Relations

$$\Delta U = \Delta Q - \Delta W$$
$$dU = TdS - pdV + \mu dN$$
$$F = U - TS$$
$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N}$$
$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}$$

Microcanonical

$$\Omega(E) = \int_{x,p} \delta(E - H(x,p)) \frac{\mathrm{d}x\mathrm{d}p}{h}$$

P_E is constant since each state has same probability

$$S = \log(\Omega(E)\Delta E) = -\log(P_E) + \log(\Delta E) = -\sum P_E \log(P_E)$$

Canonical

$$T(E) = \frac{\Omega(E)}{\frac{\mathrm{d}\Omega}{\mathrm{d}E}} = \left(\frac{\mathrm{d}S}{\mathrm{d}E}\right)^{-1}$$
$$Q = \sum_n e^{-\beta E_n}$$
$$\langle E \rangle = -\frac{\partial}{\partial \beta}\log(Q)$$
$$p_n = \frac{e^{-\beta E_n}}{Q} \Rightarrow E_n = -\frac{1}{\beta}\log(p_n) - \frac{1}{\beta}\log(Q)$$
$$\begin{aligned}
\mathrm{d}\langle E \rangle &= \sum_n \mathrm{d}p_n E_n \\
&= \sum_n \mathrm{d}p_n \left[-\frac{1}{\beta}\log(p_n) - \frac{1}{\beta}\log(Q)\right] \\
&= -\frac{1}{\beta}\sum_n \mathrm{d}p_n \log(p_n) - \frac{1}{\beta}\log(Q)\mathrm{d}\left(\sum_n p_n\right) \\
&= -\frac{1}{\beta}\sum_n \mathrm{d}p_n \log(p_n) \\
&= -\frac{1}{\beta}\mathrm{d}\left[\sum_n p_n \log(p_n)\right] \\
\Rightarrow S &= -\sum_n p_n \log(p_n)
\end{aligned}$$
$$F = E - TS = -T\log(Q)$$

Derivation of Grand Canonical

$$\log[P(E_T, N_T)] \propto \log[\Omega(E - E_T, N - N_T)]$$

$$\begin{aligned}
&\log[\Omega(E - E_T, N - N_T)] \approx \log\left[\Omega(E,N) - \frac{\mathrm{d}\Omega}{\mathrm{d}E}E_t - \frac{\mathrm{d}\Omega}{\mathrm{d}N}N_T\right] \\
&= \log\left[\Omega(E,N)\left(1 - \frac{1}{\Omega(E,N)}\frac{\mathrm{d}\Omega}{\mathrm{d}E}E_T - \frac{1}{\Omega(E,N)}\frac{\mathrm{d}\Omega}{\mathrm{d}N}N_T\right)\right] \\
&= \log[\Omega(E,N)] + \log\left(1 - \frac{1}{\Omega(E,N)}\frac{\mathrm{d}\Omega}{\mathrm{d}E}E_T - \frac{1}{\Omega(E,N)}\frac{\mathrm{d}\Omega}{\mathrm{d}N}N_T\right) \\
&= \log[\Omega(E,N)] + \log(1 - \beta E_T - \mu N_T)
\end{aligned}$$
$$\langle N \rangle = -\frac{\partial}{\partial \gamma}\log(Q)$$

Particle in a Box

$$\phi_n = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right)$$
$$E_n = \frac{n^2\pi^2\hbar^2}{2mL^2}$$

Harmonic Oscillator

$$E_n = \hbar\sqrt{\frac{k}{m}}\left(n + \frac{1}{2}\right) = \hbar\omega\left(n + \frac{1}{2}\right)$$
$$x(t) = \cos(\omega t + \phi)$$

Poisson Equation

$$\nabla^2\phi = -\frac{4\pi\rho}{\epsilon}$$

Ideal Gas Law Show that if the canonical partition function Q takes the form $Q = f(T)V^N$, the ideal gas law can be obtained.

