# **Thermodynamic integration method**

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The aim of thermodynamic integration is to compute the difference in a thermodynamic property (usually the free energy) of the system between some reference state and the state of interest. To measure the free energy change from initial to final state, thermodynamic parameters characterizing the system are changed infinitely slowly so that at each stage along the path the system is in equilibrium. This ensures that the path is reversible, i.e., the same path can be traversed in the opposite direction. In an experimental set-up, we are limited to a few thermodynamic variables such as volume, pressure, temperature in order to control the path. In a molecular simulation experiment, however, in addition to thermodynamic parameters, one can also change the interaction potential of the system and introduce suitable external potentials, making it possible to have a large variety of reversible paths and reference states [1].

In many simulation experiments, one measures the work required to change a single parameter (say  $\lambda$ ) that characterizes the path. If the path is reversible, work measured is equal to change in the appropriate free energy. This is seen from the following derivation [2]:



Figure 1. The system A is in contact with bath B. Due to exchange of heat and volume, the system A is maintained at same temperature and pressure as it undergoes a process by means of reversible work source.

Consider a system held at constant temperature T and pressure P as shown in the figure. Applying first law, reversible work done on the composite system is given by

$$W^{\text{REV}} = \Delta U_{\text{T}}$$
$$= \Delta U + \Delta U$$

where  $\Delta U$ ,  $\Delta U_B$ , and  $\Delta U_T$  are the changes in the internal energies of the system (A), bath (B), and the composite system (A+B), respectively. Since the system can exchange heat and volume with the bath:  $\Delta U_B = T\Delta S_B - P\Delta V_B$ 

But the system is isolated and the process is reversible, therefore according to 2<sup>nd</sup> law of  $\Delta S_{T} = \Delta S + \Delta S_{B} = 0$ thermodynamics :

Also.

 $\Delta V_{\rm T} = \Delta V + \Delta V_{\rm B} = 0$ Combining the above equations, we get

 $W^{REV} = \Lambda U - T\Lambda S + P \Lambda V$ 

 $= \Delta G$  (Change in Gibbs free energy)

Similarly, one can show that for a system held at constant temperature,  $W^{REV} = \Delta F$ (Change in Helmholtz free energy).

#### First order transitions and hysteresis:

The main requirement of thermodynamic integration is that the path should be reversible. i.e., it must be free from any hysteresis. Hysteresis usually occurs if one encounters a first order phase transition along the path. For example, if the density of the liquid phase is continuously reduced at constant temperature (see Fig. 2) the liquid phase becomes metastable with respect to vapor phase and at a certain density the liquid phase suddenly changes to vapor phase. (The path is shown qualitatively by line LV in Fig. 3). This leads to a discontinuous change in the derivative of free energy as shown in Fig.2. For the reverse path, as we increase the density of vapor phase beyond coexistence density, the vapor phase is suddenly converted into liquid phase again leading to discontinuity in the derivative of free energy. The presence of hysteresis indicates that the path is not reversible and hence free energy change cannot be calculated accurately.



Figure 2. The thermodynamic integration path involving first-order phase transition.



Figure 3. The typical phase diagram of a single-component system in temperature Tdensity  $\rho$  plane.

Therefore, as a general rule, any first order phase transition along the integration path must be avoided. This is the most important consideration in thermodynamic integration and hence a qualitative knowledge of underlying phase diagram helps in designing the reversible path. In case of non-physical paths, it is often helpful to choose a reference state such that its structure and energy is as close as possible to the final state of interest [2], so as to minimize the hystereis.

#### Phase diagram calculation using TDI method:

The conditions of equilibrium for coexistence of two phases of a single component system are given by : (1)  $T^{I}=T^{II}$  (2)  $P^{I} = P^{II}$  and (3)  $\mu^{I}=\mu^{II}$ . The difference in chemical potentials  $\Delta\mu=(\mu^{II}-\mu^{I})$  at a given temperature T and pressure P is related to free energy difference between the two phases by the following relations:

$$\Delta \mu = \frac{\Delta G}{N} = \frac{\Delta F + \Delta (PV)}{N}$$

where  $\Delta F$  is the Helmholtz free energy difference and  $\Delta G$  is the Gibbs free energy difference between the two phases, V is the volume and N is the number of particles.

In order to compute phase diagram, one needs chemical potentials of the bulk phases at given temperature and pressure. The chemical potentials are obtained by computing the free energy of these bulk phases with respect to suitable references states. In the following, we describe common methods to compute free energies of bulk phases.

