beta(F_C - F_C^{CM}) = -\ln\left(\frac{Q_C}{Q_C^{CM}}\right) \tag{3c}$$

In each of these formulas, Q is a partition function, $\beta = (k_B T)^{-1}$, λ is a coupling parameter, U is a λ-dependent potential energy function that interpolates between that of the EC and C systems.

A. Spring Constants and Finite Size Corrections for Einstein Crystals

When all atoms have a common spring constant (k), the Helmholtz free energy of a crystal with N_{mol} molecules composed of a total of N atoms, is given by Polson et al.[15] as:

$$\begin{aligned} \beta F_C = & \sum_{i=1}^{N} \ln\left(\frac{\beta k \Lambda_i^2}{2\pi}\right)^{3/2} \\ & + \beta \int_{\lambda=0}^{\lambda=1} \left\langle \frac{dU}{d\lambda} \right\rangle_{\lambda}^{CM} d\lambda \\ & - \ln\left[\left(\frac{\beta k}{2\pi \sum_{i=1}^{N} \mu_i^2}\right)^{3/2} \left(\frac{V}{N_{mol}}\right)\right] \end{aligned} \tag{4}$$

where $\Lambda_i = (\beta h^2/(2\pi m_i))^{1/2}$, h is Planck's constant, m_i is the mass of atom i, V is the volume of the system, and $\mu_i = m_i / \sum_{i=1}^{N} m_i$.

We have combined terms in the result as given in Polson et al. so that all arguments of logarithms are dimensionless.

Note that the corresponding equations in ref. [8], for atoms with different spring constants cannot be combined to give a dimensionless argument to the logarithm. The error introduced in that study, however, was marginal as the spring constants were similar. Using our revised result shown in equation (10), the free energy in Ref. [8] is revised to -97.44 ± 0.02 $N_{mol} k_B T$ from -97.75 ± 0.02 $N_{mol} k_B T$. Since the estimated errors in the free energy of the fluid phase were larger ($\geq 1\ N_{mol} k_B T$) than the introduced error in the Einstein crystal calculation, the melting point prediction of the study is unaffected, and indeed has been confirmed by independent density of states calculations.[21] In this work we provide a revised version of equation (4) for systems where atoms have different spring constants.

Since the part of the finite-size correction involving spring constants emerges from equation (3a), (see Appendix A), we derive the configurational partition function ratio, Z_{EC}^{CM}/Z_{EC} here for an EC with different spring constants (k_i, $i = 1, 2, ..., N$).

For 1-Dimension (x-direction), the configurational partition function of an Einstein crystal with a COM constraint is:

$$Z_{EC,x}^{CM} = \int dx^N \prod_{i=1}^{N} \exp\left[-\frac{\beta k_i}{2} x_i^2\right] \delta\left(\sum_{i=1}^{N} \mu_i x_i\right) \tag{5}$$

Without loss of generality, we are letting all particles be attached by a spring to a point at the origin. This makes x_i the displacement of atom i in the x-direction from the tether point (origin here).

We make the following variable transformation:

$$\xi_i = k_i^{1/2} x_i \tag{6}$$

with Jacobian determinant

$$J = \left| \prod_{i=1}^{N} k_i^{-1/2} \right| \tag{7}$$

Therefore,

$$\begin{aligned} Z_{EC,x}^{CM} &= \int d\xi^N J \prod_{i=1}^{N} \exp\left[-\frac{\beta}{2}\xi_i^2\right] \delta\left(\sum_{i=1}^{N} \frac{\mu_i}{k_i^{1/2}}\xi_i\right) \\ &= J\left(\frac{\beta}{2\pi\sum_{i=1}^{N}\frac{\mu_i^2}{k_i}}\right)^{1/2} \prod_{i=1}^{N}\left(\frac{2\pi}{\beta}\right)^{1/2} \\ &= \left(\frac{\beta}{2\pi\sum_{i=1}^{N}\frac{\mu_i^2}{k_i}}\right)^{1/2} \prod_{i=1}^{N}\left(\frac{2\pi}{\beta k_i}\right)^{1/2} \\ &= \left(\frac{\beta}{2\pi\sum_{i=1}^{N}\frac{\mu_i^2}{k_i}}\right)^{1/2} Z_{EC,x} \end{aligned} \tag{8}$$

where $Z_{EC,x}$ is the integral in equation (5), but without the center of mass constraint. See supplementary material for additional details. The extension to three dimensions just results in three factors of $(\beta/2\pi\sum_i[\mu_i^2/k_i])^{1/2}$.

