Chapter 3: The Canonical Ensemble

In canonical ensemble, energy is allowed to fluctuate, and we will only fix average

Section 1 Equilibrium between a system and a heat reservoir
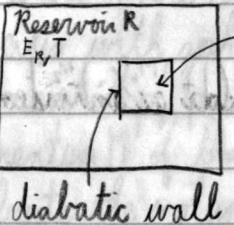
A = system

If A is in equilibrium with the reservoir, the systems have a common temperature

E_A & E_R change with time, but $E_{tot} = E_R + E_A$ is constant
- E_A, E_R characterize the different states
- Since reservoir is much larger than A, $E_A << E_R$
- From "a priori equal probability," expect
$$P(E_A) \propto \Omega_R(E_R)$$
$$S_R = k \ln \Omega_R(E_{tot} - E_A) \approx S_k(E_{tot}) - E_A \cdot \frac{\partial S_R(E)}{\partial E}\Big|_{E=E_{tot}} + \mathcal{O}\left(\frac{E_A}{E_{tot}}\right)^2$$
- If the system is in equilibrium: $\frac{\partial S_R}{\partial E} = \frac{1}{T}$
$$S_R(E_{tot} - E_A) \approx S_R(E_{tot}) - \frac{E_A}{T} = k \ln \Omega_R$$
$$P(E_A) \propto exp\left(\frac{S_R}{kT}\right) = exp(-\beta E_A)$$
$$P_r = \frac{exp(-\beta E_r)}{\sum exp(-\beta E_r)}$$

Section 2 A system in the canonical ensemble

Consider an ensemble of $\mathcal{N}$ identical systems with total energy $\mathcal{E}$. Can break $\mathcal{N}$ into the microstates n_r with associated energy E_r
$$\sum_r n_r = \mathcal{N}$$
$$\sum_r n_r E_r = \mathcal{E}$$
- $W\{n_r\} = $ # of realizations of states of whole system with a set of integers $\{n_r\}$
$$= \frac{\mathcal{N}!}{n_0! n_1! \dots n_r!}$$

$$\Gamma[\mathcal{U}, n_r; \{\omega_r\}] = \sum_{\{n_r\}}' W\{n_r\} \omega_0^{n_0} \omega_1^{n_1} \dots$$
$$\langle n_r \rangle = \frac{\partial}{\partial \omega_r} \ln \Gamma\Big|_{\omega_r = 1} \propto P_r$$
Generating function: $G(n, z) = \sum_{\mathcal{U}=0}^{\mathcal{U}} \Gamma[\mathcal{U}, n] z^{z\mathcal{U}}$
$$\Gamma = \oint \frac{dz}{2\pi i} \cdot \frac{1}{z^{n_{tot}}} \left[\sum_r \omega_r z^{E_r}\right]^n = \oint \frac{dz}{2\pi i} I(z)$$

Section 3. Physical significance of the various statistical quantities

- Call $x_0 = exp(-\beta)$
- $P_r = \frac{\langle n_r \rangle}{n} = \frac{exp(-\beta E_r)}{\sum exp(-\beta E_r)}$ Canonical distribution
- $\beta = \frac{1}{k_B T}$ Definition of temperature in canonical ensemble
- $\mathcal{U} = \frac{\sum_r E_r exp(-\beta E_r)}{\sum_r exp(-\beta E_r)} = -\frac{\partial}{\partial \beta} \ln \sum_r exp(-\beta E_r)$
- Helmholtz free energy
- $A = \mathcal{U} - TS$
$$dA = -S dT - P dV + \mu dN$$
- From this, we can determine certain thermodynamic relationships
$$S = -\left(\frac{\partial A}{\partial T}\right)_{N,V}$$
$$P = -\left(\frac{\partial A}{\partial V}\right)_{N,T}$$
$$\mu = \left(\frac{\partial A}{\partial N}\right)_{V,T}$$
$$\mathcal{U} = A + TS = A - T\left(\frac{dA}{dT}\right)_{N,V} = A + \beta \frac{\partial A}{\partial \beta}\Big|_{N,V} = \frac{\partial}{\partial \beta}(\beta A)_{N,V}$$
- $\langle n_r \rangle = n_r^*$. Large $\mathcal{N}$ makes the average the same as the most probable state
- Canonical ensemble allows much easier calculation
- Entropy of ideal gas
$$\sum_r \to \frac{1}{N!} \frac{1}{h^{3N}} \int d^3p_i d^3r_i \qquad E_r \to \sum_i \frac{p_i^2}{2m}$$
$$-\beta A = \ln \left\{\frac{1}{h^{3N}} \cdot \frac{1}{N!} V^N \prod \int exp\left(-\beta p_i^2 / 2m\right) d^3 p_i\right\}$$
$$= \ln \left\{\left[\frac{V}{h^3}\right]^N \frac{1}{N!} \left[\int exp\left(-\beta p^2 / 2m\right) d^3p\right]^N\right\}$$