Solution

$$F = -kT\log Q = -kT\log(f(T)V^N)$$
$$P = -\frac{\partial F}{\partial V} = kT\frac{f(T)NV^{N-1}}{f(T)V^N} = \frac{kTN}{V}$$

Heat Capacity Show that the heat capacity

$$C = \frac{\partial \langle E \rangle}{\partial T}$$

is given in the canonical ensemble by

$$C = \frac{\langle E^2 \rangle - \langle E \rangle^2}{kT^2}$$

Solution

$$\frac{\partial \langle E \rangle}{\partial T} = \frac{\partial \beta}{\partial T}\frac{\partial \langle E \rangle}{\partial \beta}$$
$$\frac{\partial}{\partial T}\left(\frac{1}{kT}\right) = -\frac{1}{kT^2}$$

$$\begin{aligned}
\frac{\partial \langle E \rangle}{\partial \beta} &= \frac{\partial}{\partial \beta}\left(\frac{\sum_n E_n e^{-\beta E_n}}{\sum_n e^{-\beta E_n}}\right) \\
&= \frac{\sum_n -E_n^2 e^{-\beta E_n}}{\sum_n e^{-\beta E_n}} + \left(\frac{\sum_n E_n e^{-\beta E_n}}{\sum_n e^{-\beta E_n}}\right)^2 \\
&= -\langle E^2 \rangle + \langle E \rangle^2
\end{aligned}$$

$$\begin{aligned}
C_v &= -\frac{1}{kT^2}(-\langle E^2 \rangle + \langle E \rangle^2) \\
&= \frac{1}{kT^2}(\langle E^2 \rangle - \langle E \rangle^2)
\end{aligned}$$

Enthalpy The constant pressure ensemble is defined by the enthalpy $H = E + PV$, where H is the enthalpy, E is the energy, P is the pressure (which is a parameter like the temperature in the canonical ensemble), and V is the volume, which is a variable (not constant). The weight of a configuration is given by $e^{-\beta E - \beta PV}$. Find an expression for the fluctuations of the enthalpy in terms of the derivative of the average enthalpy with respect to the temperature.

Solution Partition Function:

$$Q = \sum_j e^{-\beta E_j - \beta PV_j} = \sum_j e^{-\beta H_j}$$

Average enthalpy:

$$\langle H \rangle = \frac{\sum_j H_j e^{-\beta H_j}}{\sum_j e^{-\beta H_j}} = \frac{-\frac{\partial}{\partial \beta}(Q)}{Q} = -\frac{\partial}{\partial \beta}(\log Q)$$
$$\frac{\partial Q}{\partial \beta} = \sum_j -H_j e^{-\beta H_j}$$
$$\frac{\partial^2 Q}{\partial \beta^2} = \sum_j H_j^2 e^{-\beta H_j}$$
$$\langle H^2 \rangle = \frac{\frac{\partial^2 Q}{\partial \beta^2}}{Q}$$

$$\begin{aligned}
\frac{\partial \langle H \rangle}{\partial \beta} &= -\frac{\partial}{\partial \beta}\left(\frac{\frac{\partial Q}{\partial \beta}}{Q}\right) = -\frac{Q\frac{\partial^2 Q}{\partial \beta^2} - \left(\frac{\partial Q}{\partial \beta}\right)^2}{Q^2} \\
&= \left(\frac{\frac{\partial Q}{\partial \beta}}{Q}\right)^2 - \frac{\frac{\partial^2 Q}{\partial \beta^2}}{Q} = \langle H \rangle^2 - \langle H^2 \rangle
\end{aligned}$$

Now $\beta = \frac{1}{kT}$, so $T = \frac{1}{k\beta}$

$$\frac{\partial T}{\partial \beta} = -\frac{1}{k\beta^2} = -\frac{(kT)^2}{k} = -kT^2$$

$$\sigma_H^2 = \langle H^2 \rangle - \langle H \rangle^2 = -\frac{\partial \langle H \rangle}{\partial \beta} = -\frac{\partial T}{\partial \beta}\frac{\partial \langle H \rangle}{\partial T} = kT^2\frac{\partial \langle H \rangle}{\partial T}$$

Master Equation Given a kinetic model for the probability at state n:

$$\frac{\mathrm{d}p_n}{\mathrm{d}t} = \sum_m k(p_m - p_n)$$

show that the change in entropy $S = -\sum_n p_n \log(p_n)$ as a function of time is always nonnegative, $\frac{\mathrm{d}S}{\mathrm{d}t} \geq 0$.

