

Equilibrium Statistical Mechanics

First Law

Conservation of energy: Heat plus work equals the change in internal energy :

$$\Delta E = q + w.$$

No perpetual motion of the first kind i.e. no work without consuming fuel.

Conservation of energy: Differential form of the first law,

$$dE = dq + dw$$
$$\oint dE = 0$$

Energy is a state function.

Second Law

Entropy is a state function: No perpetual motion of the 2nd kind i.e. heat cannot be converted to work with 100% efficiency.

Differential form:

$$dS = \frac{dq_{rev}}{T}$$
$$\oint dS = 0$$

where T is the temperature and q_{rev} is the reversible heat.

Thermodynamics

Combining the First and Second Law

$$dE = dq + dw = dq_{rev} + dw_{rev} \quad (\text{E is a state function})$$

$$dE = TdS - pdV + \mu dN$$

where p is the pressure, V is the volume, μ is the chemical potential and N is the particle number.

Since Energy is a state function, dE is an exact differential. In addition, S , p and N are variables of state. Therefore,

$$dS = \frac{1}{T}dE + \frac{p}{T}dV - \frac{\mu}{T}dN$$

which implies, S(NVE), can be used to determine

$$\begin{aligned} \frac{1}{T} &= \frac{\partial S}{\partial E} \\ \frac{p}{T} &= \frac{\partial S}{\partial V} \\ \frac{\mu}{T} &= -\frac{\partial S}{\partial N} \end{aligned}$$

Third Law

In the derivation given about, it has implicitly been assumed that the integrating factor is trivial. That is, as we decrease the temperature to zero, the entropy must evolve to trivial constant. Generally, that constant is taken to be zero, and the limit of zero entropy at $T=0$ is referred to as the Third Law.

Other Conditions : Conceptual Framework

Exact Differential:

$$dE = TdS - pdV + \mu dN$$

First Derivative Relationships:

$$T = \left(\frac{\partial E}{\partial S} \right)_{VN}$$
$$p = - \left(\frac{\partial E}{\partial V} \right)_{SN}$$
$$\mu = \left(\frac{\partial E}{\partial N} \right)_{SV}$$

Thus, from derivatives of the extensive variable, E, with respect to three independent, extensive, variables (S,V,N), we obtain three corresponding dependent, intensive, thermodynamic variables T, p, μ .

Is it possible to write thermodynamics using combinations of the extensive and intensive variables as the independent parameters???

Legendre Transform

Any function, $f(x)$, can be represented at any point, x , by its derivative, and y intercept, $b(x)$,

$$f(x) = x \frac{df(x)}{dx} + b(x)$$

It is therefore correct to write

$$b(x) = f(x) - x \frac{df(x)}{dx}$$

because the intercept is determined by the function and its slope for all x .

Therefore,

$$b(y) = f(x(y)) - x(y)y$$

$$b(y) = f(y) - xy$$

where $y = df(x)/dx$ is the independent variable.

Thermodynamics: Connections

Canonical Conditions (nVT): Review

Definition of A(NVT): Helmholtz Free Energy

$$A = E - TS$$

Legendre Transform and Exact Differential:

$$dA = dE - SdT - TdS$$

$$dA = TdS - pdV + \mu dN - SdT - TdS$$

$$dA = -SdT - pdV + \mu dN$$

First Derivative Relationships:

$$S = - \left(\frac{\partial A}{\partial T} \right)_{VN}$$

$$p = - \left(\frac{\partial A}{\partial V} \right)_{TN}$$

$$\mu = \left(\frac{\partial A}{\partial N} \right)_{TV}$$

Thermodynamics: Connections

Isothermal-Isobaric Conditions (NPT):

Definition of $G(NPT)$: Gibbs Free Energy

$$G = A + PV$$

Legendre Transform and Exact Differential:

$$dG = dA + pdV + Vdp$$

$$dG = -SdT - pdV + \mu dN + pdV + Vdp$$

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

First Derivative Relationships:

$$S = - \left(\frac{\partial G}{\partial T} \right)_{pN}$$

$$V = \left(\frac{\partial G}{\partial p} \right)_{TN}$$

$$\mu = \left(\frac{\partial G}{\partial N} \right)_{TV}$$

$$G = \mu N$$

Where did the last equation come from???