$$\frac{Z_{EC}^{CM}}{Z_{EC}} = \left(\frac{\beta}{2\pi\sum_{i=1}^{N}\frac{\mu_i^2}{k_i}}\right)^{3/2} \tag{9}$$

Using equation (9) in place of equation (A.5a) in the derivation shown in Appendix A, we get

$$\begin{aligned} \beta F_C = &\sum_{i=1}^{N} \ln\left(\frac{\beta k_i \Lambda_i^2}{2\pi}\right)^{3/2} \\ &+ \beta\int_{\lambda=0}^{\lambda=1} \left\langle \frac{dU}{d\lambda}\right\rangle_{\lambda}^{CM} d\lambda \\ &- \ln\left[\left(\frac{\beta}{2\pi\sum_{i=1}^{N}\frac{\mu_i^2}{k_i}}\right)^{3/2}\left(\frac{V}{N_{mol}}\right)\right] \end{aligned} \tag{10}$$

for an Einstein crystal system with different spring constants.

Equation (10) gives the free energy of a real crystal computed using an EC system constituting different spring constants. Note that equation (10) is properly dimensionless. Moreover, equation (10) collapses to equation (4) when $k_i = k$, i.e., when all spring constants are equal.

B. Constraining the center of mass

In molecular dynamics (MD) simulations with standard force fields, the center of mass can be fixed by beginning with zero total momentum and not adding external forces. For the Einstein crystal, the springs do exert external forces so additional measures are needed.

A simple way to fix the center of mass in a system with springs begins by making the spring constants proportional to the atom masses, so that all atoms have the same frquency. When all oscillators have frequency ω, the center of mass evolves as

$$\mathbf{x}_{CM}(t) = \omega^{-1}\mathbf{v}_{CM}^{o}\sin(\omega t) + \mathbf{x}_{CM}^{o}\cos(\omega t) \tag{11}$$

where, $\mathbf{v}_{CM}^{o}$ is the initial center of mass velocity, and $\mathbf{x}_{CM}^{o}$ is the initial displacemet of the center of mass from the tether points' (lattice positions') center of mass. See supplementary material for details.

Clearly, we can maintain $\mathbf{x}_{CM} = 0$ by choosing spring constants proportional to the atom masses, so that all atoms have the same frquency and setting initial conditions such that $\mathbf{v}_{CM}^{o} = \mathbf{x}_{CM}^{o} = 0$.

We note that certain MD packages such as LAMMPS do not need to have a net zero external force on the system to constrain the center of mass. This is achieved by thermostating all degrees of freedom except the center of mass and shifting all atom coordinates after every timestep (equal to the drift in center of mass) to recenter the system to the initial value of the center of mass. This recentering does not alter the dynamics of the system or change the relative coordinates of any pair of atoms.

C. Thermodynamic Integration

To compute the free energy difference between the crystal of interest and the Einstein crystal, i.e., $F_C^{CM} - F_{EC}^{CM}$, we use thermodynamic integration (T.I.)[22] with a linear homotopy[23]

$$U(T, V_C; \lambda) = (1-\lambda)U_{EC}(T, V_C) + \lambda U_C(T, V_C) \tag{12}$$

where $U(T, V_C; \lambda)$ is the potential energy function and λ is the coupling parameter. Also, U_{EC} and U_C are the potential energy functions of the Einstein crystal and the crystal of interest (described by the chosen force field), respectively. Therefore

