

I. TEMPERATURE AND PRESSURE ESTIMATORS

From the classical virial theorem

$$\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = kT \delta_{ij}$$

we arrived at the equipartition theorem:

$$\left\langle \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i} \right\rangle = \frac{3}{2} N kT$$

where $\mathbf{p}_1, \dots, \mathbf{p}_N$ are the N Cartesian momenta of the N particles in a system. This says that the microscopic function of the N momenta that corresponds to the temperature, a macroscopic observable of the system, is given by

$$K(\mathbf{p}_1, \dots, \mathbf{p}_N) = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i}$$

The ensemble average of K can be related directly to the temperature

$$T = \frac{2}{3Nk} \langle K(\mathbf{p}_1, \dots, \mathbf{p}_N) \rangle = \frac{2}{3nR} \langle K(\mathbf{p}_1, \dots, \mathbf{p}_3) \rangle$$

$K(\mathbf{p}_1, \dots, \mathbf{p}_N)$ is known as an *estimator* (a term taken over from the Monte Carlo literature) for the temperature. An estimator is some function of the phase space coordinates, i.e., a function of microscopic states, whose ensemble average gives rise to a physical observable.

An estimator for the pressure can be derived as well, starting from the basic thermodynamic relation:

$$P = - \left(\frac{\partial A}{\partial V} \right)_{N,T} = kT \left(\frac{\partial \ln Q(N, V, T)}{\partial V} \right)_{N,T}$$

with

$$Q(N, V, T) = C_N \int dx e^{-\beta H(x)} = C_N \int d^N \mathbf{p} \int_V d^N \mathbf{r} e^{-\beta H(\mathbf{p}, \mathbf{r})}$$

The volume dependence of the partition function is contained in the limits of integration, since the range of integration for the coordinates is determined by the size of the physical container. For example, if the system is confined within a cubic box of volume $V = L^3$, with L the length of a side, then the range of each q integration will be from 0 to L . If a change of variables is made to $s_i = q_i/L$, then the range of each s integration will be from 0 to 1. The coordinates s_i are known as scaled coordinates. For containers of a more general shape, a more general transformation is

$$\mathbf{s}_i = V^{-1/3} \mathbf{r}_i$$

In order to preserve the phase space volume element, however, we need to ensure that the transformation is a canonical one. Thus, the corresponding momentum transformation is

$$\pi_i = V^{1/3} \mathbf{p}_i$$

With this coordinate/momentum transformation, the phase space volume element transforms as

$$d^N \mathbf{p} d^N \mathbf{r} = d^N \pi d^N \mathbf{s}$$

Thus, the volume element remains the same as required. With this transformation, the Hamiltonian becomes

$$H = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i} + U(\mathbf{r}_1, \dots, \mathbf{r}_N) = \sum_{i=1}^N \frac{V^{-2/3} \pi_i^2}{2m_i} + U(V^{1/3} \mathbf{s}_1, \dots, V^{1/3} \mathbf{s}_N)$$

and the canonical partition function becomes

$$Q(N, V, T) = C_N \int d^N \pi \int d^N \mathbf{s} \exp \left\{ -\beta \left[\sum_{i=1}^N \frac{V^{-2/3} \pi_i^2}{2m_i} + U(V^{1/3} \mathbf{s}_1, \dots, V^{1/3} \mathbf{s}_N) \right] \right\}$$

Thus, the pressure can now be calculated by explicit differentiation with respect to the volume, V :

$$\begin{aligned} P &= kT \frac{1}{Q} \frac{\partial Q}{\partial V} \\ &= \frac{kT}{Q} C_N \int d^N \pi \int d^N \mathbf{s} \left[\frac{2}{3} \beta V^{-5/3} \sum_{i=1}^N \frac{\pi_i^2}{2m_i} - \frac{\beta}{3} V^{-2/3} \sum_{i=1}^N \mathbf{s}_i \cdot \frac{\partial U}{\partial (V^{1/3} \mathbf{s}_i)} \right] e^{-\beta H} \\ &= \frac{kT}{Q} C_N \int d^N \mathbf{p} \int d^N \mathbf{r} \left[\frac{\beta}{3V} \sum_{i=1}^N \frac{\mathbf{p}_i^2}{m_i} - \frac{\beta}{3V} \sum_{i=1}^N \mathbf{r}_i \cdot \frac{\partial U}{\partial \mathbf{r}_i} \right] e^{-\beta H(\mathbf{p}, \mathbf{r})} \\ &= \frac{1}{3V} \left\langle \sum_{i=1}^N \left(\frac{\mathbf{p}_i^2}{m_i} + \mathbf{r}_i \cdot \mathbf{F}_i \right) \right\rangle \\ &= \left\langle -\frac{\partial H}{\partial V} \right\rangle \end{aligned}$$

