

Free energy of a harmonic crystal

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Here we derive the free energy of a harmonic crystal, which can be used as a reference state with an analytical expression for reversible pathways in molecular dynamics simulations. The harmonic crystal is a set of independent harmonic oscillators, so we assume that if a crystal consists of N harmonic oscillators, the free energy of the crystal can be written out (naively) as

$$F_{HC} = NF_{osc} \quad (1)$$

This is assuming that this is a crystal of a “single” particle type. For different types of particles in the lattice, the expression is modified as

$$F_{HC} = N_1F_{osc1} + N_2F_{osc2} + N_3F_{osc3} + \dots \quad (2)$$

So the primary concern here is to derive the free energy of a single harmonic oscillator. We assume that such an oscillator is described by the classical Hamiltonian.

$$H = \frac{p^2}{2m} + \frac{Kx^2}{2} \quad (3)$$

and that the standard expression for the Helmholtz free energy in the canonical ensemble is applicable.

$$F = -k_B T \ln Q \quad (4)$$

In a 3 dimensional space the partition function is written as

$$Q = \frac{1}{h^3} \int e^{-\beta H} d^3x d^3p \quad (5)$$

where we are substituting x in for the standard canonical variable q for ease of readability, and $\beta = \frac{1}{k_B T}$, as per thermodynamic convention.

The partition function of the harmonic oscillator can then be written out as

$$Q = \frac{1}{h^3} \int_{-\infty}^{\infty} d^3x e^{-\frac{\beta K x^2}{2}} \int_{-\infty}^{\infty} d^3p e^{-\frac{\beta p^2}{2m}} \quad (6)$$

$$\implies Q = \frac{1}{h^3} \left[\int_{-\infty}^{\infty} dx e^{-\frac{\beta K x^2}{2}} \right]^3 \left[\int_{-\infty}^{\infty} dp e^{-\frac{\beta p^2}{2m}} \right]^3 \quad (7)$$

Both momentum and position space integrals are Gaussian integrals of the form

$$I = \int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}} \quad (8)$$

Leading to an expression for the partition function as

$$Q = \frac{1}{h^3} \left(\frac{2\pi}{\beta K} \right)^{3/2} \left(\frac{2\pi m}{\beta} \right)^{3/2} \quad (9)$$

$$= \frac{1}{h^3} \left(\frac{m}{K} \right)^{3/2} \left(\frac{2\pi}{\beta} \right)^3 \quad (10)$$

At this point we find it useful to use the definitions of the angular frequency of the oscillator $\omega = \sqrt{\frac{K}{m}}$ and Planck's reduced constant $\hbar = \frac{h}{2\pi}$, and to resubstitute $\frac{1}{k_B T} = \beta$ into the expression for the partition function, leading to

$$Z = \left(\frac{k_B T}{\hbar \omega} \right)^3 \quad (11)$$

This is substituted into $F = -k_B T \ln Q$ to obtain the final expression of the free energy of a single classical harmonic oscillator in a 3 dimensional space.

$$F_{osc} = 3k_B T \ln \left(\frac{\hbar \omega}{k_B T} \right) \quad (12)$$

Then as mentioned above this expression for the individual oscillator can (naively) be scaled and summed by the number of particle types to obtain the Helmholtz free energy of the harmonic crystal.

However this expression still allows for the simulated crystal to translate back and forth as a whole - these “parts” of phase space must be excluded from the partition function integral. So a center of mass constraint must be included in the computation of the analytical free energy.

Prior work has addressed this problem, and we adapt the seven terms mentioned in equation (3) of Anwar et al's 2003 paper *Calculation of the melting point of NaCl by molecular simulation*, and note that the first four terms they mention are (after much algebra) equivalent to the expression derived above for the free energy of a single harmonic oscillator.

The final three terms in that equation can also be reduced to a form equivalent to the expression found for the free energy of a single harmonic oscillator; it can be considered the free energy of the center of mass oscillating in a direction opposite to the “net” direction of the individual oscillators in order to prevent the crystal translating as a whole.

With the inclusion of the center of mass constraint free energy term F_{COM} , the free energy of the harmonic crystal is rewritten as

$$F_{HC} = N F_{osc} - F_{COM} \quad (13)$$

The normalization factor in the expression below for the center of mass oscillator is the number of “molecular units”, and in general this expression will need to be adjusted as per stoichiometry of the crystal in question. We write out this expression in the non-general form for NaCl.

$$F_{COM} = \frac{3k_B T}{N_{NaCl}} \ln \left(\frac{\hbar \tilde{\omega}}{k_B T} \right) \quad (14)$$

where the center of mass frequency is defined as

$$\tilde{\omega} \equiv \frac{1}{\mu_{Na}\mu_{Cl}} \sqrt{\frac{K_{Na}K_{Cl}}{2\pi M N_{Na} N_{Cl}}} \quad (15)$$

where $M = m_{Na}N_{Na} + m_{Cl}N_{Cl}$ is the total mass of all particles in the simulation box, and $\mu_i = \frac{m_i}{\sum m_i}$ is the fractional mass of each species. Note that both M and μ_i depend on the number of particles being simulated.

There is also a final $\ln N/N$ term in equation (5) of Anwar et al's paper, which is supposed to correct for the finite-size of the center of mass oscillator. However we note that this $\ln N/N$ term as indicated in Table II of that paper only accounts for around 0.37% of the total free energy of the crystal, and when we include it in our calculations we find a similar negligible effect.

It is this author's opinion that regardless of whether or not this $\ln N/N$ term is included in post-hoc analysis of the molecular dynamics simulations, the proper way to account for finite size effects is to run the reversible pathway to the harmonic crystal at multiple system sizes, then empirically fit the observed *Gibbs* free energy of the crystal in question as a function of system size curve to an appropriate functional form to extrapolate to a macroscopic limit.

Example curves (without error bars) for finite-size extrapolation and the resulting $G_{sol}(T)$ curve we observe for Fumi-Tosi NaCl (the template material used to test out this methodology) are included on the following pages of this document.

Although not directly related to the harmonic crystal itself, we note that we that the observed $G_{sol}(T)$ curve for our simulated NaCl increases as a function of temperature, as opposed to the typical pedagogical curves which show a monotonic decrease in the free energy as a function of temperature. Here we feel it pertinent to mention the definition of the thermodynamic potential $G = U + PV - TS$.

Since NaCl is an ionic crystal where the majority of the internal energy U comes from long-range $1/r$ interactions, it is possible that at the larger equilibrium volumes at higher temperatures, there is some sort of cumulative, density-dependent decrease in the magnitude of the internal energy U , which is larger than the increase in the magnitude of the entropy term TS , resulting in an increase in the Gibbs free energy as a function of temperature. This "cumulative, density-dependent" effect on the internal energy U will not be present in other classes of materials not primarily bound together by $1/r$ interactions, such as metals, covalently bonded solids, and molecular crystals.

Note that while this is merely a hypothesis, this is also hinted at in the conclusion of Anwar et al's paper, and the author thinks it may be worth investigating the relevant $U(T)$ and $S(T)$ curves for different classes of materials to confirm.