### Liquid phase free energy :

When the gas phase of a given substance is sufficiently rarefied, it approaches ideal gas behavior and this state can then be used as a reference state. However, one cannot directly reduce the density of the liquid phase to gas-like densities due to first order transition. In order to avoid the phase transition, the integration is done in two stages. In the first stage, the temperature of the liquid is increased till it becomes supercritical. This is shown in figure by line L-S. The change in free energy in this process is given as:

$$\Delta(\beta F) = \int_{L}^{S} d\beta U(\beta(V, N))$$

where  $\beta=1/kT$  is the inverse temperature, k is the Boltzmann constant, and U is the internal energy of the liquid at given temperature T, volume V and number of particles N. The integrand in above equation, i.e., U can be computed by simulation at number of coexistence points along the path.

$$\beta(\Delta F)_{s} = \int_{D}^{S} d\rho \left(\frac{P - \rho kT}{\rho^{2}}\right)$$

where,

$$\beta(\Delta F)_s = F_s - F^I$$

Here,  $F^{I}$  is the Helmholtz free energy for ideal gas with the same temperature and density as the supercritical state S. The term  $\rho kT$  in above equation represents the ideal gas pressure. Note that  $\beta(\Delta F)_{D}=0$ , since at point D the gas phase behaves as ideal gas. By computing the integrands in the above equations by canonical-ensemble simulations, we can calculate the liquid free energy.

#### Solid phase free energy:

Unlike the liquid phase, the solid phase cannot be connected to ideal gas state by a reversible path. Thus, a non-physical path must be constructed to a reference phase whose free energy can be computed analytically. The most common method used is called Einstein crystal method [2,3] which we describe below:

In an Einstein crystal (see Fig. 4), particles are attached by harmonic springs to their respective lattice sites. The interaction potential is given by [3],

$$\varphi_{\rm R} = N\varphi_0 + \frac{K}{2}\sum_{i=1}^{\rm N} (\vec{r}_i - \vec{R}_i)^2$$

Here,  $\phi_0$  is the static lattice energy of the Einstein crystal phase, and K is the harmonic spring constant. Both these parameters are chosen so that the properties of Einstein crystal phase are similar to the actual crystal phase. The free energy of Einstein crystal F<sub>E</sub> can be computed analytically and is given by the following equation [3]:



Figure 4. The path from crystal phase of interest to the Einstein crystal phase. In Einstein crystal, the springs represent the (external) harmonic potential.between the particle and lattice site.

$$\beta F_{\rm E} = 3 \,{\rm Nln} \left( \frac{\beta h \sqrt{K}}{2\pi} \right) + \beta N \varphi_0$$

where h is the Planck constant. The free energy of a solid phase is obtained by connecting it to Einstein crystal phase through a non-physical path defined by the following equation:

$$\varphi(\lambda) = \lambda \varphi_{\rm S} + (1 - \lambda) \varphi_{\rm E}$$

Here  $\phi_S$  is the intermolecular potential function of the solid phase of interest and  $\phi_E$  is that of the Einstein crystal whose free energy is exactly known.

The free energy difference is computed by:

$$\beta(\mathbf{F} - \mathbf{F}_{\mathrm{E}}) = \int_{0}^{1} d\lambda \left(\frac{\partial \mathbf{F}}{\partial \lambda}\right) = \int_{0}^{1} d\lambda \left\langle\frac{\partial \varphi}{\partial \lambda}\right\rangle$$

The integrand on right hand side above equation is computed by canonical ensemble simulation as a function of  $\lambda$  values. Then, the integral is evaluated by numerical integration using, for example, a Gaussian quadrature scheme. By computing the value of  $F_E$ , one can then obtain free energy F of solid phase. This method has been applied to phase diagram calculations of several molecular systems including Nitrogen, Helium [2] and water [4].

There are other methods to compute the free energy of solids such as Single occupancy cell (SOC) method and Harmonic crystal method [2]. In the SOC method, the crystal is expanded to gas-like densities while imposing the single occupancy constraint to prevent melting and thus avoiding a first-order transition along the path. In the single-occupancy constraint, each particle is constrained to a volume equal to that of the Weigner-Seitz cell around its lattice point. The free energy of the constrained solid in the dilute gas limit can be computed analytically. In the harmonic crystal method, the crystal is cooled to

very low temperatures, where it effectively behaves as a harmonic crystal. The free energy of low temperature harmonic crystal can be computed analytically.