Solution

$$\begin{aligned}
\frac{\mathrm{d}S}{\mathrm{d}t} &= -\sum_n \left[\frac{\mathrm{d}p_n}{\mathrm{d}t} + \frac{\mathrm{d}p_n}{\mathrm{d}t}\log(p_n)\right] \\
&= -\frac{\mathrm{d}}{\mathrm{d}t}\sum_n p_n - \sum_n \frac{\mathrm{d}p_n}{\mathrm{d}t}\log(p_n) \\
&= -\sum_n \frac{\mathrm{d}p_n}{\mathrm{d}t}\log(p_n) \\
&= -\sum_n \log(p_n)\sum_m k(p_m - p_n) \\
&= -\sum_m \log(p_m)\sum_n k(p_n - p_m) \\
&= -\frac{1}{2}k\sum_{m,n}[\log(p_n)(p_m - p_n) + \log(p_m)(p_n - p_m)] \\
&= -\frac{1}{2}k\sum_{m,n}[(\log(p_n) - \log(p_m))(p_m - p_n)] \\
&= \frac{1}{2}k\sum_{m,n}[(\log(p_m) - \log(p_n))(p_m - p_n)]
\end{aligned}$$

Liouville Theorem The probability density of phase space in classical mechanics is $\rho(x,p,t)$. Write down the complete derivative of the density with respect to time. Use the Hamilton equations. Integrate overa phase space volume element $\Delta x \Delta p$ and use the conservation of probability and Gauss therorem to prove the Liouville theorem.

Solution

$$\dot{x} = \frac{\partial H}{\partial p}$$

$$\dot{p} = -\frac{\partial H}{\partial x}$$

$$\begin{aligned}
\frac{\mathrm{d}\rho(x,p,t)}{\mathrm{d}t} &= \frac{\partial \rho}{\partial t} + \frac{\partial \rho}{\partial x}\frac{\partial x}{\partial t} + \frac{\partial \rho}{\partial p}\frac{\partial p}{\partial t} \\
&= \frac{\partial \rho}{\partial t} + \frac{\partial \rho}{\partial x}\frac{\partial H}{\partial p} - \frac{\partial \rho}{\partial p}\frac{\partial H}{\partial x}
\end{aligned}$$

$$P = \int_{\Delta x \Delta p} \rho \mathrm{d}x\mathrm{d}p$$

$$\begin{aligned}
\frac{\partial P}{\partial t} &= \int_{\Delta x \Delta p} \frac{\partial \rho}{\partial t}\mathrm{d}x\mathrm{d}p \\
&= -\int_S \rho(x,p,t)(\dot{x}, \dot{p}) \cdot \begin{pmatrix} \mathrm{d}A_x \\ \mathrm{d}A_p \end{pmatrix}
\end{aligned}$$

By Gauss Theorem

$$\begin{aligned}
&= -\int_{\Delta x \Delta p} \frac{\partial \rho}{\partial x}\dot{x} + \frac{\partial \rho}{\partial p}\dot{p} + \rho\left(\cancel{\frac{\partial^2 H}{\partial x \partial p} - \frac{\partial^2 H}{\partial p \partial x}}\right)\mathrm{d}x\mathrm{d}p \\
&= \int_{\Delta x \Delta p} \frac{\partial \rho}{\partial p}\frac{\partial H}{\partial x} - \frac{\partial \rho}{\partial x}\frac{\partial H}{\partial p}
\end{aligned}$$

$$\frac{\partial \rho}{\partial t} = \frac{\partial \rho}{\partial p}\frac{\partial H}{\partial x} - \frac{\partial \rho}{\partial x}\frac{\partial H}{\partial p}$$

Substituting this into the original equation, everything cancels, and we get

$$\frac{\mathrm{d}\rho}{\mathrm{d}t} = 0$$

Lagrange Multipliers The weight of a particular arrangement from an ensemble is given by

$$W = \frac{L!}{\prod_j n_j!}$$

where L is the number of subsystems and n_j is the number of times a system with energy E_j is observed in the arrangement. Find the most probable arrangement under the constraints that the total number of systems and total energy are fixed. Determine the probability to sample energy E_j.

