

Free-energy calculation

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This text was based on following references [1] [2] [3] [4] [5] and it was written so it matches the computation procedure applied in attached python module.

1 Harmonic approximation to the free-energy

In general sense, the free energy $F(N, V, T)$ is defined as:

$$F(N, V, T) = \frac{1}{\beta} \ln Q(N, V, T) \equiv \frac{1}{\beta} \ln \left(\frac{V^N \int e^{-\beta \mathcal{H}(\mathbf{p}^N, \mathbf{r}^N)} d\mathbf{p}^N d\mathbf{r}^N}{\Lambda^{3N} N!} \right) \quad (1)$$

where $\beta = (k_B T)^{-1}$, $\Lambda = \sqrt{2\pi\hbar^2\beta/m}$ is the thermal de Broigle wavelength. Due to the computational limitations this definition is impractical and can be solved analytically only for simplified system like Debye crystal - with atoms interconnected with harmonic, spring-like force; or Einstein crystal - where independent atoms interacts with lattice by means of harmonic interaction. For the isolated system of N atoms, the harmonic, classical free energy $F_h^c(T)$ at temperature T can be defined as:

$$F_h^c(T) = k_B T \sum_{i=1}^{3N-3} \ln \frac{\hbar\omega_i}{k_B T} \quad (2)$$

here the ω_i denotes phonon frequency of vibrating atoms that can be obtained from lattice dynamics calculations. Eq.(2) can be also presented for when not only the eigenvalues of dynamical matrix is available but also when vibrational Density of States (vDOS) $g(\omega)$ is used:

$$F_h^c(T) = k_B T \int g(\omega) \ln \frac{\hbar\omega}{k_B T} d\omega \quad (3)$$

Similarly, the harmonic free-energy of the Debay crystal can be described within quantum approximation:

$$F_h^q(T) = \sum_{i=1}^{3N-3} \left(\frac{\hbar\omega_i}{2} + k_B T \ln(1 - e^{-\frac{\hbar\omega_i}{k_B T}}) \right) \quad (4)$$

$$F_h^q(T) = \int g(\omega) \left(\frac{\hbar\omega}{2} + k_B T \ln(1 - e^{-\frac{\hbar\omega}{k_B T}}) \right) d\omega \quad (5)$$

In practice, this approximation gives acceptable approximation to the free-energy only for low values of T , for which the system is still quasi-harmonic and the rotational or diffusive degrees of freedom are not active.

2 Thermodynamic integration

For the sake of this document, two paths will be discussed in their general formulation: potential and temperature.

2.1 Potential path

In the potential path (i.e.: harmonic→anharmonic or FF→DFT) we consider molecular system governed by the mixed potential:

$$U_\lambda = \lambda U_A + (1 - \lambda) U_B \quad (6)$$

with $\lambda \in (0, 1)$. Let us consider a free-energy derivative with respect to λ of a system with potential U_λ within a canonical ensemble:

$$\left. \frac{\partial F(\lambda)}{\partial \lambda} \right|_{N,V,T} = -\beta^{-1} \frac{\partial}{\partial \lambda} \ln Q(N, V, T, \lambda) = -\frac{\beta^{-1}}{Q(N, V, T, \lambda)} \frac{\partial Q(N, V, T, \lambda)}{\partial \lambda} \quad (7)$$

using the partition function definition as in Eq.1:

$$\left. \frac{\partial F(\lambda)}{\partial \lambda} \right|_{N,V,T} = \frac{\int \frac{\partial \mathcal{H}(\mathbf{p}^N, \mathbf{r}^N, \lambda)}{\partial \lambda} e^{-\beta \mathcal{H}(\mathbf{p}^N, \mathbf{r}^N, \lambda)} d\mathbf{p}^N d\mathbf{r}^N}{\int e^{-\beta \mathcal{H}(\mathbf{p}^N, \mathbf{r}^N, \lambda)} d\mathbf{p}^N d\mathbf{r}^N} = \left\langle \frac{\partial \mathcal{H}(\mathbf{p}^N, \mathbf{r}^N, \lambda)}{\partial \lambda} \right\rangle_\lambda \quad (8)$$

where $\langle \cdot \rangle_\lambda$ denotes ensemble average of a system governed by the mixed potential U_λ . This leads to the free energy difference:

$$F(1) = F(0) + \int_{\lambda=0}^{\lambda=1} \left\langle \frac{\partial \mathcal{H}(\mathbf{p}^N, \mathbf{r}^N, \lambda)}{\partial \lambda} \right\rangle_\lambda d\lambda \quad (9)$$

where $F(1)$ and $F(0)$ are free-energy values for $\lambda=1$ and $\lambda=0$, respectively. Since only the potential energy depends on λ , Eq.9 can be presented as:

$$F(1) = F(0) + \int_{\lambda=0}^{\lambda=1} \left\langle \frac{\partial U(\mathbf{r}^N, \lambda)}{\partial \lambda} \right\rangle_\lambda d\lambda \quad (10)$$