$$Z = \sum_r \exp(-\beta E_r) \qquad \text{Partition function}$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V} = -T\left(\frac{\partial^2 A}{\partial T^2}\right)_{N,V}$$

$$G = A + PV = A - V\left(\frac{\partial A}{\partial V}\right)_{N,T} = N\left(\frac{\partial A}{\partial N}\right)_{V,T} = N\mu$$

$$S = k \ln \Omega$$

Section 9. Alternative expressions for the partition function

· Quantum paramagnet

   Dilute gas of atoms with magnetic dipole moment $\vec{\mu}$

$$\vec{\mu} = \left(\frac{ge}{2mc}\right)\vec{l}$$

$$l^2 = \hbar^2 J(J+1) \qquad J = \text{non-negative integer or half-integer}$$

$g = $ "Landé g-factor"

$g \cdot \frac{e}{2mc} = $ gyromagnetic ratio

$\mu_B = \frac{e\hbar}{2mc}$ Bohr magneton

Quantized value of $l_z \Rightarrow$ discrete values of $\mu_z = g\mu_B j_z$

Hamilton: $\mathcal{H} = \sum_i \frac{p_i^2}{2m} - H \sum_i \mu_{i,z}$

Partition function

$$Z = \frac{1}{N!}\left(\sum_{j_{z,1}=-J}^{\ldots} \cdots \sum_{j_{z,N}=-J}\right) \exp\left(\beta H \mu_0 \sum_i j_{z,i}\right) \cdot \exp\left(-\beta \sum_i \frac{p_i^2}{2m}\right) \frac{1}{h^{3N}} d^3p_1 \ldots d^3p_N$$

$$= Z_{\text{ideal gas}} \cdot \left[\sum_{j_z=-N}^{N} \exp(\beta H g \mu_0 j_z)\right]^N$$

$$Z_{1, \text{dipole}} = \sum_{j_z=-J}^{J} \exp(x j_z / J)$$

$$x = \beta g \mu_0 H J$$

· Virial and Equipartition function

Valid for classical system following Hamiltonian

dynamics with Hamiltonian $\mathcal{H}\{q_i, p_i\}$

Thermal average $\left\langle x_i \frac{\partial \mathcal{H}}{\partial x_j}\right\rangle = \frac{\int x_i \frac{\partial \mathcal{H}}{\partial x_j} \exp(-\beta \mathcal{H}) d\omega}{\int \exp(-\beta \mathcal{H}) d\omega}$

$$= kT \delta_{ij}$$

· Equipartition: Use $\left\langle p_i \frac{\partial \mathcal{H}}{\partial p_i}\right\rangle = k_B T$

$$\left\langle q_i \frac{\partial \mathcal{H}}{\partial q_i}\right\rangle = k_B T$$

Suppose $\mathcal{H} = \sum_{ij}(\dot{p}_i \ q_i) A_{ij} \binom{p_i}{q_j}$

$\binom{P_i}{Q_i} = \sum_j T_{ij} \binom{p_i}{q_i}$ Canonical transformation

   such that $\mathcal{H} = \sum_i \{A_i P_i^2 + B_i Q_i^2\}$

$\left\langle \sum_i \left(P_i \frac{\partial \mathcal{H}}{\partial P_i} + Q_i \frac{\partial \mathcal{H}}{\partial Q_i}\right)\right\rangle = \langle 2\mathcal{H}\rangle = f \cdot kT$

   where $f = $ #'s $A \neq B \neq 0$

$\langle \mathcal{H}\rangle = \frac{1}{2} f k_B T$

i.e. $\langle \mathcal{H}\rangle = N k_0 T \cdot$ degrees of freedom

· Virial Theorem: $\left\langle \sum_i q_i \frac{\partial \mathcal{H}}{\partial q_i}\right\rangle = -\left\langle \sum_i q_i \dot{p}_i\right\rangle$