Interlude : Homogeneous Functions

If a function, $f(x_1 \dots x_M)$ is homogeneous function of degree one in the variables $x_1 \dots x_M$ then scaling the x_i by a constant will result in the scaling of f by the same constant

$$f(\lambda x_1 \dots \lambda x_M) = \lambda f(x_1 \dots x_M)$$

In addition, taking the λ derivative of both sides

$$\begin{aligned}\lambda f(x_1 \dots x_M) &= f(\lambda x_1 \dots \lambda x_M) \\ f(x_1 \dots x_M) &= \sum_i \frac{\partial(\lambda x_i)}{\partial \lambda} \frac{\partial f(\lambda x_1 \dots \lambda x_M)}{\partial \lambda x_i} \\ f(x_1 \dots x_M) &= \sum_i x_i \frac{\partial f(\lambda x_1 \dots \lambda x_M)}{\partial \lambda x_i} \\ f(x_1 \dots x_M) &= \sum_i x_i \frac{\partial f(x_1 \dots x_M)}{\partial x_i}\end{aligned}$$

where the value $\lambda = 1$ was inserted in the last step.

Alternative Definitions

$G(T,p,N)$ is extensive function. However, it depends on only **one** extensive variable, N . Therefore, G must be a homogeneous function of degree 1 in N . That is decreasing/increasing the amount of material in a system by a scaling factor must increase the Free energy by the same scaling factor.

Thus,

$$G = N \left(\frac{\partial G}{\partial N} \right)_{T,p} = \mu N$$

for a one component system.

Thermodynamics: Connections

Grand Canonical Conditions (μVT):

Definition of ϕ :

$$\phi = A - \mu N$$

Legendre Transform and Exact Differential of $\phi(nPH)$:

$$d\phi = dA - \mu dN - Nd\mu$$

$$d\phi = -SdT - pdV + \mu dN - \mu dN - Nd\mu$$

$$d\phi = -SdT - pdV - Nd\mu$$

First Derivative Relationships:

$$S = - \left(\frac{\partial \phi}{\partial T} \right)_{V\mu}$$

$$p = - \left(\frac{\partial \phi}{\partial V} \right)_{T\mu}$$

$$N = \left(\frac{\partial \phi}{\partial \mu} \right)_{TV}$$

$$\phi = -pV$$

The function ϕ is never used. It is rather always replaced by “ $-pV$ ”.

Thermodynamics: Connections

Unphysical Conditions (μpT):

Systems cannot exist under μpT . Free energies must be extensive functions. None of the variables, μpT , are extensive. Therefore, any function which depends on μpT cannot be extensive. Mathematically, we cannot form a thermodynamic function of μpT by Legendre transform

$$\begin{aligned}\psi &= \phi + pV = -pV + pV = 0 \\ \psi &= G - \mu N = \mu N - \mu N = 0.\end{aligned}$$

Physically, a system separated from a particle reservoir by a semipermeable membrane, connected to a heat bath with the walls of the membrane moving in response to pressure variations of the system is **not** at equilibrium. Any fluctuation can give rise to explosive growth or decay.

Quandary

How does thermodynamics arise from the complex dynamical motions of atoms/molecules around us? Lets start by examining the dynamical equations:

Newton's Laws

Newton's stated that for every reaction there is an equal and opposite reaction. For the most basic case, we write, the mass of a particle times its acceleration equals the force

$$ma = F$$

$$m\ddot{q} = F$$

which can be written in the form

$$\dot{q} = \frac{p}{m}$$

$$\dot{p} = F$$

where q is the particle position and p its momentum.

Hamilton's Equations

Hamilton's equations are a generalization/reformulation of Newton's equations. Briefly, the Hamiltonian, $H(p, q)$ is defined such that

$$\begin{aligned}\dot{q} &= \frac{\partial H}{\partial p} \\ \dot{p} &= -\frac{\partial H}{\partial q}\end{aligned}$$

which yields

$$\begin{aligned}\frac{dH}{dt} &= \dot{q} \frac{\partial H}{\partial q} + \dot{p} \frac{\partial H}{\partial p} = 0 \\ &= \frac{\partial H}{\partial p} \frac{\partial H}{\partial q} - \frac{\partial H}{\partial q} \frac{\partial H}{\partial p} = 0\end{aligned}$$

and defines the Poisson Bracket

$$\{A, H\} = \frac{dA}{dt} = \frac{\partial H}{\partial p} \frac{\partial A}{\partial q} - \frac{\partial H}{\partial q} \frac{\partial A}{\partial p}$$

Hamilton's Equations.