Solution

$$L = \sum_i n_i$$

$$E = \sum_i n_i E_i$$

We will use Lagrange multipliers and Sterlings approx: $\log(x!) = x\log x - x$ Maximize $\log W$:

$$\begin{aligned}
\log W - \alpha L - \beta E &= \log\left(\frac{L!}{\prod_j n_j!}\right) - \alpha\sum_i n_i - \beta\sum_i n_i E_i \\
&= \log(L!) - \sum_i \log(n_i!) - \alpha\sum_i n_i - \beta\sum_i n_i E_i \\
&= \left(\sum_i n_i\right)\log\left(\sum_i n_i\right) - \sum_i n_i \\
&\quad - \sum_i (n_i \log n_i - n_i + \alpha n_i + \beta n_i E_i)
\end{aligned}$$

$$\frac{\partial}{\partial n_i}(\log W - \alpha L - \beta E) = -\log n_i - \alpha - \beta E_i = 0$$

$$n_i = e^{-\alpha - \beta E_i}$$

$$P_{E_j} = \frac{e^{-\alpha - \beta E_j}}{\sum_n e^{-\alpha - \beta E_n}} = \frac{e^{-\beta E_j}}{\sum_n e^{-\beta E_n}}$$

$$\Omega(E) \propto E^N$$

$$P(E) \propto \Omega(E)e^{-\beta E} \propto E^N e^{-\beta E}$$

$$\begin{aligned}
\frac{\mathrm{d}}{\mathrm{d}E}\log P(E) &= \frac{\mathrm{d}}{\mathrm{d}E}\left[\log(E^N) - \beta E\right] \\
&= \frac{NE^{N-1}}{E^N} - \beta = 0
\end{aligned}$$

Most probable energy

$$E^* = \frac{N}{\beta}$$

Equilibrium Use the Liouvill equation to show that if the phase space probability density in classical mechanics is a function of the Hamiltonian only, then the system must be in equilibrium.

Solution Liouville Equation:

$$\frac{\partial \rho}{\partial t} = \frac{\partial \rho}{\partial x}\frac{\partial H}{\partial p} - \frac{\partial \rho}{\partial p}\frac{\partial H}{\partial x}$$

$$\frac{\partial \rho}{\partial x} = \frac{\partial \rho}{\partial H}\frac{\partial H}{\partial x}$$

$$\frac{\partial \rho}{\partial p} = \frac{\partial \rho}{\partial H}\frac{\partial H}{\partial p}$$

$$\begin{aligned}
\frac{\partial \rho}{\partial t} &= \frac{\partial \rho}{\partial H}\frac{\partial H}{\partial x}\frac{\partial H}{\partial p} - \frac{\partial \rho}{\partial H}\frac{\partial H}{\partial p}\frac{\partial H}{\partial x} \\
&= \frac{\partial \rho}{\partial H}\left(\frac{\partial H}{\partial x}\frac{\partial H}{\partial p} - \frac{\partial H}{\partial p}\frac{\partial H}{\partial x}\right) \\
&= 0
\end{aligned}$$

Harmonic Oscillator Consider a quantum harmomic oscillator with Hamiltonian

$$H = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + \frac{1}{2}m\omega^2 x^2$$

Write down the energy levels and derive the partition function in the canonical ensemble.

