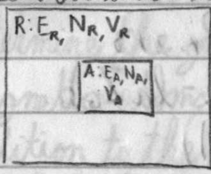
He sleeps. Though fate dealt with him strongly, he lived. Bereft of his angel, he died. It came about simply, of itself, as night follows when the day is ended. - Jean val Jean's epitaph (Victor Hugo, The Wretched).

Chapter 4: The Grand Canonical Ensemble

We've seen the microcanonical and canonical ensembles, so now let's introduce the final ensemble: the grand canonical ensemble. In the grand canonical ensemble, the thermodynamic variables are μ, V, and T. Imagine we have a system embedded in a reservoir with the walls permeable to heat and particles.



The total number of particles in both should be constant as well as the total energy. In addition, we assume the system is small, i.e.

$$E_R + E_A = E_{tot} = \text{constant} \qquad E_A/E_{tot} \ll 1$$
$$N_R + N_A = N_{tot} = \text{constant} \qquad N_A/N_{tot} \ll 1$$

We expect that the probability of the system to have E_A + N_A to be related to the number of microstates available to the reservoir.

$$P(E_A, N_A) \propto \Omega_R(E_{tot} - E_A, N_{tot} - N_A)$$

Let's attempt to calculate the entropy of the reservoir

$$\begin{aligned} S_R &= k_B \ln \Omega_R(E_{tot} - E_A, N_{tot} - N_A) \\ &\simeq k_B \ln \Omega_R(E_{tot}, N_{tot}) - E_A\left(\frac{\partial S}{\partial E}\right)_{E_{tot}, N_{tot}} - N_A\left(\frac{\partial S}{\partial N}\right)_{E_{tot}, N_{tot}} \\ &= k_B \ln \Omega_R(E_{tot}, N_{tot}) - E_A/T + \mu N_A/T \end{aligned}$$

$$P_{E_A, N_A} = \frac{\exp\left(-(E_A - \mu N_A)/k_B T\right)}{\sum_r \exp\left(-(E_A(r) - \mu N_A(r))/k_B T\right)}$$

where $Z_G = \sum_r \exp\left(-(E_A(r) - \mu N_A(r))/k_B T\right)$ is the grand partition function.

If we do a little bit of rearranging,

$$\begin{aligned} Z_G &= \sum_{N_A} \exp(\mu N_A/k_B T) \exp(-E_A/k_B T) \\ &= \sum_{N_A} z^{N_A} Z_C(N_A) \end{aligned}$$

where Z_C is the canonical partition function, and $z = \exp(\mu/k_B T)$ is the fugacity.

Let's now define $\alpha = -\mu/k_B T$ and $\beta = 1/k_B T$, which lets us rewrite

$$Z_G = \sum_r \exp(-\alpha N_A - \beta E_A)$$

$$\langle E_A \rangle = -\frac{\partial}{\partial\beta} \ln Z_G = -\sum_r -E_A \exp(-\beta E_A - \alpha N_A)$$
$$= \sum_r E_A \exp(-\beta E_A - \alpha N_A)$$
$$\langle N_A \rangle = -\frac{\partial}{\partial\alpha} \ln Z_G = -\sum_r -N_A \exp(-\beta E_A - \alpha N_\alpha)$$
$$= \sum_r N_A \exp(-\beta E_A - \alpha N_A)$$

☆ Entropy in Grand Canonical Ensemble

We recall from before that $S = -k_B \sum_r P_r \ln P_r$

$$S = -k_B \sum_r \frac{1}{Z_G} \exp(-\alpha N - \beta E)\cdot(-\alpha N - \beta E - \ln Z_G)$$
$$= k_B\{\alpha\langle N\rangle + \beta\langle E\rangle + \ln Z_G\}$$
$$= -\mu N/T + \mathcal{U}/T + k_B \ln Z_G$$
$$\Phi_G = -k_B T \ln Z_G = \mathcal{U} - \mu N - TS = A - \mu N$$

where we have defined Φ_G to be the grand potential.