For the most basic case,

$$\begin{aligned}H &= \frac{p^2}{2m} + \phi(q) \\ \dot{q} &= \frac{p}{m} \\ \dot{p} &= -\frac{\partial\phi(q)}{\partial q} = F\end{aligned}$$

where $p^2/2m$ is the kinetic energy and $\phi(q)$ is the potential energy.

Liouville's Theorem.

Hamilton's equations can be written in the form

$$\dot{\Gamma} = \xi(\Gamma, t)$$

where Γ is an $2n$ -dimensional vector, $\Gamma = (q_t^1, \dots, p_t^n)$, and $\xi(\Gamma, t)$ is an $2n$ -dimensional vector function of Γ and t . The formal solution can be written in terms of the initial conditions

$$\Gamma_t^i = \Gamma_t^i(t; \Gamma_0^1, \dots, \Gamma_0^{2n})$$

Liouville's Theorem.

We can consider the solution as a transformation from the initial coordinates at time, t_0 , to the coordinates at time, t and determine the evolution of the volume element

$$d\Gamma_t = J(\Gamma_t; \Gamma_0) d\Gamma_0$$

where

$$\mathbf{M} = \frac{\partial(\Gamma_t^1 \cdots \Gamma_t^{2n})}{\partial(\Gamma_0^1 \cdots \Gamma_0^{2n})}$$
$$J(\Gamma_t; \Gamma_0) = \det \mathbf{M}$$

Liouville's Theorem.

The Jacobian is the determinant of a matrix \mathbf{M} according to:

$$J(\Gamma_t; \Gamma_0) = \det(\mathbf{M}) = e^{\text{Tr}(\ln \mathbf{M})}$$

An equation of motion for $J(\Gamma_t; \Gamma_0)$ can be derived by

$$\frac{dJ}{dt} = J \text{Tr} \left(\mathbf{M}^{-1} \frac{d\mathbf{M}}{dt} \right) = J \sum_{i,j} M_{ij}^{-1} \frac{dM_{ji}}{dt}$$

subject to the obvious initial condition $J(0) = 1$.

Here, the matrix elements of \mathbf{M}^{-1} and $d\mathbf{M}/dt$ are:

$$M_{ij}^{-1} = \frac{\partial \Gamma_0^i}{\partial \Gamma_t^j}$$
$$\frac{dM_{ji}}{dt} = \frac{\partial \dot{\Gamma}_t^j}{\partial \Gamma_0^i}$$

Liouville's Theorem.

The equation of motion for J reduce to

$$\begin{aligned}\frac{dJ}{dt} &= J \sum_{i,j} \frac{\partial \Gamma_0^i}{\partial \Gamma_t^j} \frac{\partial \dot{\Gamma}_t^j}{\partial \Gamma_0^i} \\ &= J \sum_{i,j,k} \frac{\partial \Gamma_0^i}{\partial \Gamma_t^j} \frac{\partial \dot{\Gamma}_t^j}{\partial \Gamma_t^k} \frac{\partial \Gamma_t^k}{\partial \Gamma_0^i} \\ &= J \sum_{j,k} \delta_{jk} \frac{\partial \dot{\Gamma}_t^j}{\partial \Gamma_t^k} \\ &= J \sum_i \frac{\partial \dot{\Gamma}_t^i}{\partial \Gamma_t^i} \\ &= J \kappa(\Gamma_t)\end{aligned}$$

The quantity

$$\kappa(\Gamma, t) = \nabla_{\Gamma} \cdot \dot{\Gamma} = \nabla_{\Gamma} \cdot \xi(\Gamma, t)$$

is known as the *compressibility* of the dynamical system.

Liouville's Theorem.

Using the definition of $\xi(\Gamma, t)$

$$\kappa(\Gamma, t) = -\sum_i \frac{\partial^2 H}{\partial p_i \partial q_i} + \sum_i \frac{\partial^2 H}{\partial q_i \partial p_i} = 0$$

and $J(t) \equiv 1$.

Thus, Hamiltonian system preserve the phase space volume,

$$d\Gamma_0 = d\Gamma_t$$

which completes the proof Liouville's theorem!!!