Solution

$$E_n = \hbar\omega\left(n+\frac{1}{2}\right)$$

$$\begin{aligned}Q &= \sum_n e^{-\beta\hbar\omega\left(n+\frac{1}{2}\right)} \\ &= e^{-\frac{\beta\hbar\omega}{2}}\sum_n e^{-\beta\hbar\omega n} \\ &= \frac{e^{-\frac{\beta\hbar\omega}{2}}}{1-e^{-\beta\hbar\omega}}\end{aligned}$$

As $\beta \to 0$

$$Q \to \frac{1-\beta\hbar\omega/2}{1-1+\beta\hbar\omega} = \frac{1}{\beta\hbar\omega} - \frac{1}{2} \to \frac{2\pi}{\beta h\omega}$$

Classical:

$$\begin{aligned}\int e^{-\beta H}\mathrm{d}x\mathrm{d}p &= \int e^{-\frac{\beta p^2}{2m}}\mathrm{d}p \int e^{-\frac{\beta m\omega^2 x^2}{2}}\mathrm{d}x \\ &= \sqrt{\frac{2m\pi}{\beta}}\sqrt{\frac{2\pi}{\beta m\omega^2}} \\ &= \frac{2\pi}{\beta\omega}\end{aligned}$$

Ergodic Hypothesis Consider the classical harmonic oscillator with energy

$$E = \frac{1}{2}m\dot{x}^2 + \frac{1}{2}\underbrace{k}_{m\omega^2}x^2$$

Compute the average of the kinetic energy over time and over the microcanonical ensemble. Show that both averages are the same.

Solution Temporal average:

$$\begin{aligned}x(t) &= A\cos(\omega t+\phi) \\ v(t) &= -\omega A\sin(\omega t+\phi)\end{aligned}$$

$$\begin{aligned}E &= \frac{1}{2}m\omega^2 A^2 \\ K &= E\sin^2(\omega t+\phi)\end{aligned}$$

$$\begin{aligned}\langle K\rangle_t &= \frac{1}{t}\int_{t_0}^{t_0+t} E\sin^2(\omega\tau+\phi)\mathrm{d}\tau \\ &= \frac{E}{\omega t}\left[-\frac{1}{4}\sin(2\omega\tau+2\phi)+\frac{\omega\tau+\phi}{2}\right]_{\omega t_0}^{\omega t_0+\omega t} \\ &= \frac{E}{\omega t}\left[-\frac{1}{4}\sin(2\omega t+\Delta)+\frac{1}{4}\sin(\Delta)+\frac{\omega t}{2}\right] \\ &= \frac{E}{2} - \frac{E}{4\omega t}\left[\sin(2\omega t+\Delta)-\sin(\Delta)\right]\end{aligned}$$

$$\lim_{t\to\infty}\langle K\rangle_t = \frac{E}{2}$$

Phase space average:

$$\langle K\rangle_S = \frac{\int \frac{1}{2}mv^2\delta\left(E-\frac{1}{2}mv^2-\frac{1}{2}kx^2\right)\mathrm{d}x\mathrm{d}v}{\int \delta\left(E-\frac{1}{2}mv^2-\frac{1}{2}kx^2\right)\mathrm{d}x\mathrm{d}v}$$

Let $Z_1 = \sqrt{\frac{m}{2}}v$, $Z_2 = \sqrt{\frac{k}{2}}x$.

$$\int \delta\left(E-\frac{1}{2}mv^2-\frac{1}{2}kx^2\right)\mathrm{d}x\mathrm{d}v = \frac{2}{\sqrt{mk}}\int\delta\left(E-Z_1^2-Z_2^2\right)\mathrm{d}Z_1\mathrm{d}Z_2$$

Let $R^2 = Z_1^2+Z_2^2$ and $\cos(\theta) = Z_1/R$.