$$\begin{aligned} F_C^{CM} - F_{EC}^{CM} &= \int_{\lambda=0}^{\lambda=1} \left\langle \frac{dU}{d\lambda}\right\rangle_{\lambda}^{CM} d\lambda \\ &= \int_{\lambda=0}^{\lambda=1} \langle U_C - U_{EC}\rangle_{\lambda}^{CM} d\lambda \end{aligned} \tag{13}$$

where, $\langle dU/d\lambda\rangle_{\lambda}^{CM}$ is evaluated by computing an average of $(U_C - U_{EC})$ over configurations in the λ state canonical ensemble. Note, for $0 < \lambda < 1$, equation (11) is still applicable. See supplementary material for details.

III. SIMULATION DETAILS

We model LiI and NaCl using the Joung Cheatham force field (the version optimized for SPC/E).[24] All MD simulations were carried out using LAMMPS.[19]

The NVT simulations for computing the free energies were setup using the interionic distances reported by

Joung et al.[24], of 3.05 Å, and 2.89 Å for LiI and NaCl, respectively. A super cell measuring 36.6 Å × 36.6 Å × 36.6 Å comprising 864 ion pairs was used for LiI, and a super cell measuring 34.68 Å × 34.68 Å × 34.68 Å comprising 864 ion pairs was used for NaCl. This is equivalent to 6 × 6 × 6 unit cells for both crystal systems. To compute the intrinsic finite-size effects, systems comprising 7 × 7 × 7, 8 × 8 × 8, and 9 × 9 × 9 unit cells were used for both crystals.

The Lorentz-Berthelot mixing rules were used for computing the interatomic pair coefficients. We used a time step of 1 fs. Nonbonded interactions were cutoff at 1.6 nm, and 1.1 nm for LiI and NaCl, respectively, with long range electrostatics handled by LAMMPS' Particle-Particle-Particle-Mesh (PPPM) summation [25,26] and a switching function applied for Lennard-Jones interactions between 1.4-1.6 nm, and 0.9-1.1 nm for LiI and NaCl, respectively.

A 25 point Gauss Legendre quadrature method[27] was used to evaluate the integral in equation 13. The NVT simulations were run for a total of 8 ns, of which the initial 2 ns were used for equilibration and then discarded. Data every 1 ps was used to compute the thermodynamic averages for LiI and NaCl systems (the autocorrelation times for $\langle dU/d\lambda \rangle_\lambda$ were approximately in the range of 50 - 400 fs, therefore a 1 ps sampling frequency provides independent samples for each λ state. See supplementary material for autocorrelation time calculations). The spring constants for the reference Einstein crystals are chosen to reproduce the mean square displacement of lithium and sodium ions at 300K. For the different springs case, respective spring constants are scaled to compute the counter ion's spring constant such that k_i/m_i is constant. Table I reports the numerical values used in this study.

TABLE I: Masses (a.m.u) & spring constants ($k_BT/Å^2$)

	LiI		***NaCl***	
	Li^+	**I^-**	**Na^+**	**Cl^-**
mass	6.941	126.904	22.990	35.450
k_i using mass-scaled springs	35.866	655.749	77.543	119.581
k_i using MSD-based springs	35.866	67.121	77.543	85.167
k_i using equal springs	35.866	35.866	77.543	77.543

For the MSD-based and equal springs cases, to constrain the center of mass in LAMMPS, we use the *temp/com* command in conjuction with the langevin thermostat to thermostat all degrees of freedom except the center of mass. We use the *recenter* command to correct for the drift in the center of mass after every time step.