Liouville Equation

It is now possible to consider a normalized distribution function, $f(\Gamma, t)$, describing an ensemble of systems evolving according to Hamilton's equations.

An equation of motion for the distribution function can be derived by balancing the rate of change of the number of ensemble members inside a volume, V , by the flux through the boundary surface

$$\begin{aligned} \frac{d}{dt} \int_{D(V)} d\Gamma f(\Gamma, t) &= - \int_{\partial V} dS_{\Gamma} [\hat{n} \cdot \xi(\Gamma, t)] f(\Gamma, t) \\ \int_{D(V)} d\Gamma \frac{\partial f(\Gamma, t)}{\partial t} &= - \int_{D(V)} \sum_i \nabla_i [\xi_i(\Gamma) f(\Gamma, t)] \\ &= - \int_{D(V)} \sum_i \xi_i(\Gamma, t) \nabla_i f(\Gamma, t) \end{aligned}$$

where phase space is assumed to be Euclidean or flat (it is).

In order for the result to hold for all possible Volumes, the local results follows

$$\begin{aligned} \frac{\partial f(\Gamma, t)}{\partial t} + \sum_i \xi_i(\Gamma, t) \nabla_i f(\Gamma, t) &= 0 \\ \frac{df(\Gamma, t)}{dt} &= 0 \end{aligned}$$

Liouville Equation : Equilibrium solutions

We wish to examine equilibrium solutions, $f(\Gamma)$ or $\partial f/\partial t = 0$. Clearly, any function consisting of conserved quantities of the dynamics, $f(H, C_1 \dots C_M)$ will satisfy the Liouville Equation where $dC_k/dt = 0$.

We wish to consider a distribution function that will allow us to visit **all** points in phase space with equal a priori probability subject to the constraints embodied by the conserved quantity, H (and possibly others). Clearly,

$$f(H, C_1 \dots C_M) = K \delta(H - E) \prod_k \delta(C_k - C_k^{(0)})$$

where K is a constant.

Liouville Equation : Equilibrium solutions

Therefore, we can define the phase space volume

$$\Omega(NVE) = \frac{1}{N!h^N} \int d\Gamma \delta(H - E)$$

and static or phase space averages

$$\langle A \rangle = \frac{E_0}{N!h^N \Omega(NVE)} \int d\Gamma \delta(H - E) A(\Gamma)$$

where h is Plank's constant, only the Hamiltonian is assumed to be conserved, and E_0 is a constant.

The time average of a single trajectory will produce the phase space average

$$\langle A \rangle = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T dt A(\Gamma_t)$$

if and only if the system is **ergodic**.

We are now ready to connect to thermodynamics!!

Gibbs Postulates

(1) Thermodynamic quantities can be mapped into averages over all possible microstates consistent with the few macroscopic parameters required to specify the state of the system (here, NVE).

(2) We construct the averages using an “ensemble”. An ensemble is a collection of systems identical on the macroscopic level but different on the microscopic level.

(3) The ensemble members obey the principle of “equal a priori probability”. That is, no one ensemble member is more important or probable than another.

Boltzmann Entropy and Partition Function

It is clear from the derivation presented above that the phase space average is exactly equal to the desired ensemble average. That is all phase points with energy, E are included with equal probability.

Consider the phase space volume, $\Omega(NVE)$, the “number of states” with energy E given physical volume, V and N particles. As the phase space volume increases, obviously, the number of microstates increases and the entropy should increase. This suggest that we postulate that $S(NVE) = F(\Omega(NVE))$ where $\Omega(NVE)$ is now referred to as the partion function and F is a monotonically increasing, function.

Connection to Thermodynamics

From thermodynamics, we know that

$$\begin{aligned}\frac{1}{T} &= \frac{\partial S}{\partial E} \\ \frac{p}{T} &= \frac{\partial S}{\partial V} \\ \frac{\mu}{T} &= -\frac{\partial S}{\partial N}\end{aligned}$$

From our postulates these quantities MUST arise from phase space averages.