Thus, the pressure estimator is

$$\Pi(\mathbf{p}_1, \dots, \mathbf{p}_N, \mathbf{r}_1, \dots, \mathbf{r}_N) = \Pi(\mathbf{x}) = \frac{1}{3V} \sum_{i=1}^N \left[\frac{\mathbf{p}_i^2}{2m_i} + \mathbf{r}_i \cdot \mathbf{F}_i(\mathbf{r}) \right]$$

and the pressure is given by

$$P = \langle \Pi(\mathbf{x}) \rangle$$

For periodic systems, such as solids and currently used models of liquids, an absolute Cartesian coordinate q_i is ill-defined. Thus, the virial part of the pressure estimator $\sum_i q_i F_i$ must be rewritten in a form appropriate for periodic systems. This can be done by recognizing that the force F_i is obtained as a sum of contributions F_{ij} , which is the force on particle i due to particle j . Then, the classical virial becomes

$$\begin{aligned} \sum_{i=1}^N \mathbf{r}_i \cdot \mathbf{F}_i &= \sum_{i=1}^N \mathbf{r}_i \cdot \sum_{j \neq i} \mathbf{F}_{ij} \\ &= \frac{1}{2} \left[\sum_i \mathbf{r}_i \sum_{j \neq i} \cdot F_{ij} + \sum_j \mathbf{r}_j \cdot \sum_{i \neq j} \mathbf{F}_{ji} \right] \\ &= \frac{1}{2} \left[\sum_i \mathbf{r}_i \cdot \sum_{j \neq i} \mathbf{F}_{ij} - \sum_j \mathbf{r}_j \cdot \sum_{i \neq j} \mathbf{F}_{ij} \right] \\ &= \frac{1}{2} \sum_{i,j, i \neq j} (\mathbf{r}_i - \mathbf{r}_j) \cdot \mathbf{F}_{ij} = \frac{1}{2} \sum_{i,j, i \neq j} \mathbf{r}_{ij} \cdot \mathbf{F}_{ij} \end{aligned}$$

where \mathbf{r}_{ij} is now a relative coordinate. \mathbf{r}_{ij} must be computed consistent with periodic boundary conditions, i.e., the relative coordinate is defined with respect to the closest periodic image of particle j with respect to particle i . This gives rise to surface contributions, which lead to a nonzero pressure, as expected.

II. ENERGY FLUCTUATIONS IN THE CANONICAL ENSEMBLE

In the canonical ensemble, the total energy is not conserved. ($H(\mathbf{x}) \neq \text{const}$). What are the fluctuations in the energy? The energy fluctuations are given by the root mean square deviation of the Hamiltonian from its average $\langle H \rangle$:

$$\Delta E = \sqrt{\langle (H - \langle H \rangle)^2 \rangle} = \sqrt{\langle H^2 \rangle - \langle H \rangle^2}$$

$$\langle H \rangle = -\frac{\partial}{\partial \beta} \ln Q(N, V, T)$$

$$\begin{aligned} \langle H^2 \rangle &= \frac{1}{Q} C_N \int d\mathbf{x} H^2(\mathbf{x}) e^{-\beta H(\mathbf{x})} \\ &= \frac{1}{Q} C_N \int d\mathbf{x} \frac{\partial^2}{\partial \beta^2} e^{-\beta H(\mathbf{x})} \\ &= \frac{1}{Q} \frac{\partial^2}{\partial \beta^2} Q \\ &= \frac{\partial^2}{\partial \beta^2} \ln Q + \frac{1}{Q^2} \left(\frac{\partial Q}{\partial \beta} \right)^2 \\ &= \frac{\partial^2}{\partial \beta^2} \ln Q + \left[\frac{1}{Q} \frac{\partial Q}{\partial \beta} \right]^2 \\ &= \frac{\partial^2}{\partial \beta^2} \ln Q + \left[\frac{\partial}{\partial \beta} \ln Q \right]^2 \end{aligned}$$