· A divergence on Information entropy
S can be used to create a measure of ignorance about
the state of some system. Characterizes how hard it
is to encode a message and send it
$S_s = -\sum_i p_i \log_2 p_i$ Shannon entropy
1. Maximum if all possibilities are equally likely
2. Expect no change in entropy if adding events of zero
   probability
3. Additivity

Problems.

1. Pathria 3.4
Verify that the quantity $(k/N) \ln \Gamma$, where $\Gamma(N, U) = \sum'_{\{n_r\}} W\{n_r\}$
is equal to the (mean) entropy of the given system. Show
that this leads to essentially the same result for
$\ln \Gamma$ if we take, in the foregoing summation, only the largest
term of the sum, namely the term $W\{n_r^*\}$ that
corresponds to the most probable distribution set.
$\frac{1}{N} \ln \Gamma(N, U) = \ln\{\sum_r \omega_r \exp(-\beta E_r)\} + \beta U$
$\quad S = -k \langle \ln P_r \rangle = -k \sum_r P_r \ln P_r$
$\quad P_r = \frac{\exp(-\beta E_r)}{\sum_r \exp(-\beta E_r)}$
$\quad S = -k \sum_r \left(\frac{\exp(-\beta E_r)}{\sum_r \exp(-\beta E_r)} \cdot \ln \frac{\exp(-\beta E_r)}{\sum_r \exp(-\beta E_r)}\right)$ (1)

$U = A + TS$
$A = U - TS = -kT \sum_r \exp(-\beta E_r)$
$U = -\frac{d}{d\beta} \ln\{\sum_r \exp(-\beta E_r)\}$
$\quad = \beta \frac{\sum_r \exp(-\beta E_r)}{\sum_r \exp(-\beta E_r)}$

$\frac{k}{N} \ln \Gamma(N, U) = k \ln\{\sum_r \omega_r \exp(-\beta E_r)\} + k\beta U$
$\quad = -\frac{A}{T} + k\beta U$
$\quad = -\frac{A}{T} + \frac{U}{T}$
$\quad = \frac{U-A}{T} = S$
$\frac{k}{N} \ln \Gamma(N, U) = S$

$\ln W^* = \ln \Gamma = N \ln N - \sum_r C \exp(-\beta E_r) \ln[C \exp(-\beta E_r)]$
$\quad = N \ln N - \sum_r C \exp(-\beta E_r)[\ln C + \ln \exp(-\beta E_r)]$
$\quad = N \ln N + \sum_r \beta E_r C \exp(-\beta E_r) - \sum_r C \ln C \exp(-\beta E_r)$
$N = \sum_r n_r = \sum_r C \exp(-\beta E_r) = CQ$
$\ln W^* = CQ \ln(CQ) + \beta\langle E_r \rangle CQ - CQ \ln C$
$\quad = CQ \ln Q + CQ \beta \langle E_r \rangle$
$\frac{k}{N} \ln \Gamma = \frac{k}{CQ}(CQ \ln Q + CQ \beta \langle E_r \rangle)$
$\quad = k[\ln Q + \beta \langle E_r \rangle]$
$\quad = k\beta[U - A] = \frac{U-A}{T} = S$
$\frac{k}{N} \ln \Gamma = S$

2. Pathria 3.15
Show that the partition function $Q_N(V, T)$ of an extreme
relativistic gas consisting of N monatomic molecules with
energy-momentum relationship $\varepsilon = pc$, c being the speed of
light, is given by $Q_N(V, T) = \frac{1}{N!}\{8\pi V(\frac{kT}{hc})^3\}^N$. Study the
thermodynamics of this system, checking in particular
that $PV = \frac{U}{3}$, $\frac{U}{N} = 3kT$, & $\gamma = \frac{4}{3}$.
Next, using the inversion formula (3.4.7), derive an
expression for the density of states $g(E)$ of this
system.