Now making use of entropy as an extensive function, i.e.

$$S[\lambda\mathcal{U}, \lambda V, \lambda N] = \lambda S[\mathcal{U}, V, N]$$

If we differentiate by λ but then set $\lambda = 1$,

$$S[\mathcal{U},V,N] = \frac{\partial S}{\partial(\lambda\mathcal{U})}\cdot\frac{\partial(\lambda\mathcal{U})}{\partial\lambda} + \frac{\partial S}{\partial(\lambda V)}\cdot\frac{\partial(\lambda V)}{\partial\lambda} + \frac{\partial S}{\partial(\lambda N)}\cdot\frac{\partial(\lambda N)}{\partial\lambda}$$
$$= 1/T\cdot\mathcal{U} + P/T\cdot V - \mu/T\cdot N = S$$
$$TS = \mathcal{U} + PV - \mu N$$
$$-PV = \mathcal{U} - \mu N = -TS = \Phi$$

Thus we see that $\Phi = -k_B T \ln Z_G = -PV$

☆ Example: The Ideal Gas

$$Z_C = \frac{1}{N!}\left\{\frac{1}{h^3}\int \exp(-\beta p^2/2m)\, d^3x\, d^3p\right\}^N$$
$$= \frac{1}{N!}\left\{\frac{V}{h^3}\left(\frac{2\pi m}{\beta}\right)^{3/2}\right\}^N$$

Let's now define the de Broglie thermal wavelength

$$\lambda = \frac{h}{\sqrt{2\pi m k_B T}} = \left(\frac{2\pi\hbar^2}{m k_B T}\right)^{1/2}$$
$$Z_C = \frac{1}{N!}(V/\lambda^3)^N$$
$$Z_G = \sum_{n=0}^{\infty} z^n \cdot \frac{1}{n!}\left(\frac{V}{\lambda^3}\right)^n = \exp(zV/\lambda^3)$$
$$-\Phi_G = k_B T \ln Z_G = PV$$
$$k_B T z V/\lambda^3 = PV$$

Since $N = -\frac{\partial}{\partial\alpha} \ln Z_G = -\frac{\partial}{\partial\alpha} \frac{V}{\lambda^3} \exp(-\alpha)$

$$= \frac{V}{\lambda^3} \exp(\beta\mu) = Vz/\lambda^3$$

Which returns the ideal gas law

$$PV = N k_B T$$

☆ Example: Pathria 4.8

Determine the grand partition function of a gaseous system of "magnetic" atoms (with $J = 1/2$ and $g = 2$) that can have, in addition to the kinetic energy, a magnetic potential energy equal to $\mu_B H$ or $-\mu_B H$, depending on their orientation with respect to an applied magnetic field H. Derive an expression for the magnetization of the system, and calculate how much heat will be given off by the system when the magnetic field is reduced from H to 0 at constant volume and constant temperature.

The first thing we want to do is find the partition function

$$Z_1 = \sum_{s=\pm1} \frac{1}{h^3}\int \exp(-\beta p^2/2m)\exp(s\beta\mu_B H)\, d^3x\, d^3p$$
$$= \frac{V}{\lambda^3}\cdot 2\cosh(\beta\mu_B H)$$
$$Z_N = \frac{1}{N!} Z_1^N$$
$$Z_G = \sum_{N=0}^{\infty} \frac{1}{N!}\cdot z^N Z_1^N = \exp(zZ_1)$$

which is just $\exp(zVf(T))$

$$f(T) = \frac{1}{\lambda^3}\cdot 2\cosh(\mu_0 H/k_B T) = f_{gas}(T)\, f_{spin}(T)$$
$$\Phi_G = -k_B T z V f(T) = A - \mu N$$
$$dA = -S\,dT - P\,dV + \mu\,dN$$
$$d\Phi_G = -S\,dT - P\,dV + \mu\,dN - N\,d\mu - \mu\,dN$$
$$= -S\,dT - P\,dV - N\,d\mu$$
$$N = -\left(\frac{d\Phi}{d\mu}\right)_{T,V} = +k_B T\cdot\frac{1}{k_B T} zVf(T)$$
$$= zVf(T)$$

$$M = \frac{1}{\beta}\cdot\frac{\partial \ln Z_G}{\partial H}$$
$$= k_B T\cdot zVf_{gas}(T)\cdot\frac{\partial}{\partial H} f_{spin}(T)$$
$$= k_B T z V\cdot 1/\lambda^3\cdot 2\cdot\frac{\mu_B}{k_B T}\tanh(\mu_0 H/k_B T)$$
$$= N\mu_B \tanh(\mu_0 H/k_B T)$$

$$\Delta Q = T\Delta S$$

$$A = \Phi_G + \mu N = -k_B T N + (k_B T \ln z) N$$
$$= Nk_B T(\ln z - 1) = k_B T N\left(\ln \frac{N}{Vf(T)} - 1\right)$$