Therefore, $S = F(\Omega)$ must be a constant times the logarithm, $S = k \log(\Omega)$, so that,

$$\begin{aligned}\frac{1}{T} &= \frac{\partial S}{\partial E} \\ \frac{1}{T} &= \frac{E_0}{N!h^N \Omega(NVE)} \int d\Gamma \delta(H - E) \frac{\partial k \log \delta(H - E)}{\partial E} \\ &= \langle \hat{T}^{-1} \rangle\end{aligned}$$

where k is Boltzmann's constant and \hat{T}^{-1} is the inverse temperature "estimator".

Ideal Gas

We next consider the ideal gas in three spatial dimensions, in the large N limit

$$\begin{aligned}\Omega(NVE) &= \frac{E_0}{N!h^{3N}} \int d\mathbf{p}^N d\mathbf{q}^N \delta(\sum_k \mathbf{p}_k^2/2m - E) \\ &= [3NE_0] \left[\frac{V}{h^3} (2\pi mE)^{3/2} \right]^N \left[\frac{1}{N! \Gamma\left(\frac{3N}{2}\right)} \right] \\ S(NVE) &= Nk \log \left[\frac{V}{Nh^3} \left(\frac{4\pi mE}{3N} \right)^{3/2} \right] + \frac{5}{2} Nk + \mathcal{O}(N^0)\end{aligned}$$

Thus,

$$\begin{aligned}\frac{1}{T} &= \frac{3k}{2E} \\ \frac{p}{T} &= \frac{Nk}{V}\end{aligned}$$

so that

$$\begin{aligned}E &= \frac{3kT}{2} \\ p &= \frac{NkT}{V}\end{aligned}$$

as expected!!

The Thermodynamic Limit

Statistical mechanics is defined at finite N . How then does it produce the thermodynamics limit $N \rightarrow \infty$? In thinking about the ensemble hypothesis consider that ensemble members can be thought of as very small chunks of a giant system. Thus, by averaging quantities over many small chunks, it should be possible to produce thermodynamic quantities as ensemble averages with small N . That is, we just need each chunk of the giant system to be large enough to be statistically independent,

In addition, it can be shown that as $N \rightarrow \infty$ statistical mechanics predicts (properly) that average quantities such pressure approach their average, $\langle p \rangle = p_{ext}$, and all thermodynamic quantities are the same in all ensembles.

NVT Partition Function

Canonical ensemble: NVT

1. Imagine a system surrounded by a thermal reservoir with:

$$(H = H_I + H_{II}), \{H_I, H_{II}\} = 0$$

2. The probability of having energy E_I in system I **and** the E_{II} in II must be $P_I P_{II} = P_{I,II}$. Hence,

$$\begin{aligned} Q(NV\beta) &= \int dE_I \int dE_{II} P(E_I; \beta) \Omega_I(NV E_I) P(E_{II}; \beta) \Omega_{II}(NV E_{II}) \\ &= \int dE \int_{-2E}^{2E} d\epsilon P\left(E + \frac{\epsilon}{2}; \beta\right) P\left(E - \frac{\epsilon}{2}; \beta\right) \\ &\quad \Omega_I\left(NV\left(E + \frac{\epsilon}{2}\right)\right) \Omega_{II}\left(NV\left(E - \frac{\epsilon}{2}\right)\right) \end{aligned}$$

3. We also know that

$$Q(NV\beta) = \int dE P(E; \beta) \Omega_{I,II}(NV E)$$

which implies

$$\begin{aligned} P(E; \beta) &= P\left(E + \frac{\epsilon}{2}; \beta\right) P\left(E - \frac{\epsilon}{2}; \beta\right) \\ P(E; \beta) &= \exp(-\beta E) \end{aligned}$$

where $\beta = \beta(T)$.

4. Combining results we obtain

$$\begin{aligned} Q(NV\beta) &= \int d\Gamma \int dE \exp(-\beta E) \Omega(NV E) \\ &= \frac{C_N}{h^{3n}} \int d\Gamma \exp[-\beta H(\Gamma)] \end{aligned}$$

Statistical Mechanics Review

Thermodynamic Connection: NVT

1. Define the average energy:

$$-\frac{\partial \log[Q(V\beta)]}{\partial \beta} = \int d\Gamma H(V, \Gamma) \left[\frac{K \exp[-\beta H(V, \Gamma)]}{Q(V\beta)} \right] = \langle E \rangle$$