$$\mathcal{H} = \sum_{i=1}^{N} p_i c$$

$$Q_N = \frac{1}{N! h^{3N}} \int \exp\left(-\beta \sum p_i c\right) d^3 q_1 \ldots d^3 q_N \, d^3 p_1 \ldots d^3 p_N$$

Note that Pathria uses Q_N to denote the partition function while Fertig uses Z (from the German Zustandssumme)

$$= \frac{V^N}{N! h^{3N}}\left[\int_0^\infty \exp(-pc\beta) \cdot 4\pi p^2 \, dp\right]^N$$

$$= \frac{V^N}{N! h^{3N}}\left[4\pi \left(\frac{-(c^2\beta^2 p^2 + 2c\beta p + 2)\exp(-pc\beta)}{(c\beta)^3}\right)\Big|_0^\infty\right]^N$$

$$= \frac{V^N}{N! h^{3N}}\left[\frac{4\pi \cdot 2}{(c\beta)^3}\right]^N = \frac{1}{N!}\left[8\pi V\left(\frac{kT}{hc}\right)^3\right]^N$$

$$A = -kT \ln Q_N = -kT\left[N \ln\left(8\pi V\left(\tfrac{kT}{hc}\right)^3\right) - N\ln N + N\right]$$

$$= -kT\left[N\ln\left(\tfrac{8\pi V}{N}\left(\tfrac{kT}{hc}\right)^3\right) + N\right] = -kTN\left[\ln\left(\tfrac{8\pi V}{N}\left(\tfrac{kT}{hc}\right)^3\right) + 1\right]$$

$$P = -\left(\tfrac{\partial A}{\partial V}\right)_{N,T} = \frac{kTN}{\tfrac{8\pi}{N}\left(\tfrac{kT}{hc}\right)^3} \cdot \frac{8\pi}{N} \cdot \left(\tfrac{kT}{hc}\right)^3 = \frac{kTN}{V}$$

$$PV = kTN$$

$$U = -T^2\left[\tfrac{\partial}{\partial T}\left(\tfrac{A}{T}\right)\right]_{N,V} = -T^2 \tfrac{\partial}{\partial T}\left(-kN\ln\left(\tfrac{8\pi V}{N}\left(\tfrac{kT}{hc}\right)^3\right) + 1\right)$$

$$= \frac{T^2 kN}{\tfrac{8\pi}{N}\left(\tfrac{kT}{hc}\right)^3} \cdot \tfrac{8\pi V}{N}\left(\tfrac{k}{hc}\right)^3 \cdot 3T^2 = 3kNT$$

$$PV = \tfrac{1}{3}U$$

$$U/N = 3kT$$

$$C_v = \left(\tfrac{\partial U}{\partial T}\right)_{N,V} = 3kN$$

$$C_p = \left(\tfrac{\partial(U+PV)}{\partial T}\right)_{N,V} = 4kN$$

$$\gamma = C_p/C_v = 4/3$$

$$g(E) = \tfrac{1}{2\pi i}\int_{\beta'-i\infty}^{\beta'+i\infty} \exp(\beta E) Q(\beta)\, d\beta$$

$$= \tfrac{1}{2\pi i}\int_{\beta'-i\infty}^{\beta'+i\infty} \exp(\beta E) \cdot \tfrac{1}{N!}\left\{8\pi V\left(\tfrac{1}{hc\beta}\right)^3\right\}^N d\beta$$

$$= \frac{(8\pi V)^N}{2\pi i (hc)^{3N} N!}\int_{\beta'-i\infty}^{\beta'+i\infty} \frac{\exp(\beta E)}{\beta^{3N}}\, d\beta \qquad \text{pole at } \beta = 0$$