IV. RESULTS AND DISCUSSION

For each crystal system (i.e., LiI and NaCl) we compute free energies using mass-scaled, MSD-based and equal spring constants. Table II shows the dimensionless Helmholtz free energies per ion pair. All components of equation 10 are reported to show the relative magnitudes of corrections. See supplementary material for plots of the T.I. integrands. The free energies should match for the two procedures, i.e., with different and equivalent springs. As seen in Table II the free energies computed using different spring constants are in excellent agreement with the free energies computed using equivalent spring constants, thereby successfully testing the theory. Also, the use of MSD-based spring constants optimizes the calculations as can be seen in the near 24% uncertainty reduction for LiI when compared to the equal spring case. This is because the MSD of the Li and I atoms differ significantly as can be seen by the MSD-based spring constants. In the NaCl calculations, the MSD of the two atoms are similar, leading to marginal accuracy gains on using MSD-based springs. We also compute the free energy of NaCl crystal at 298 K to compare with Aragones et al.[6] Our free energy estimate at 298 K is -311.0340 ± 0.0002 $N_{mol}k_BT$ (using $\Lambda_{Na} = \Lambda_{Cl} = 1Å$), which is in excellent agreement with their result of -311.10 ± 0.1 $N_{mol}k_BT$.

As seen in Figures 1 and 2, the solid free energies of LiI and NaCl demonstrate a significant system size dependence, i.e. the free energy size dependence is greater than the calculation uncertainty. Tables III and IV show the accounting of the COM constraint finite size correction for each system size for LiI and NaCl, respectively.

We use a linear model to capture the intrinsic finite size effect and predict free energy in the thermodynamic limit:[4]

$$\beta f(N_{mol}) = \beta f(N_{mol} \to \infty) + \frac{d_1}{N_{mol}} \tag{14}$$

The value of the slopes (d_1) for LiI and NaCl are -13.1 ± 0.2, and -14.7 ± 0.2, respectively.

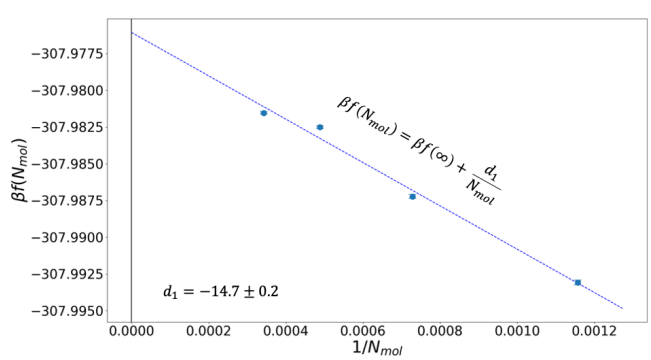

FIG. 1: Intrinsic system-size dependence of LiI crystal's free energy

TABLE II: Absolute dimensionless Helmholtz free energy ($\beta f = \beta F/N_{mol}$) calculation of LiI and NaCl (per ion pair) at 300 K. See supplementary material for details of the column headings shown in this table.

Crystal system	βf_{EC}	$\beta(f_{EC}^{CM} - f_{EC})^*$	$\beta\Delta f_{EC\to C}^{CM}$	$\beta(f_C - f_C^{CM})^*$	βf_C
LiI mass-scaled springs	-0.53908	-0.01990	-307.42991 ± 0.00028	-0.00467	-307.99356 ± 0.00028
LiI MSD-based springs	-3.95800	-0.01603	-304.01438 ± 0.00016	-0.00467	-307.99308 ± 0.00016
LiI equiv. springs	-4.89807	-0.01494	-303.07519 ± 0.00021	-0.00467	-307.99286 ± 0.00021
NaCl mass-scaled springs	-1.81876	-0.01772	-317.07633 ± 0.00015	-0.00449	-318.91719 ± 0.00015
NaCl MSD-based springs	-2.32772	-0.01734	-316.56798 ± 0.00015	-0.00449	-318.91753 ± 0.00015
NaCl equiv. springs	-2.46850	-0.01723	-316.42744 ± 0.00016	-0.00449	-318.91755 ± 0.00016

TABLE III: Absolute dimensionless Helmholtz free energy ($\beta f = \beta F/N_{mol}$) calculation of LiI (per ion pair) at 300 K for varying system size using MSD-based springs. See supplementary material for details of the column headings shown in this table.