2. Define the average Pressure:

$$\frac{\partial \log[Q(V\beta)]}{\partial V} = \beta \int d\Gamma P(V, \Gamma) \left[\frac{K \exp[-\beta H(V, \Gamma)]}{Q(V\beta)} \right] = \beta \langle P \rangle$$

3. Perform a Legendre Transformation: Assume averages are equivalent to thermodynamic quantities

$$\begin{aligned} d(\beta E + \log[Q(V\beta)]) &= \beta dE + \beta P dV \\ dS &= \frac{1}{T} dE + \frac{p}{T} dV \\ \beta &= \frac{1}{kT} \\ S &= E/T - A/T \\ A &= -kT \log[Q(VT)]. \end{aligned}$$

4. Here, the universal constant k is the familiar Boltzmann's constant.

NVT Partition Function : The free particle

The canonical partition function for the free particle is

$$\begin{aligned} Q(NVT) &= \frac{1}{N!h^{3n}} \int d\Gamma \exp[-\beta \sum_k \mathbf{p}_k^2/2m] \\ &= \frac{V^N}{N!} \left[\frac{m}{2\pi\hbar^2\beta} \right]^{3N/2} \end{aligned}$$

Using our standard relationships:

$$\begin{aligned} p &= kT \frac{\partial \log Q(NVT)}{\partial T} = \frac{NkT}{V} \\ E &= -\frac{\partial \log Q(NVT)}{\partial \beta} = \frac{3NkT}{2} \end{aligned}$$

NPT Partition Function

Using the similar arguments to those used to construct the canonical and microcanonical partition functions, it can be shown that

$$\begin{aligned}
 \Delta(NPT) &= \frac{C_N}{h^{dN}} \int_0^\infty dV e^{-\beta P_{\text{ext}} V} \int d^N \mathbf{p} \int_{D(V)} d^N \mathbf{r} e^{-\beta H(\mathbf{p}, \mathbf{r})} \\
 &= \frac{C_N}{h^{dN}} \int_0^\infty dV e^{-\beta P_{\text{ext}} V} \int dE e^{-\beta E} \\
 &\quad \times \int d^N \mathbf{p} \int_{D(V)} d^N \mathbf{r} \delta(H(\mathbf{p}, \mathbf{r}) - E) \\
 &= \int_0^\infty dV e^{-\beta P_{\text{ext}} V} \int dE e^{-\beta E} \Omega(NVE) \\
 &= \int_0^\infty dV e^{-\beta P_{\text{ext}} V} Q(NVT)
 \end{aligned}$$

is the isothermal-isobaric partition function where C_N a combinatorial factor, $Q(NVT)$ is the canonical partition function and the $\Omega(NVE)$ is the microcanonical partition function.

The connection to thermodynamics is, also, standard,

$$G = -kT \log \Delta(NPT)$$

NPT Partition Function : The free particle

The partition function is

$$\begin{aligned}
 \Delta(NPT) &= \frac{1}{N!h^{dN}} \int_0^\infty dV e^{-\beta PV} \int d^N \mathbf{p} \int_{D(V)} d^N \mathbf{r} e^{-\beta \sum_k p_k^2/2m} \\
 &= \left[\frac{m}{2\pi\hbar^2\beta} \right]^{3N/2} \int_0^\infty dV e^{-\beta PV} \frac{V^N}{N!} \\
 &= \left[\frac{m}{2\pi\hbar^2\beta} \right]^{3N/2} [\beta P]^{-(N+1)}
 \end{aligned}$$

This result yields

$$\begin{aligned}
 V &= -kT \left(\frac{\partial \log \Delta(NPT)}{\partial P} \right) = \frac{(N+1)kT}{P} \\
 H_{enthal} &= - \left(\frac{\partial \log \Delta(NPT)}{\partial \beta} \right) = \left[\frac{5N}{2} + 1 \right] kT
 \end{aligned}$$

which in the large N limit yields

$$\begin{aligned}
 PV &= NkT \\
 H_{enthal} &= \frac{5NkT}{2}
 \end{aligned}$$

Note, that

$$V^{-1} = \langle V^{-1} \rangle = \frac{P}{NkT}$$

because in small systems $[\langle V \rangle]^{-1} \neq \langle V^{-1} \rangle!$

Thermodynamic Estimators : More detail!