Using Cauchy's integral formula $f^{(n)}(a) = \frac{n!}{2\pi i}\oint \frac{f(z)}{(z-a)^{n+1}}\,dz$

$$f(z) = \exp(\beta E)$$
$$3N = n+1$$

$$g(E) = \frac{(8\pi V)^N}{2\pi i (hc)^{3N} N!} \cdot \frac{2\pi i}{(3N-1)!}\, f^{3N-1}(0)$$

$$= \frac{(8\pi V)^N}{(hc)^{3N}(3N-1)! N!} \cdot E^{3N-1}\,\exp(0)$$

$$= \frac{(8\pi V)^N}{(hc)^{3N}(3N-1)! N!} \cdot E^{3N-1} \qquad E > 0$$

$$= 0 \qquad E < 0 \;\; \text{since the contour does not enclose a pole}$$

3. Interacting Spins

A system consists of N clusters. Each cluster is made up of two spin-½ particles, each having a magnetic moment $\vec{\mu} = \frac{2\mu S}{\hbar}$. The system is placed in an external magnetic field H at temperature T. The Hamiltonian for each cluster is
$$\mathcal{H} = \frac{J}{\hbar^2} S_z(1) S_z(2) - \frac{2\mu}{\hbar} H[S_z(1) + S_z(2)],$$
where $J \neq \mu$ are positive constants.

a. List all possible microscopic states (corresponding to $S_z = \pm\frac{\hbar}{2}$ for each spin, so there should be a total of four) for each cluster, and give their energies. Sketch the energy levels as a function of H.

$$\left(\tfrac{\hbar}{2}, \tfrac{\hbar}{2}\right): \mathcal{H} = \tfrac{J}{4} - 2\mu H$$

$$\left(\tfrac{\hbar}{2}, -\tfrac{\hbar}{2}\right) = \left(-\tfrac{\hbar}{2}, \tfrac{\hbar}{2}\right): \mathcal{H} = -\tfrac{J}{4}$$
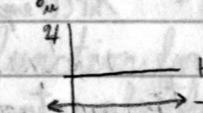
$$\left(-\tfrac{\hbar}{2}, -\tfrac{\hbar}{2}\right): \mathcal{H} = \tfrac{J}{4} + 2\mu H$$
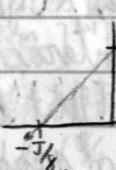
b. Obtain the partition function for this system $Z(T, H)$ in the canonical ensemble, and determine the Helmholtz free energy A.

$$Z = \left(\sum_i \exp(-\beta E_i) \right)^N$$
$$= \left[\exp\left(\beta\left(-\tfrac{J}{4} + 2\mu H\right)\right) + 2\exp\left(\tfrac{\beta J}{4}\right) + \exp\left(\beta\left(-\tfrac{J}{4} - 2\mu H\right)\right) \right]^N$$
$$= \left(\exp\left(\tfrac{-J\beta}{4}\right)\right)^N \left[\exp(2\beta\mu H) + 2\exp\left(\tfrac{J\beta}{2}\right) + \exp(-2\beta\mu H) \right]^N$$
$$= \left(2\exp\left(\tfrac{-J\beta}{4}\right)\right)^N \left[\cosh(2\beta\mu H) + \exp\left(\tfrac{J\beta}{2}\right)\right]^N \cdot \tfrac{1}{N!}$$

$$A = -kTN \ln\left[\tfrac{1}{N!}\left(2\exp\left(\tfrac{-J\beta}{4}\right)\left\{\cosh(2\beta\mu H) + \exp\left(\tfrac{J\beta}{2}\right)\right\}\right) \right]$$

c. Obtain an expression for the magnetization $M(T, H)$ for this system, and find the spin susceptibility $\chi(T) = \lim\limits_{H\to 0} \frac{\partial M}{\partial H}$.