2.2 Temperature path

In the temperature path, we consider temperature (or β) change of the free-energy by calculating:

$$\frac{\partial \beta F}{\partial \beta} = -\frac{\partial \ln Q}{\partial \beta} = -\frac{1}{Q} \frac{\partial Q}{\partial \beta} = \frac{\int \mathcal{H}(\mathbf{p}^N, \mathbf{r}^N, \beta) e^{-\beta \mathcal{H}(\mathbf{p}^N, \mathbf{r}^N, \beta)} d\mathbf{p}^N d\mathbf{r}^N}{\int e^{-\beta \mathcal{H}(\mathbf{p}^N, \mathbf{r}^N, \beta)} d\mathbf{p}^N d\mathbf{r}^N} \quad (11)$$

which leads to:

$$\frac{\partial \beta F}{\partial \beta} = \left\langle \mathcal{H}(\mathbf{p}^N, \mathbf{r}^N, \beta) \right\rangle_{\beta} \quad (12)$$

where $\langle \dots \rangle_{\beta}$ denotes ensemble average at temperature β . By integrating both side one gets:

$$\int \frac{\partial \beta F}{\partial \beta} d\beta = \beta_2 F_2 - \beta_1 F_1 = \frac{F_2}{k_B T_2} - \frac{F_1}{k_B T_1} = \int \left\langle \mathcal{H}(\mathbf{p}^N, \mathbf{r}^N, \beta) \right\rangle_{\beta} d\beta \quad (13)$$

where F_1 and F_2 are free-energy values at temperature T_1 and T_2 , respectively. This finally leads to:

$$F_2 = \frac{T_2}{T_1} F_1 + k_B T_2 \int_{\beta_1}^{\beta_2} \left\langle \mathcal{H}(\mathbf{p}^N, \mathbf{r}^N, \beta) \right\rangle_{\beta} d\beta \quad (14)$$

3 Anharmonic approximation to the free-energy

Similarly to Eq.12 the anharmonic, classical free-energy can be described as:

$$F_{anh}^c(T_2) = \frac{T_2}{T_1} F_{anh}^c(T_1) + k_B T_2 \int_{\beta_1}^{\beta_2} \langle U \rangle_{V,T} + \langle K \rangle_{V,T} d\beta \quad (15)$$

where $\langle U \rangle_{V,T}$ and $\langle K \rangle_{V,T}$ are potential and kinetic ensemble averaged energies. With the $\beta = \frac{1}{k_B T}$ variable substitution, Eq.15 can be also expressed as:

$$F_{anh}^c(T_2) = \frac{T_2}{T_1} F_{anh}^c(T_1) - T_2 \int_{T_1}^{T_2} \frac{\langle U \rangle_{V,T} + \langle K \rangle_{V,T}}{T^2} dT \quad (16)$$

In order to improve the convergence of Eq.16 one can consider that the ensemble average of kinetic energy in crystal structures can be defined as $\langle K \rangle_{V,T} = \frac{3N-3}{2} k_B T$. Moreover, if the potential was fully harmonic, the $\langle U \rangle_{V,T}$ would also be of the same value. In anharmonic case, the $\langle U \rangle_{V,T}$ can be expressed as:

$$\langle U \rangle_{V,T} = U_{latt} + \frac{3N-3}{2} k_B T + \langle U \rangle_{V,T}^{ah} \quad (17)$$

where U_{latt} is the lattice energy, $\frac{3N-3}{2} k_B T$ is the harmonic potential energy and $\langle U \rangle_{V,T}^{ah}$ is the anharmonic contribution to the total potential energy. After inserting Eq. (17) into Eq.16 and performing integration analytically one gets:

$$\begin{aligned} F_{anh}^c(T_2) = & U_{latt} + \frac{T_2}{T_1} (F_{anh}^c(T_1) - U_{latt}) \\ & - k_B T_1 (3N-3) \ln\left(\frac{T_2}{T_1}\right) - T_2 \int_{T_1}^{T_2} \frac{\langle U_{ah} \rangle_{V,T}}{T^2} dT \end{aligned} \quad (18)$$

Here the $F_{anh}^c(T_1)$ is the initial, low temperature anharmonic free-energy, that can be calculated based on the Eq.10 for which the of the reference crystal free-energy $F(0)$ can be described with harmonic approximation as in Eq.1:

$$F_{anh}^c(T_1) = k_B T_1 \int g(\omega) \ln \frac{\hbar \omega}{k_B T_1} d\omega + \int_{\lambda=0}^{\lambda=1} \left\langle \frac{\partial U^{D \rightarrow A}(\lambda)}{\partial \lambda} \right\rangle_{\lambda} d\lambda \quad (19)$$

with $U^{D \rightarrow A}(\lambda)$ being the potential energy of the model with mixed potential where $\lambda = 0$ is the Debye potential and $\lambda = 1$ is the anharmonic potential. Often, the low temperature anharmonic free energy $F_{anh}^c(T_1)$ can be approximated by the harmonic component exclusively, neglecting the integral in the Eq.19. This gives final equation for the anharmonic, classical free energy:

$$\begin{aligned} F_{anh}^c(T_2) = & U_{latt} + \frac{T_2}{T_1} (k_B T_1 \int g(\omega) \ln \frac{\hbar \omega}{k_B T_1} d\omega - U_{latt}) \\ & - k_B T_1 (3N-3) \ln\left(\frac{T_2}{T_1}\right) - T_2 \int_{T_1}^{T_2} \frac{\langle U_{ah} \rangle_{V,T}}{T^2} dT \end{aligned} \quad (20)$$