In the isothermal-isobaric ensemble, the average Volume can be written as

$$\begin{aligned}\langle V \rangle &= \left(\frac{\partial G}{\partial P_{\text{ext}}} \right)_{TN} \\ &= \frac{C_N}{h^{dN} \Delta(NPT)} \int_0^\infty dV e^{-\beta P_{\text{ext}} V} \int d^N \mathbf{p} \int_{D(V)} d^N \mathbf{r} e^{-\beta H(\mathbf{p}, \mathbf{r})} V \\ &= \langle V \rangle_{\text{extended phase space}}\end{aligned}$$

Thermodynamic Estimators

The average Enthalpy ($H_{enthal} = E + P_{ext}V$),

$$\begin{aligned}
 G &= A + P_{ext}V = E - TS + P_{ext}V = H_{enthal} - TS \\
 H_{enthal} &= G + TS \\
 &= G - T \frac{\partial G}{\partial T} \\
 &= G + T \frac{\partial kT \log \Delta(NPT)}{\partial T} \\
 &= G + kT \log \Delta(NPT) + kT^2 \frac{\partial \log \Delta(NPT)}{\partial T} \\
 &= G - G - \frac{\partial \log \Delta(NPT)}{\partial \beta} \\
 &= - \frac{\partial \log \Delta(NPT)}{\partial \beta}
 \end{aligned}$$

can be written as

$$\begin{aligned}
 \langle H_{enthal} \rangle &= \frac{C_N}{h^{dN} \Delta(NPT)} \int_0^\infty dV e^{-\beta P_{ext}V} \\
 &\quad \times \int d^N \mathbf{p} \int_{D(V)} d^N \mathbf{r} e^{-\beta H(\mathbf{p}, \mathbf{r})} [H(\mathbf{p}, \mathbf{r}) + P_{ext}V] \\
 &= \langle H \rangle_{\text{phase space}} + \langle P_{ext}V \rangle_{\text{extended phase space}}
 \end{aligned}$$

Thermodynamic Estimators

Consider,

$$\begin{aligned}
 \left\langle -kT \frac{\partial \log Q(NVT)}{\partial V} \right\rangle &= -\frac{kT}{\Delta(NPT)} \int_0^\infty dV e^{-\beta P_{\text{ext}} V} Q(NVT) \frac{\partial \log Q(NVT)}{\partial V} \\
 &= -\frac{kT}{\Delta(NPT)} \int_0^\infty dV e^{-\beta P_{\text{ext}} V} \frac{\partial Q(NVT)}{\partial V} \\
 &= -\frac{kT}{\Delta(NPT)} \int_0^\infty dV e^{-\beta P_{\text{ext}} V} Q(NVT) (-\beta P_{\text{ext}}) \\
 &= P_{\text{ext}}
 \end{aligned}$$

Inserting the definition of $Q(NVT)$ yields

$$\begin{aligned}
 \left\langle -kT \frac{\partial \log Q(NVT)}{\partial V} \right\rangle &= \frac{C_N}{h^{dN} \Delta(NPT)} \int_0^\infty dV e^{-\beta P_{\text{ext}} V} \\
 &\quad \times \frac{\partial}{\partial V} \int d^N \mathbf{p} \int_{D(V)} d^N \mathbf{r} e^{-\beta H(\mathbf{p}, \mathbf{r})} \\
 P_{\text{ext}} &= \langle P_{\text{int}} \rangle_{\text{extended phase space}}
 \end{aligned}$$

where

$$P_{\text{int}} = \frac{1}{dV} \left[\sum_{i=1}^N \frac{\mathbf{p}_i^2}{m_i} + \sum_{i=1}^N \mathbf{r}_i \cdot \mathbf{F}_i - (dV) \frac{\partial \phi(\mathbf{r}, V)}{\partial V} \right]$$

Thermodynamic Estimators

Finally,

$$\begin{aligned} \left\langle -kTV \frac{\partial \log Q(NVT)}{\partial V} \right\rangle &= \langle P_{int} V \rangle \\ &= P_{ext} \langle V \rangle - kT \end{aligned}$$

using similar arguments to those employed above.