$$M = \frac{1}{\beta Z} \cdot \frac{\partial Z}{\partial H}$$
$$Z = \tfrac{1}{N!}\left[2\exp\left(\tfrac{-J\beta}{4}\right)\left\{\cosh(2\beta\mu H) + \exp\left(\tfrac{J\beta}{2}\right)\right\}\right]^N$$
$$\frac{\partial Z}{\partial H} = \frac{(2\exp(\tfrac{-J\beta}{4}))^N}{N!} \cdot N\left[\cosh(2\beta\mu H) + \exp\left(\tfrac{J\beta}{2}\right)\right]^{N-1} \sinh(2\beta\mu H) \cdot 2\beta\mu$$
$$M = \frac{N!\,(2\exp(\tfrac{-J\beta}{4}))^N}{\beta(2\exp(\tfrac{-J\beta}{4}))^N} \cdot \frac{2\beta\mu N}{N!} \cdot \frac{\left[\cosh(2\beta\mu H) + \exp(\tfrac{J\beta}{2})\right]^{N-1}}{\left[\cosh(2\beta\mu H) + \exp(\tfrac{J\beta}{2})\right]^N}\sinh(2\beta\mu H)$$
$$= \frac{2\mu N \sinh(2\beta\mu H)}{\cosh(2\beta\mu H) + \exp(\tfrac{J\beta}{2})}$$
$$\frac{\partial M}{\partial H} = \frac{2\mu\cdot 2\beta\mu N\cosh(2\beta\mu H)\left[\cosh(2\beta\mu H) + \exp(\tfrac{J\beta}{2})\right] + 2\beta\mu\sinh(2\beta\mu H)\cdot 2\mu N\sinh(2\beta\mu H)}{\left(\cosh(2\beta\mu H) + \exp(\tfrac{J\beta}{2})\right)^2}$$
$$= \frac{4\beta\mu^2 N(1 + \exp(\tfrac{J\beta}{2}))}{\left(\cosh(2\beta\mu H) + \exp(\tfrac{J\beta}{2})\right)^2}$$
$$\chi(T) = \frac{4\beta\mu^2 N}{1 + \exp(\tfrac{J\beta}{2})} = \frac{4\mu^2 N}{kT(1 + \exp(\tfrac{J\beta}{2}))}$$

d. Show that at a high temperature, $\chi^{-1}(T) = \frac{T + \Theta}{C}$ where $C \propto \mu^2$ is the Curie constant for non-interacting spins, and $\Theta \propto J$. This shows that measuring $\chi(T)$ at high temperatures can reveal both the presence of magnetic moments in the material, and, by determining Θ, the energy scale characterizing interactions between the moments.

$$\chi^{-1}(T) = \frac{kT + kT\exp(\tfrac{J/2}{kT})}{4\mu^2 N} \approx \frac{kT + kT(1 + \tfrac{J/2}{kT})}{4\mu^2 N} \qquad \exp(x) \approx 1 + x \text{ by Taylor expansion}$$
$$= \frac{2kT + \tfrac{J}{2}}{4\mu^2 N} \approx \frac{T + \Theta}{C}$$

4. Toy Model for Diatomic Molecules

Consider a classical system of N noninteracting diatomic molecules in a box of volume V at temperature T. The Hamiltonian for a single molecule is taken to be

$$\mathcal{H}(\vec{p}_1, \vec{p}_2, \vec{r}_1, \vec{r}_2) = \tfrac{1}{2m}(p_1^2 + p_2^2) + \tfrac{1}{2}K|\vec{r}_1 - \vec{r}_2|^2, \text{ where}$$

$\vec{p}_1, \vec{p}_2, \vec{r}_1, \vec{r}_2$ are the momenta and coordinates of the two atoms in a molecule. (Note that this is a poor model of an actual diatomic molecule due to the fact that the equilibrium displacement of the spring is 0. The results you obtain will not correspond to the expected results for a real diatomic gas).

a. Obtain the partition function for a single molecule, $Q_1(T, V)$.
$$\mathcal{H} = \tfrac{1}{2m}(p_1^2 + p_2^2) + \tfrac{K}{2}r^2 \quad \text{where } r = |\vec{r}_1 - \vec{r}_2|$$
$$Z_1 = \tfrac{1}{2!}\cdot\tfrac{1}{h^6}\int \exp(-\beta\mathcal{H})\,dp_1\,dp_2\,dr\,dR$$
$$= \tfrac{1}{2h^6}\cdot V(4\pi)^3\left(\int_0^\infty p^2\exp\left(\tfrac{-\beta p^2}{2m}\right)dp\right)^2\left(\int_0^\infty r^2\exp\left(\tfrac{-\beta Kr^2}{2m}\right)dr\right)$$
$$= \frac{V(4\pi)^3}{2h^6}\cdot\frac{1}{4^2(\tfrac{\beta}{2m})^2}\cdot\frac{\pi}{\tfrac{\beta}{2m}}\cdot\frac{1}{4(\tfrac{\beta K}{2})}\left(\frac{\pi}{\tfrac{\beta K}{2}}\right)^{1/2}$$
$$= \frac{V}{2}\left[\frac{2\pi m}{h^2\beta}\right]^3\left[\frac{2\pi}{K\beta}\right]^{3/2}$$