Therefore

$$\langle H^2 \rangle - \langle H \rangle^2 = \frac{\partial^2}{\partial \beta^2} \ln Q$$

But

$$\frac{\partial^2}{\partial \beta^2} \ln Q = kT^2 C_V$$

Thus,

$$\Delta E = \sqrt{kT^2 C_V}$$

Therefore, the relative energy fluctuation $\Delta E/E$ is given by

$$\frac{\Delta E}{E} = \frac{\sqrt{kT^2 C_V}}{E}$$

Now consider what happens when the system is taken to be very large. In fact, we will define a formal limit called the *thermodynamic limit*, in which $N \rightarrow \infty$ and $V \rightarrow \infty$ such that N/V remains constant.

Since C_V and E are both extensive variables, $C_V \sim N$ and $E \sim N$,

$$\frac{\Delta E}{E} \sim \frac{1}{\sqrt{N}} \rightarrow 0 \quad \text{as } N \rightarrow \infty$$

But $\Delta E/E$ would be exactly 0 in the microcanonical ensemble. Thus, in the thermodynamic limit, the canonical and microcanonical ensembles are equivalent, since the energy fluctuations become vanishingly small.

III. ISOTHERMAL-ISOBARIC ENSEMBLE

A. Basic Thermodynamics

The Helmholtz free energy $A(N, V, T)$ is a natural function of N , V and T . The isothermal-isobaric ensemble is generated by transforming the volume V in favor of the pressure P so that the natural variables are N , P and T (which are conditions under which many experiments are performed – “standard temperature and pressure,” for example).

Performing a Legendre transformation of the Helmholtz free energy

$$\tilde{A}(N, P, T) = A(N, V(P), T) - V(P) \frac{\partial A}{\partial V}$$

But

$$\frac{\partial A}{\partial V} = -P$$

Thus,

$$\tilde{A}(N, P, T) = A(N, V(P), T) + PV \equiv G(N, P, T)$$

where $G(N, P, T)$ is the Gibbs free energy.

The differential of G is

$$dG = \left(\frac{\partial G}{\partial P} \right)_{N, T} dP + \left(\frac{\partial G}{\partial T} \right)_{N, P} dT + \left(\frac{\partial G}{\partial N} \right)_{P, T} dN$$

But from $G = A + PV$, we have

$$dG = dA + PdV + VdP$$

but $dA = -SdT - PdV + \mu dN$, thus

$$dG = -SdT + VdP + \mu dN$$

Equating the two expressions for dG , we see that

$$\begin{aligned} V &= \left(\frac{\partial G}{\partial P} \right)_{N, T} \\ S &= - \left(\frac{\partial G}{\partial T} \right)_{N, P} \\ \mu &= \left(\frac{\partial G}{\partial N} \right)_{P, T} \end{aligned}$$

B. The partition function and relation to thermodynamics

In principle, we should derive the isothermal-isobaric partition function by coupling our system to an infinite thermal reservoir as was done for the canonical ensemble and also subject the system to the action of a movable piston under the influence of an external pressure P . In this case, both the temperature of the system and its pressure will be controlled, and the energy and volume will fluctuate accordingly.

However, we saw that the transformation from E to T between the microcanonical and canonical ensembles turned into a Laplace transform relation between the partition functions. The same result holds for the transformation from V to T . The relevant “energy” quantity to transform is the work done by the system against the external pressure P in changing its volume from $V = 0$ to V , which will be PV . Thus, the isothermal-isobaric partition function can be expressed in terms of the canonical partition function by the Laplace transform:

$$\Delta(N, P, T) = \frac{1}{V_0} \int_0^\infty dV e^{-\beta PV} Q(N, V, T)$$

where V_0 is a constant that has units of volume. Thus,

$$\Delta(N, P, T) = \frac{1}{V_0 N! h^{3N}} \int_0^\infty dV \int dx e^{-\beta(H(x)+PV)}$$

The Gibbs free energy is related to the partition function by

$$G(N, P, T) = -\frac{1}{\beta} \ln \Delta(N, P, T)$$

This can be shown in a manner similar to that used to prove the $A = -(1/\beta) \ln Q$. The differential equation to start with is

$$G = A + PV = A + P \frac{\partial G}{\partial P}$$

Other thermodynamic relations follow:

Volume:

$$V = -kT \left(\frac{\partial \ln \Delta(N, P, T)}{\partial P} \right)_{N, T}$$

Enthalpy:

$$\bar{H} = \langle H(x) + PV \rangle = -\frac{\partial}{\partial \beta} \ln \Delta(N, P, T)$$

Heat capacity at constant pressure

$$C_P = \left(\frac{\partial \bar{H}}{\partial T} \right)_{N, P} = k\beta^2 \frac{\partial^2}{\partial \beta^2} \ln \Delta(N, P, T)$$

Entropy:

$$\begin{aligned} S &= - \left(\frac{\partial G}{\partial T} \right)_{N, P} \\ &= k \ln \Delta(N, P, T) + \frac{\bar{H}}{T} \end{aligned}$$

The fluctuations in the enthalpy $\Delta \bar{H}$ are given, in analogy with the canonical ensemble, by

$$\Delta \bar{H} = \sqrt{kT^2 C_P}$$

so that

$$\frac{\Delta \bar{H}}{\bar{H}} = \frac{\sqrt{kT^2 C_P}}{\bar{H}}$$

so that, since C_P and \bar{H} are both extensive, $\Delta \bar{H}/\bar{H} \sim 1/\sqrt{N}$ which vanish in the thermodynamic limit.

C. Pressure and work virial theorems

As noted earlier, the quantity $-\partial H/\partial V$ is a measure of the instantaneous value of the internal pressure P_{int} . Let us look at the ensemble average of this quantity

$$\begin{aligned}\langle P_{\text{int}} \rangle &= -\frac{1}{\Delta} C_N \int_0^\infty dV e^{-\beta PV} \int dx \frac{\partial H}{\partial V} e^{-\beta H(\mathbf{x})} \\ &= \frac{1}{\Delta} C_N \int_0^\infty dV e^{-\beta PV} \int dx kT \frac{\partial}{\partial V} e^{-\beta H(\mathbf{x})} \\ &= \frac{1}{\Delta} \int_0^\infty dV e^{-\beta PV} kT \frac{\partial}{\partial V} Q(N, V, T)\end{aligned}$$

Doing the volume integration by parts gives

$$\begin{aligned}\langle P_{\text{int}} \rangle &= \frac{1}{\Delta} [e^{-\beta PV} kT Q(N, V, T)]|_0^\infty - \frac{1}{\Delta} \int_0^\infty dV kT \left(\frac{\partial}{\partial V} e^{-\beta PV} \right) Q(N, V, T) \\ &= P \frac{1}{\Delta} \int_0^\infty dV e^{-\beta PV} Q(N, V, T) = P\end{aligned}$$

Thus,

$$\langle P_{\text{int}} \rangle = P$$

This result is known as the pressure virial theorem. It illustrates that the average of the quantity $-\partial H/\partial V$ gives the fixed pressure P that defines the ensemble.

Another important result comes from considering the ensemble average $\langle P_{\text{int}} V \rangle$

$$\langle P_{\text{int}} V \rangle = \frac{1}{\Delta} \int_0^\infty dV e^{-\beta PV} kT V \frac{\partial}{\partial V} Q(N, V, T)$$

Once again, integrating by parts with respect to the volume yields

$$\begin{aligned}\langle P_{\text{int}} V \rangle &= \frac{1}{\Delta} [e^{-\beta PV} kT V Q(N, V, T)]|_0^\infty - \frac{1}{\Delta} \int_0^\infty dV kT \left(\frac{\partial}{\partial V} V e^{-\beta PV} \right) Q(N, V, T) \\ &= \frac{1}{\Delta} \left[-kT \int_0^\infty dV e^{-\beta PV} Q(N, V, T) + P \int_0^\infty dV e^{-\beta PV} V Q(N, V, T) \right] \\ &= -kT + P \langle V \rangle\end{aligned}$$

or

$$\langle P_{\text{int}} V \rangle + kT = P \langle V \rangle$$

This result is known as the work virial theorem. It expresses the fact that equipartitioning of energy also applies to the volume degrees of freedom, since the volume is now a fluctuating quantity.