$$\begin{aligned}\frac{2}{\sqrt{mk}}\int\delta\left(E-Z_1^2-Z_2^2\right)\mathrm{d}Z_1\mathrm{d}Z_2 &= \frac{2}{\sqrt{mk}}\int\delta\left(E-R^2\right)\mathrm{d}\theta R\mathrm{d}R \\ &= \frac{2\pi}{\sqrt{mk}}\int\delta(E-R^2)\mathrm{d}R^2 \\ &= \frac{2\pi}{\sqrt{mk}}\end{aligned}$$

$$\begin{aligned}\int\frac{1}{2}mv^2\delta\left(E-\frac{1}{2}mv^2-\frac{1}{2}kx^2\right)\mathrm{d}x\mathrm{d}v &= \frac{1}{\sqrt{mk}}\int R^2\cos^2\theta\,\delta(E-R^2)\mathrm{d}\theta\mathrm{d}R^2 \\ &= \frac{E\pi}{\sqrt{mk}}\end{aligned}$$

$$\langle K\rangle_S = \frac{E}{2}$$

Imperfect Gas

$$Z = \int e^{-\beta U(r_1,r_2,\ldots,r_N)}\prod_i \mathrm{d}r_i$$

$$U = \frac{1}{2}\sum_{i\neq j}u_{ij}(r_{ij})$$

$$f_{ij} = 1-e^{-\beta u_{ij}}$$

$$\begin{aligned}Z &\approx \int e^{-\beta\sum_{j,k}u_{jk}(r_{jk})}\prod_i\mathrm{d}r_i \\ &= \int\prod e^{-\beta u_{jk}(r_{jk})}\prod_i\mathrm{d}r_i \\ &= \int\prod(1-f_{jk}(r_{jk}))\prod_i\mathrm{d}r_i \\ &\approx \int\left(1-\frac{1}{2}\sum_{i\neq j}f_{ij}\right)\prod_i\mathrm{d}r_i \\ &= V^N - \frac{V^{N-2}}{2}\sum_{i\neq j}\int f_{ij}(r_{ij})\mathrm{d}r_i\mathrm{d}r_j \\ &= V^N\left(1-\frac{N(N-1)}{2V}\int\left(1-e^{-\beta u(r_{12})}\right)\mathrm{d}r_{12}\right)\end{aligned}$$

$$\begin{aligned}p &= -\frac{\partial F}{\partial V} = \beta^{-1}\frac{\partial}{\partial V}\log(Q) = \beta^{-1}\frac{\partial}{\partial V}\log(Z) \\ &= \beta^{-1}\frac{\partial}{\partial V}\left[V^N\left(1-\frac{N(N-1)}{2V}\int 4\pi r^2\left(1-e^{-\beta u(r)}\right)\mathrm{d}r\right)\right] \\ &\approx \beta^{-1}\left[NV^{-1}-\frac{\partial}{\partial V}\frac{N^2}{V}\int 2\pi r^2\left(1-e^{-\beta u(r)}\right)\mathrm{d}r\right] \\ &= \beta^{-1}\frac{N}{V}+\beta^{-1}\frac{N^2}{V^2}\int 2\pi r^2\left(1-e^{-\beta u(r)}\right)\mathrm{d}r \\ &= kT\rho + kT\rho^2 B_2(T)\end{aligned}$$

Liquids

$$p = kT\frac{\partial}{\partial V}\log(Z) = kT\frac{\frac{\partial Z}{\partial V}}{Z}$$

$$r_k = V\bar{r}_k$$

$$Z = \int^V\cdots\int^V e^{-\beta U}\prod_i\mathrm{d}r_i = V^N\int^1\cdots\int^1 e^{-\beta U}\prod_i\mathrm{d}\bar{r}_i$$

$$\frac{\partial Z}{\partial V} = NV^{N-1}\int^1 e^{-\beta U}\prod_i\mathrm{d}\bar{r}_i - \beta V^N\int^1\frac{\partial U}{\partial V}e^{-\beta U}\prod_i\mathrm{d}\bar{r}_i$$

$$\frac{\partial U}{\partial V} = \sum_{i>j}\frac{\partial u(r_{ij})}{\partial V} = \sum_{i>j}\frac{\partial u(r_{ij})}{\partial r_{ij}}\frac{\partial r_{ij}}{\partial V}$$