b. Determine the partition function for N molecules, and find the Helmholtz free energy of the system
$$Z_N = \frac{(Z_1)^N}{N!} = \frac{1}{N!}\left(\frac{V}{2}\right)^N\left[\frac{2\pi m}{h^2\beta}\right]^{3N}\left[\frac{2\pi}{K\beta}\right]^{3N/2}$$
$$A = -k_B T\ln Z_N = -k_B T\left[-\ln N! + N\ln\left(\tfrac{V}{2}\right) + 3N\ln\left(\tfrac{2\pi m}{h^2\beta}\right) + \tfrac{3N}{2}\ln\left(\tfrac{2\pi}{K\beta}\right)\right]$$
$$= -k_B T\left[-N\ln N + N + N\ln\left(\tfrac{V}{2}\right) + 3N\ln\left(\tfrac{2\pi m}{h^2\beta}\right) + \tfrac{3N}{2}\ln\left(\tfrac{2\pi}{K\beta}\right)\right]$$
$$= -k_B T N\left\{\ln\left[\frac{V}{2N}\left(\frac{2\pi m}{h^2}\right)^3\left(\frac{2\pi}{K}\right)^{3/2}(k_B T)^{9/2}\right] + 1\right\}$$

c. Show that this gas obeys the same equation of state as that of a monatomic ideal gas

$$P = -\left(\frac{\partial A}{\partial V}\right) = k_B T N \cdot \frac{2N}{V}\left(\frac{h^2}{2\pi m}\right)^3 \left(\frac{K}{2\pi}\right)^{3/2} (k_B T)^{-9/2} \cdot \frac{1}{2N}\left(\frac{2\pi m}{h^2}\right)^3 \left(\frac{2\pi}{K}\right)^{3/2} (k_B T)^{9/2}$$

$$= k_B T N / V$$

$$PV = N k_B T$$

d. Determine the internal energy of this gas and show that your result is consistent with the equipartition theorem

$$U = \frac{\partial}{\partial \beta}(\beta A) = \frac{\partial}{\partial \beta}\left(-N \ln\left[\frac{V}{2N}\left(\frac{2\pi m}{h^2}\right)^3 \left(\frac{2\pi}{K}\right)^{3/2} (\beta)^{-9/2}\right] - N\right)$$

$$= -N \cdot \frac{2N}{V}\left(\frac{h^2}{2\pi m}\right)^3 \left(\frac{2\pi}{K}\right) \beta^{9/2} \cdot \frac{V}{2N}\left(\frac{2\pi m}{h^2}\right)^3 \left(\frac{2\pi}{K}\right)^{3/2} \cdot -9/2 \beta^{-11/2}$$

$$= 9/2\, N k_B T$$

Equipartition theorem: # quadratic terms in H. 3 from p_1, 3 from p_2, 3 from r for 9 total

$$\Rightarrow E = 9/2\, N k_B T$$

e. Find the specific heat at constant volume for this gas. Note this result is different than what you may have learned in the past about specific heat of a real diatomic gas at room temperature. We will discuss in detail the correct treatment of a gas of diatomic molecules later.

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V} = 9/2\, N k_B$$

f. Find the mean square molecular diameter $\langle |\vec{r}_1 - \vec{r}_2|^2 \rangle$ as a function of temperature.

$$\langle |\vec{r}_1 - \vec{r}_2| \rangle = -1/\beta \frac{\partial}{\partial K}(\ln Z_1)$$

$$= -1/\beta \cdot N \cdot \frac{2}{V}\left(\frac{h^2}{2\pi m k_B T}\right)^3 \left(\frac{K}{2\pi k_B T}\right)^{3/2} \cdot \frac{V}{2}\left(\frac{2\pi m k_B T}{h^2}\right)^3 \cdot (2\pi k_B T)^{3/2} \cdot -3/2 K^{-5/2}$$

$$= 3 k_B T / K$$