Eq.20 is defined with nuclei treated on the classical level of theory. In order to move to the quantum description of nuclei one can perform an approximation in which the harmonic classical part is substituted by the harmonic quantum part:

$$\begin{aligned} F_{anh}^q(T_2) = & U_{latt} + \frac{T_2}{T_1} (k_B T_1 \int g(\omega) \ln \frac{\hbar \omega}{k_B T_1} d\omega - U_{latt}) \\ & - k_B T_1 (3N-3) \ln\left(\frac{T_2}{T_1}\right) - T_2 \int_{T_1}^{T_2} \frac{\langle U_{ah} \rangle_{V,T}}{T^2} dT \\ & - k_B T_2 \int g(\omega) \ln \frac{\hbar \omega}{k_B T_2} d\omega \\ & + \int g(\omega) \left(\frac{\hbar \omega_i}{2} + k_B T \ln(1 - e^{-\frac{\hbar \omega_i}{k_B T}}) \right) d\omega \end{aligned} \quad (21)$$

4 FF-DFT

As calculations presented in the Eq.20 and Eq.21 requires long molecular dynamics trajectories, one can perform them on the classical level of force-field potentials. In order to account for the quantum contributions one can calculate the difference between quantum and classical free-energy as it is presented in Eq.10:

$$\Delta F^{FF \rightarrow DFT} = \int_{\lambda=0}^{\lambda=1} \left\langle \frac{\partial U^{FF \rightarrow DFT}(\lambda)}{\partial \lambda} \right\rangle_{\lambda} d\lambda \quad (22)$$

with $U^{FF \rightarrow DFT}$ being the mixed potential energy where $\lambda = 0$ is the FF potential and $\lambda = 1$ is the DFT one.

If the studied crystal is fairly harmonic at low temperature and the Debye \rightarrow Anharmonic term can be omitted, the full form for the anharmonic, quantum free-energy is:

$$\begin{aligned} F_{anh}^{c,DFT}(T_2) = & U_{latt} + \frac{T_2}{T_1} (k_B T_1 \int g(\omega) \ln \frac{\hbar \omega}{k_B T_1} d\omega - U_{latt}) \\ & - k_B T_1 (3N - 3) \ln \left(\frac{T_2}{T_1} \right) - T_2 \int_{T_1}^{T_2} \frac{\langle U_{ah} \rangle_{V,T}}{T^2} d\beta \\ & + \int_{\lambda=0}^{\lambda=1} \left\langle \frac{\partial U^{FF \rightarrow DFT}(\lambda)}{\partial \lambda} \right\rangle_{\lambda} d\lambda \end{aligned} \quad (23)$$

Similarly to the Eq.21 the quantum approximation to the Eq.23 can be obtained by substituting the harmonic classical part with the harmonic quantum. However, in this case, the lattice dynamics calculations has to be performed on the DFT level. The final expression for the DFT anharmonic quantum free energy is given by:

$$\begin{aligned} F_{anh}^{c,DFT}(T_2) = & U_{latt} + \frac{T_2}{T_1} (k_B T_1 \int g(\omega) \ln \frac{\hbar \omega}{k_B T_1} d\omega - U_{latt}) \\ & - k_B T_1 (3N - 3) \ln \left(\frac{T_2}{T_1} \right) - T_2 \int_{T_1}^{T_2} \frac{\langle U_{ah} \rangle_{V,T}}{T^2} d\beta \\ & + \int_{\lambda=0}^{\lambda=1} \left\langle \frac{\partial U^{FF \rightarrow DFT}(\lambda)}{\partial \lambda} \right\rangle_{\lambda} d\lambda \\ & - k_B T_2 \int g(\omega) \ln \frac{\hbar \omega}{k_B T_2} d\omega \\ & + \int g(\omega) \left(\frac{\hbar \omega_i}{2} + k_B T \ln(1 - e^{-\frac{\hbar \omega_i}{k_B T}}) \right) d\omega \end{aligned} \quad (24)$$

5 NVT→NPT

In order to evaluate the Helmholtz free-energy at isobaric-isothermal ensemble one can extend previously discussed formulations for isohoric-isothermal ensemble by calculating the free-energy difference of NVT→NPT transition:

$$\Delta F^{NVT \rightarrow NPT} = k_B T_2 \ln \rho(V|P, T) \quad (25)$$

where $\rho(V|P, T)$ is the normalized probability of observing the system with volume V under the condition of given P and T . This probability is defined as:

$$\rho(V|P, T) = \frac{e^{-\frac{PV + A(V, T)}{k_B T}}}{\int e^{-\frac{PV + A(V, T)}{k_B T}} dV} \quad (26)$$

References

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