$$r_{ij} = \sqrt{(x_i-x_j)^2+(y_i-y_j)^2+(z_i-z_j)^2} = V^{1/3}\bar{r}_{ij}$$

$$\frac{\partial r_{ij}}{\partial V} = \frac{\partial}{\partial V}V^{1/3}\bar{r}_{ij} = \frac{\bar{r}_{ij}}{3V^{2/3}} = \frac{r_{ij}}{3V}$$

$$\begin{aligned}\frac{\partial}{\partial V}\log(Z) &= \frac{N}{V} - \frac{N(N-1)}{6VkT}\int_V r_{12}\frac{\mathrm{d}u}{\mathrm{d}r_{12}}e^{-\beta\sum_{i\neq j}u_{ij}}\mathrm{d}r_1\ldots\mathrm{d}r_N \\ &= \frac{N}{V} - \frac{N(N-1)}{6VkTZ}\int_V r_{12}\frac{\mathrm{d}u}{\mathrm{d}r_{12}}\left[\int_V e^{-\beta U}\mathrm{d}r_3\ldots\mathrm{d}r_N\right]\mathrm{d}r_1\mathrm{d}r_2\end{aligned}$$

Particle in a Box

$$\begin{aligned}Q &= \sum_{n_x,n_y,n_z}e^{-\beta\frac{\hbar^2\pi^2}{2MV^{2/3}}(n_x^2+n_y^2+n_z^2)} \\ &\approx \int_0^\infty e^{-\beta\frac{\hbar^2\pi^2}{2MV^{2/3}}(n_x^2+n_y^2+n_z^2)}\mathrm{d}n_x\mathrm{d}n_y\mathrm{d}n_z \\ &= \frac{1}{8}\left(\frac{2MV^{2/3}}{\beta\hbar^2\pi}\right)^{3/2} = \left(\frac{M}{2\beta\hbar^2\pi}\right)^{3/2}V\end{aligned}$$

N indistinguishable particles:

$$Q = \frac{1}{N!}\left(\frac{M}{2\beta\hbar^2\pi}\right)^{3N/2}V^N$$

Reaction

$$K = \frac{P_{Na_2}}{P_{Na}^2} = \frac{V}{kT}\frac{N_{Na_2}}{N_{Na}^2}$$
$$dN = dN_{Na_2} = -1/2 dN_{Na}$$
$$dF = -\mu_{Na}dN_{Na} - \mu_{Na_2}dN_{Na_2} = (2\mu_{Na} - \mu_{Na_2})dN = 0$$

$2\mu_{Na} = \mu_{Na_2}$

$$\begin{aligned}\mu_{Na} &= -kT\frac{\partial}{\partial N_{Na}}\log\left[\frac{Q_{Na}^{N_{Na}}Q_{Na_2}^{N_{Na_2}}}{N_{Na}!N_{Na_2}!}\right]\\ &\approx -kT\frac{\partial}{\partial N_{Na}}[N_{Na}\log(Q_{Na})] + kT\frac{\partial}{\partial N_{Na}}[N_{Na}\log(N_{Na}) - N_{Na}]\\ &= -kT\log(Q_{Na}) + kT\log(N_{Na})\\ &= kT\log\left(\frac{N_{Na}}{Q_{Na}}\right)\end{aligned}$$

$$\frac{Q_{Na_2}}{Q_{Na}^2} = \frac{N_{Na_2}}{N_{Na}^2}$$

Poisson-Boltzman Equation

$$\begin{aligned}\nabla^2\phi(r) &= -\frac{4\pi}{\epsilon}\sum_s c_s q_s e^{-\beta q_s \phi(r)}\\ &\approx -\frac{4\pi}{\epsilon}\sum_s c_s q_s[1-\beta q_s\phi(r)]\\ &= \frac{4\pi\beta}{\epsilon}\sum_s c_s q_s^2\phi(r) = \kappa^2\phi(r)\end{aligned}$$

$$\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}\phi}{\mathrm{d}r}\right) = \kappa^2\phi(r)$$
$$\phi(r) = A\frac{e^{-\kappa r}}{r} + \cancel{B\frac{e^{\kappa r}}{r}}$$
$$\phi(r) = \frac{q}{\epsilon r(1+\kappa a)}e^{-\kappa(r-a)}$$
$$Q = \int_a^\infty \rho(r)4\pi r^2\mathrm{d}r = -\frac{\epsilon}{4\pi}\int_a^\infty(\nabla^2\phi)4\pi r^2\mathrm{d}r$$