### Direct computation of crystal-melt free energy difference:

The methods that we described above entail computation of liquid and crystal free energies *separately* by connecting these phases to suitable reference states via reversible paths. However, for phase diagram calculation, we only need the *difference* in free energies between crystal and liquid phases and not their absolute free energies. Thus it will be desirable to have a method that directly calculates the free energy difference by connecting the two phases by reversible path. Such a method was first proposed by Grochola [5]. In this method, one directly connects liquid and crystal phases by a reversible path. The integrand is evaluated by performing canonical ensemble simulations along the path and subsequent numerical integration yields directly the Helmholtz free energy difference  $\Delta F = (F_C - F_L)$  between liquid and crystal phases. Based on the computed  $\Delta F$ , one can calculate the crystal-melt coexistence point. This method has an advantage over the previously discussed methods in that analytical expression for the free energy of a reference state is not required and this gives more flexibility in terms of designing the thermodynamic integration path. This method was later adopted to isothermal-isobaric (NPT) ensemble to yield directly  $\Delta G$ , i.e., Gibbs free energy difference between liquid and crystal phases [6]. In the following, we describe this NPT version of the method.

The reversible path connecting liquid and crystal phases consists of 3 stages (see Fig. 5). In the first stage, the liquid phase is converted into high density gas phase by reducing the strength of the interaction according to following equation

$$\varphi_1 = (1 - \eta \lambda_1) \varphi$$

where  $\eta$  is a parameter that decides the extent to which interaction strength is reduced. The corresponding change in free energy for the first stage is obtained by numerical integration of the following equation:

$$\Delta G_1 = \int_0^1 d\lambda_1 \frac{\partial G}{\partial \lambda_1} = \int_0^1 d\lambda_1 < -\eta \varphi >$$

where <...> represents isothermal isobaric ensemble average which is computed by NPT simulations A constraint on maximum possible volume is imposed (as depicted by the stops in the figure), while performing NPT simulations along the path. In the absence of this constraint, the volume of the system would expand to gas like densities at the end of the first stage leading to significant hysteresis in the second stage. In the second stage, external potential consisting of Gaussian potential wells at the crystal lattice points is introduced linearly while maintaining the reduced strength of the interaction potential between the molecules.

The interaction potential for the second stage is given by

$$\varphi_2(\lambda_2) = (1 - \eta)\varphi + \lambda_2\varphi_E$$

Here,  $\phi_E$  is the Gaussian external potential. The change in Gibbs free energy for the second stage is given by

$$\Delta G_2 = \int_0^1 d\lambda_2 < \varphi_E >$$

In the third stage, the strength of the intermolecular potential is restored while the Gaussian external potential is linearly reduced to zero according to the following equation:

$$\varphi_3(\lambda_3) = (1 - \eta + \lambda_3 \eta)\varphi + (1 - \lambda_3)\varphi_E$$

The change in Gibbs free energy for the third stage is given by

$$\Delta G_3 = \int_0^1 d\lambda_3 < \eta \varphi - \varphi_E >$$

Finally, the Gibbs free energy difference between crystal and melt phases is obtained by adding contribution from the three stages, i.e.,  $\Delta G = \Delta G_1 + \Delta G_2 + \Delta G_3$ .

The method has been extended to binary mixtures [7] and also to sublimation temperature computation [8]. This method (in canonical ensemble formulation) has been applied to compute melting temperature of molecular systems such as Sodium chloride [9], trizole and Benzene [10].



Figure 5. The reversible path from liquid to crystal phase. The stops represent the maximum volume constraint. The grid represents external potential in the form of Gaussian wells located at the lattice points.

## Cleaving wall method to compute crystal-melt interfacial energy $(\gamma)$ :

Crystal-melt interfacial energy ( $\gamma$ ) plays an important role in the process of crystallization from the melt. Particularly, the morphology of the crystal and the rate of crystallization depend on  $\gamma$ . However, experimental determination of this quantity is difficult and hence simulations can play a crucial role in predicting the value of  $\gamma$ . Thermodynamically,  $\gamma$  is defined as the excess Helmholtz free energy associated with the interface:

$$\gamma = F_{\rm CL} - F_{\rm C} - F_{\rm I}$$

where  $F_{CL}$  is the Helmholtz free energy of the combined crystal-melt system with an interface,  $F_C$  is the free energy of bulk crystal phase, and  $F_L$  is that of the bulk liquid phase.