N_{mol}	βf_{EC}	$\beta(f_{EC}^{CM} - f_{EC})^*$	$\beta\Delta f_{EC\to C}^{CM}$	$\beta(f_C - f_C^{CM})^*$	βf_C
864	-3.95800	-0.01603	-304.01438 ± 0.00016	-0.00467	-307.99308 ± 0.00016
1372	-3.95800	-0.01060	-304.01569 ± 0.00013	-0.00294	-307.98723 ± 0.00013
2048	-3.95800	-0.00739	-304.01515 ± 0.00010	-0.00197	-307.98251 ± 0.00010
2916	-3.95800	-0.00537	-304.01679 ± 0.00009	-0.00138	-307.98154 ± 0.00009
$N_{mol} \to \infty$	-3.95800	0.00000	-304.01730 ± 0.00021	0.00000	-307.97607 ± 0.00014

TABLE IV: Absolute dimensionless Helmholtz free energy ($\beta f = \beta F/N_{mol}$) calculation of NaCl (per ion pair) at 300 K for varying system size computed using MSD-based springs. See supplementary material for details of the column headings shown in this table.

N_{mol}	βf_{EC}	$\beta(f_{EC}^{CM} - f_{EC})^*$	$\beta\Delta f_{EC\to C}^{CM}$	$\beta(f_C - f_C^{CM})^*$	βf_C
864	-2.32772	-0.01734	-316.56798 ± 0.00015	-0.00449	-318.91753 ± 0.00015
1372	-2.32772	-0.01143	-316.56964 ± 0.00012	-0.00283	-318.91162 ± 0.00012
2048	-2.32772	-0.00795	-316.57104 ± 0.00010	-0.00189	-318.90860 ± 0.00010
2916	-2.32772	-0.00576	-316.57206 ± 0.00008	-0.00133	-318.90687 ± 0.00008
$N_{mol} \to \infty$	-2.32772	0.00000	-316.57449 ± 0.00013	0.00000	-318.90223 ± 0.00013

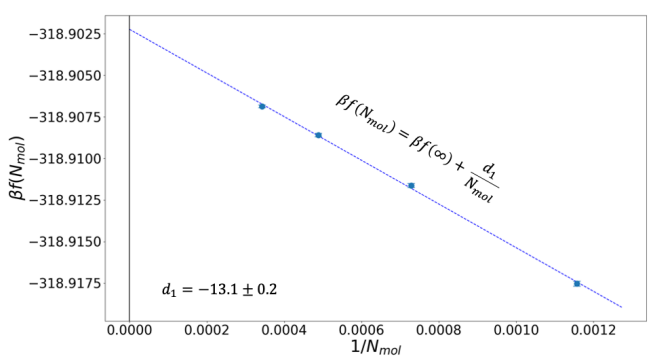

FIG. 2: Intrinsic system-size dependence of NaCl crystal's free energy

V. CONCLUSIONS

In this paper we extend the work of Polson et al.[15] to compute free energies of crystals using an Einstein crystal with fixed center of mass and *different* spring constants. For calculations that make use of different spring constants, our result provides a revised equation to be used in place of equation (3) in ref. [8]. We also provide necessary conditions to help constrain the center of mass in a molecular dynamics simulations (using MD packages with no built-in capabilities to do the same) employing springs to tether atoms. The free energies of LiI and NaCl crystals computed using *different* and equal spring constants are in excellent agreement, thus successfully testing the theory. Our results also demonstrate a reduction in error bars when MSD-based springs are used to optimize the calculations. The significant system size

dependence of the solid free energy after applying the COM-constraint corrections helps demonstrate the relative magnitudes of the intrinsic and COM-constraint finite-size corrections relative to other contributions to the absolute free energy of the crystals.