Probability to find ion within $r + \mathrm{d}r$ is

$$\rho(r)4\pi r^2\mathrm{d}r = \frac{q\kappa^2 r}{1+\kappa a}e^{-\kappa(r-a)}\mathrm{d}r$$

Boltzmann Equation

$$\frac{\partial f_i}{\partial t} + v_i\frac{\partial f_i}{\partial r} + \frac{F_i}{m_i}\frac{\partial f_i}{\partial v_i} = \sum_j\int[f_i'f_j' - f_if_j]g_{ij}2\pi b\mathrm{d}b\mathrm{d}v_i$$

$$H(t) = \int f(r,v,t)\log[f(r,v,t)]\mathrm{d}r\mathrm{d}v$$

$$\begin{aligned}\frac{\mathrm{d}H}{\mathrm{d}t} &= \int\frac{\partial f}{\partial t}\log(f)\mathrm{d}r\mathrm{d}v + \cancel{\int\frac{\partial f}{\partial t}\mathrm{d}r\mathrm{d}v}\\ &= \cancel{-\int\log(f)v\frac{\partial f}{\partial r}\mathrm{d}r\mathrm{d}v - \int\log(f)\frac{F}{m}\frac{\partial f}{\partial v}\mathrm{d}r\mathrm{d}v}\\ &+\int\log(f)[f'f_1' - ff_1]g2\pi b\mathrm{d}b\mathrm{d}v\mathrm{d}r\\ &= \int\log(f)[f'f_1' - ff_1]g2\pi b\mathrm{d}b\mathrm{d}v\mathrm{d}r\\ &= \int\log(f_1)[f'f_1' - ff_1]g2\pi b\mathrm{d}b\mathrm{d}v\mathrm{d}r\\ &= -\int\log(f')[f'f_1' - ff_1]g2\pi b\mathrm{d}b\mathrm{d}v\mathrm{d}r\\ &= -\int\log(f_1')[f'f_1' - ff_1]g2\pi b\mathrm{d}b\mathrm{d}v\mathrm{d}r\\ &= \frac{1}{4}\int\log\left(\frac{ff_1}{f'f_1'}\right)[f'f_1' - ff_1]2\pi b\mathrm{d}b\mathrm{d}r\mathrm{d}v\end{aligned}$$

Work out Verlet Algorithm on paper

Umbrella Sampling

$$\begin{aligned}P(q_0) &= \frac{\left\langle\delta(q(X)-q_0)e^{\beta V(q)}\right\rangle_{U+V}}{\left\langle e^{\beta V(q)}\right\rangle_{U+V}}\\ &= \frac{e^{\beta V(q_0)}\left\langle\delta(q(X)-q_0)\right\rangle_{U+V}}{\left\langle e^{\beta V(q)}\right\rangle_{U+V}}\end{aligned}$$

Prokaryotic cell Primitive cell without a nucleus

Cytoplasm Internal cell fluid - no compartments

Cell wall Rigid layer surrounding some cells. Prevents over expansion due to osmotic pressure

Cell membrane Collection of phospholipids that form a bilayer and define the boundary between inside and outside of all cells

Capsule External layer on prokaryotic cells. Made of sugar, extra protection

Ribosome Compartment in which protein synthesis takes place from information provided by RNA

Golgi apparatus Organelle that packages biomolecules for delivery.

Golgi vesicles Vesicles that transport enzymes and other material through ER to Golgi body

Smooth ER Synthesizes lipids and steroids

Rough ER Synthesizes proteins

Nucleus Where genetic material is stored

Mitochondrion Organelle that generates ATP

Lysosome Organelle that breaks up waste materails