Thus, for the ideal gas,

$$\begin{aligned} \langle V \rangle &= \frac{C_N}{h^{dN} \Delta(NPT)} \int_0^\infty dV V e^{-\beta P_{ext} V} \int d^N \mathbf{p} \int_{D(V)} d^N \mathbf{r} e^{-\beta H(\mathbf{p}, \mathbf{r})} \\ &= \frac{\int_0^\infty dV V^{N+1} e^{-\beta P_{ext} V}}{\int_0^\infty dV V^N e^{-\beta P_{ext} V}} \\ &= \frac{(N+1)kT}{P_{ext}} \end{aligned}$$

$$\begin{aligned} \langle P_{int} V \rangle &= P_{ext} \langle V \rangle - kT \\ &= (N+1)kT - kT = NkT \end{aligned}$$

NPT/NVT : Thermodynamic Limit

Note, while the thermodynamics independent variables are changed via Legendre Transform, partition functions are changed via Laplace Transforms. In the thermodynamics limit, only the maximum term contributes to the integrals, and the two transformations become manifestly identical $E \rightarrow E_{thermo}$, $V \rightarrow V_{thermo}$ and $A \rightarrow A_{thermo}$.

Thus, in the thermodynamic limit,

$$\begin{aligned}\Delta(NPT) &= e^{-\beta P_{\text{ext}}V} e^{-\beta E} \Omega(NVE) \\ G &= PV + E - TS = H - TS\end{aligned}$$

and

$$\begin{aligned}\Delta(NPT) &= e^{-\beta P_{\text{ext}}V} Q(NVT) \\ G &= PV + A\end{aligned}$$

Similarly, for the canonical ensemble

$$\begin{aligned}Q(NVT) &= e^{-\beta E} \Omega(NVE) \\ A &= E - TS =\end{aligned}$$

Generalized NPT ensemble

Virial Theorems

1. The canonical partition function:

$$\begin{aligned} Q(\mathbf{h}) &\propto \int d\mathbf{r} \exp[-\beta\phi(\mathbf{r}, \mathbf{h})] \\ \mathbf{r} &= \mathbf{h}\mathbf{s} \\ Q(\mathbf{h}) &\propto \int d\mathbf{s} V^N \exp[-\beta\phi(\mathbf{h}\mathbf{s}, \mathbf{h})] \end{aligned}$$

2. Tensorial Virial Theorem:

(a) Note the relation:

$$\begin{aligned} kT \frac{\partial \log[Q(V)]}{\partial V} &= kT \frac{\partial \log[Q(V)]}{\partial V} \left(\frac{V}{dV} \right) \sum_{\alpha,\beta} h_{\beta\alpha}^{-1} h_{\alpha\beta} \\ &= \left(\frac{kT}{dV} \right) \sum_{\alpha,\beta} \frac{\partial \log[Q(V)]}{\partial h_{\alpha\beta}} h_{\alpha\beta} \\ &= \frac{1}{d} \text{Tr} \mathbf{P}_{int} \end{aligned}$$

(b) Understand:

$$\langle (P_{int})_{\alpha\beta} - P_{ext} \delta_{\alpha\beta} \rangle = \left\langle \frac{kT}{V} \sum_{l=1}^d \frac{\partial \log[Q(\mathbf{h})]}{\partial h_{\alpha l}} h_{\beta l} - P_{ext} \delta_{\alpha\beta} \right\rangle = 0$$

Generalized NPT Ensemble

Pressure

1. Internal Pressure Tensor, $(P_{int})_{\alpha\beta}$:

$$\begin{aligned} \langle (P_{int})_{\alpha\beta} \rangle &= \frac{1}{\Delta} \int d\mathbf{h} \exp[-\beta P_{ext} V] V^{1-d} Q(\mathbf{h}) \\ &\times \left[\frac{kT}{V} \sum_{l=1}^d \frac{\partial \log[Q(\mathbf{h})]}{\partial h_{\alpha l}} h_{\beta l} \right] \end{aligned}$$

$$(P_{int})_{\alpha\beta} = \frac{1}{V} \left[\sum_{i=1}^N \frac{(\mathbf{p}_i)_\alpha (\mathbf{p}_i)_\beta}{m_i} + (\mathbf{F}_i)_\alpha (\mathbf{r}_i)_\beta - \left(\overset{\leftrightarrow}{\phi} \overset{\leftrightarrow}{\mathbf{h}} \right)_{\alpha\beta} \right]$$

where

$$(\phi')_{\alpha\beta} = \frac{\partial \phi(\mathbf{r}, \mathbf{h})}{\partial h_{\alpha\beta}}$$