Appendix A: Revisiting the Finite Size Correction Derivation[15]

1. Computing Q_{EC}^{CM}/Q_{EC}:

For an N atom Einstein crystal system with uniform spring constants (k) and distinguishable particles,

$$Q_{EC} = \frac{1}{h^{3N}} Z_{EC}\ P_{EC} \tag{A.1}$$

where,

$$Z_{EC} = \int d\mathbf{r}^N \prod_{i=1}^{N} \exp\left[-\frac{\beta k}{2}\left\|\mathbf{r}_i\right\|^2\right] = \prod_{i=1}^{N}\left(\frac{2\pi}{\beta k}\right)^{3/2} \tag{A.2a}$$

$$P_{EC} = \int d\mathbf{p}^N \prod_{i=1}^{N} \exp\left[-\frac{\beta}{2m_i}\left\|\mathbf{p}_i\right\|^2\right] = \prod_{i=1}^{N}\left(\frac{2\pi m_i}{\beta}\right)^{3/2} \tag{A.2b}$$

Similarly,

$$Q_{EC}^{CM} = \frac{1}{h^{3(N-1)}} Z_{EC}^{CM}\ P_{EC}^{CM} \tag{A.3}$$

Note that in the above equation we have $h^{3(N-1)}$ because with a hard constraint of a fixed center of mass, the system "lives in" a $6N-6$ dimensional phase space. Equation (A.3) differs from a harmonically restrained system in $6N$ dimensions, in which case we would still have h^{3N}.

Z_{EC}^{CM} and P_{EC}^{CM} are

$$\begin{aligned} Z_{EC}^{CM} &= \int d\mathbf{r}^N \prod_{i=1}^{N} \exp\left[-\frac{\beta k}{2} r_i^2\right] \delta\left(\sum_{i=1}^{N} \mu_i \mathbf{r}_i\right) \\ &= \left(\frac{\beta k}{2\pi \sum_{i=1}^{N} \mu_i^2}\right)^{3/2} \prod_{i=1}^{N}\left(\frac{2\pi}{\beta k}\right)^{3/2} \\ &= \left(\frac{\beta k}{2\pi \sum_{i=1}^{N} \mu_i^2}\right)^{3/2} Z_{EC} \end{aligned} \tag{A.4a}$$

$$\begin{aligned} P_{EC}^{CM} &= \int d\mathbf{p}^N \prod_{i=1}^{N} \exp\left[-\frac{\beta}{2m_i} p_i^2\right] \delta\left(\sum_{i=1}^{N} \mathbf{p}_i\right) \\ &= \left(\frac{\beta}{2\pi M}\right)^{3/2} \prod_{i=1}^{N}\left(\frac{2\pi m_i}{\beta}\right)^{3/2} \\ &= \left(\frac{\beta}{2\pi M}\right)^{3/2} P_{EC} \end{aligned} \tag{A.4b}$$

where $M = \sum_{i=1}^{N} m_i$.
Therefore,

$$\frac{Z_{EC}^{CM}}{Z_{EC}} = \left(\frac{\beta k}{2\pi \sum_{i=1}^{N} \mu_i^2}\right)^{3/2} \tag{A.5a}$$

$$\frac{P_{EC}^{CM}}{P_{EC}} = \left(\frac{\beta}{2\pi M}\right)^{3/2} \tag{A.5b}$$

Now, using (A.1) and (A.3),

$$\begin{aligned} \frac{Q_{EC}^{CM}}{Q_{EC}} &= h^3 \left(\frac{Z_{EC}^{CM}}{Z_{EC}}\right)\left(\frac{P_{EC}^{CM}}{P_{EC}}\right) \\ &= \left(\frac{\beta k}{2\pi \sum_{i=1}^{N} \mu_i^2}\right)^{3/2} \left(\frac{\beta h^2}{2\pi M}\right)^{3/2} \end{aligned} \tag{A.6}$$