In recent years, cleaving wall method [11] has been developed as a general molecular simulation method for computing  $\gamma$ . In this technique, the crystal and melt phases are combined reversibly starting from separated bulk phases. In the first two stages, the cleaving walls are brought near to the bulk liquid and crystal phases under periodic boundary conditions. The purpose of this step is to prevent the particles from crossing the sides of the simulation box. In the third stage, the periodic boundary conditions in the z-directions are rearranged so as to reversibly combine the cleaved liquid and crystal phases. In the final stage, walls are removed and one gets the desired crystal-melt interface. The reversible work done per unit area along the four stage path yields the crystal-melt interfacial energy. For the first, second, and fourth stages, the work done on the system is given by:

$$W_{1,2,4}^{\text{REV}} = \int_{zi}^{zf} dz \frac{\partial F}{\partial z}$$

Here,  $(\partial F/\partial z)$  is the derivative of the Helmholtz free energy with respect to the distance z of the wall from the cleaving plane and it measures the force exerted on the system. The limits on the integrand,  $z_i$  and  $z_f$  represent the initial and final positions of the walls. The work done in the third stage is given by,

$$W_{3}^{\text{REV}} = \int_{0}^{1} d\lambda \frac{\partial F}{\partial \lambda}$$

where  $\lambda$  is a parameter controlling the rearrangement of the boundary conditions in the third stage. The crystal melt interfacial energy is equal to the total reversible work for the four stages per unit area of the interface created. The method is sufficiently precise and enables one to compute the dependence of  $\gamma$  on crystal orientation. The method has been applied to Lennard-Jones potential [11], Stillinger-Weber potential of silicon [12] and TIP4P potential of water molecules [13].

# Gibbs-Duhem integration method:

The methods described so far require many simulations along the reversible path to compute free energy difference between bulk phases from which a single coexistence point can be obtained. Hence this procedure is highly computationally intensive, if one wants to calculate the entire phase diagram. In 1993, Kofke [14] invented an efficient and general method to trace out the entire coexistence curve starting from an initial (known) coexistence point by thermodynamic integration. In this method, one performs numerical integration of the clapeyron equation, which for a single component system takes the following form [1,14]:

$$\frac{\mathrm{dP}}{\mathrm{d\beta}} = -\frac{\Delta h}{\beta \Delta v}$$

The derivative on the left hand side of the above equation is the rate of change of pressure P with respect to inverse temperature  $\beta = 1/kT$  along the coexistence line of the bulk phases 1 and 2. The terms  $\Delta h = h_2 \cdot h_1$  and  $\Delta v = v_2 \cdot v_1$  are the differences between

specific enthalpies and specific volumes of the two phases, respectively. The right hand side of the above equation is evaluated by performing isothermal isobaric simulations for the two phases. Then, the above first order differential equations is integrated by means of standard predictor-corrector method starting from an initially known coexistence point  $(\beta_0, P_0)$ . The method can be extended to binary system [15] by integrating the generalized Clapeyron equation applicable for a mixture. The advantage of Gibbs Duhem integration method is that, one needs to perform only a few simulations (about 2 simulations for each phase) for obtaining a single coexistence point. Thus the method is highly efficient compared to traditional TDI methods. Another advantage of GDI method is that it does not require parameterization of interaction potential or introduction of external potentials and is relatively simpler to implement than TDI method. However, these is a possibility of systematic drift from the true coexistence line as the integration of Clapeyron equation proceeds, specially if the integration step size in the predictorcorrector algorithm is not taken to be sufficiently small. Hence it is desirable to countercheck the accuracy of the method by obtaining two or more coexistence points independently by TDI method. Thus the combination of TDI and GDI methods offers a powerful tool for accurate and efficient computation of entire coexistence line. GDI method is very general and has been applied to numerous phase diagram calculations [2].

### Summary:

In this lecture, we have discussed various common thermodynamic integration (TDI) methods for phase diagram and interfacial free energy computation. TDI methods gives very accurate estimates of these properties, provided that there is no hysteresis along the path. Molecular simulations imparts great flexibility and versatility to thermodynamic integration due to possibility of employing non-physical paths. Since one needs to simulate only the equilibrium states along the path, both Monte Carlo and Molecular Dynamics simulations can be used. In case of physical paths, a qualitative knowledge of phase diagram is helpful in designing a reversible path. If one wants to compute free energy of a condensed (liquid or crystal) phase by a non-physical path, phase diagram of the intermediate states is not generally known. For such paths, hysteresis is minimized by choosing a reference state which is very similar in structure (as determined, for example, by radial distribution functions) and energy to the desired condensed phase. With the discovery of highly efficient methods and increase of computing power, the utility of TDI methods is bound to increase.

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