2. Computing Q_C/Q_C^{CM}:

$$Q_C = \frac{1}{h^{3N}} Z_C\ P_C \tag{A.7}$$

where:

$$Z_C = \int d\mathbf{r}^N \prod_{i=1}^{N} \exp\left[-\beta U(\mathbf{r}^N)\right] \tag{A.8a}$$

$$P_C = \int d\mathbf{p}^N \prod_{i=1}^{N} \exp\left[-\frac{\beta}{2m_i}\left\|\mathbf{p}_i\right\|^2\right] = \prod_{i=1}^{N}\left(\frac{2\pi m_i}{\beta}\right)^{3/2} \tag{A.8b}$$

now using equation (13) from Polson et al.[15],

$$\begin{aligned} \frac{Z_C}{Z_C^{CM}} &= \frac{\int d\mathbf{r}^N \prod_{i=1}^{N} \exp\left[-\beta U(\mathbf{r}^N)\right]}{\int d\mathbf{r}^N \prod_{i=1}^{N} \exp\left[-\beta U(\mathbf{r}^N)\right] \delta\left(\sum_{i=1}^{N} \mu_i \mathbf{r}_i\right)} \\ &= \frac{1}{\left\langle \delta\left(\sum_{i=1}^{N} \mu_i \mathbf{r}_i\right)\right\rangle} \\ &= \frac{1}{\wp(\mathbf{r}_{CM} = 0)} \\ &= \frac{V}{N_{mol}} \end{aligned} \tag{A.9}$$

Note[15] that $\wp(\mathbf{r}_{CM})$ is the probability distribution function of the center of mass. Since, the probability distribution of the center of mass of the lattice is evenly distributed over a volume equal to that of the Wigner–Seitz cell of the lattice positioned at the center of the volume

over which we carry out the integration in the partition function. It follows for one molecule per Wigner-Seitz cell: $\wp(\mathbf{r}_{CM}=0)=N_{mol}/V$.

Since $P_C = P_{EC}$ we have from equation (A.5b)

$$\frac{P_C}{P_C^{CM}} = \left(\frac{\beta}{2\pi M}\right)^{-3/2} \tag{A.10}$$

Therefore,

$$\begin{aligned}\frac{Q_C}{Q_C^{CM}} &= h^{-3}\left(\frac{Z_C}{Z_C^{CM}}\right)\left(\frac{P_C}{P_C^{CM}}\right)\\ &= \left(\frac{V}{N_{mol}}\right)\left(\frac{\beta h^2}{2\pi M}\right)^{-3/2}\end{aligned} \tag{A.11}$$

3. Free energy of the crystal:

Using equations (A.6) and (A.11), we have

$$\begin{aligned}\beta F_C = &\sum_{i=1}^{N}\ln\left(\frac{\beta k\Lambda_i^2}{2\pi}\right)^{3/2}\\ &-\ln\left[\left(\frac{\beta k}{2\pi\sum_{i=1}^{N}\mu_i^2}\right)^{3/2}\left(\frac{\beta h^2}{2\pi M}\right)^{3/2}\right]\\ &+\beta\int_{\lambda=0}^{\lambda=1}\left\langle\frac{dU}{d\lambda}\right\rangle_\lambda d\lambda\\ &-\ln\left[\left(\frac{V}{N_{mol}}\right)\left(\frac{\beta h^2}{2\pi M}\right)^{-3/2}\right]\end{aligned} \tag{A.12a}$$

$$\begin{aligned}\beta F_C = &\sum_{i=1}^{N}\ln\left(\frac{\beta k\Lambda_i^2}{2\pi}\right)^{3/2}\\ &+\beta\int_{\lambda=0}^{\lambda=1}\left\langle\frac{dU}{d\lambda}\right\rangle_\lambda^{CM} d\lambda\\ &-\ln\left[\left(\frac{\beta k}{2\pi\sum_{i=1}^{N}\mu_i^2}\right)^{3/2}\left(\frac{V}{N_{mol}}\right)\right]\end{aligned} \tag{A.12b}$$

where, $\Lambda_i = (\beta h^2/(2\pi m_i))^{1/2}$

Note that the log terms in equation (A.12b) have been combined to give a dimensionless argument to the logarithms.

SUPPLEMENTARY MATERIAL

See supplementary material for details of the column headings shown in Table II, III, and IV, Mathematica result of $Z_{EC,x}^{CM}$, details to ensure zero net external force due to springs, plots of the T.I. integrands, details of the error propagation and autocorrelation time results.

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DATA AVAILABILITY

The data that supports the findings of this study are available within the article [and its supplementary material]

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