$$S = -\left(\frac{\partial A}{\partial T}\right)_{N,V} = Nk_B\left[1 - \ln\left(\frac{N}{Vf(T)}\right) + T\frac{\partial \ln f(T)}{\partial T}\right]$$
$$= Nk_B\left[1 - \ln\left(N/Vf_{gas}(T)\right) + T\frac{\partial \ln f_{gas}}{\partial T} + \ln f_{spin} + T\frac{\partial \ln f_{spin}}{\partial T}\right]$$

$$S = S_{gas} + Nk_B\left\{\ln\left(2\cosh\left(\mu_0 H/k_B T\right)\right) - \frac{\mu_0 H}{k_0 T}\tanh\left(\mu_0 H/k_B T\right)\right\}$$

$$\Delta S = S_{spin}(T, H=0) - S_{spin}(T,H)$$
$$= Nk_B\left(\frac{\mu_0 H}{k_0 T}\tanh\left(\mu_0 H/k_0 T\right) - \ln\left(\cosh\left(\mu_B H/k_0 T\right)\right)\right)$$

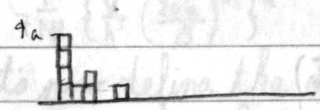
$$\Delta Q = Nk_B T\left[\mu_B H/k_0 T \tanh\left(\mu_0 H/k_0 T\right) - \ln\cosh\left(\mu_0 H/k_0 T\right)\right]$$

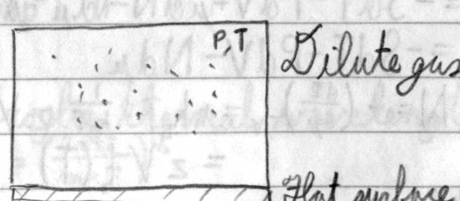
for $\mu_B H \gg k_B T$

$$\tanh\left(\mu_0 H/k_0 T\right) \to 1$$
$$\cosh\left(\mu_0 H/k_0 T\right) = \tfrac{1}{2}\exp(\beta\mu_B H)\left(1 + \exp(-2\beta\mu_B H)\right)$$
$$\ln\cosh\left(\mu_0 H/k_0 T\right) = -\ln 2 + \mu_0 H/k_0 T$$
$$\Delta Q = Nk_B T\left[\mu_0 H/k_0 T + \ln 2 - \mu_B H/k_0 T\right]$$
$$= Nk_B T\ln 2$$

☆ Example: Thin metallic film

To first order (I'm probably going to butcher this, so if you want to know more about this, ask your resident condensed matter physicist), there is a line on which atoms may be deposited. Each deposited atom has energy $-\varepsilon_0$, and atoms can stack. Each atom contributes height a to thickness $h(\vec{r})$





We would like to know the average height $\langle h\rangle$ as a function of P, T

In equilibrium, μ must be the same for atoms on the surface and in the gas (the ideal gas)

$$zV/\lambda^3 = N$$
$$PV = Nk_B T = zVk_B T/\lambda^3$$
$$e^{\beta\mu} = P\lambda^3/k_B T$$
$$\mu = k_B T\ln\left(\frac{P\lambda^3}{k_B T}\right)$$

$$Z_G^{surface} = \sum_{n_{site}}\exp\left\{-\beta\sum_{sites}(-\varepsilon_0 n_{site}) + \beta\mu\sum_{site} n_{site}\right\}$$

State characterized by $\{n_{site}\}$, the # atoms determines the height of the column

$$Z_G^{surf} = \sum_{n_0=0}^{\infty}\sum_{n_1=0}^{\infty}\cdots\exp\left\{-\beta\sum_{site=1}[-\varepsilon_0 - \mu]n_i\right\}$$
$$= \left[\sum_{n_0=0}^{\infty}\exp\{\beta[\varepsilon_0 + \mu]n\}\right]^A$$

$$\varepsilon_0 + \mu < 0$$
$$\mu < -\varepsilon_0$$
$$k_0 T\ln\left(\frac{P\lambda^3}{k_0 T}\right) < -\varepsilon_0$$
$$P \le \frac{k_B T}{\lambda^3}\exp\left(-\varepsilon_0/k_B T\right) = P_0$$

$$S = \sum_{n=0}^{\infty} e^{nx} = \frac{1}{1-e^x}$$
$$Z_G^{surf} = \left[1/1-\exp[\beta(\varepsilon_0-\mu)]\right]^A$$
$$\langle h\rangle = a\langle n\rangle = \frac{1}{A}\cdot\frac{a}{Z_G}\cdot\frac{1}{\beta}\cdot\frac{d}{d\mu}Z_G = a\exp[\beta(\varepsilon_0+\mu)]/1-\exp[\beta(\varepsilon_0-\mu)]$$
$$= \frac{a\,P/P_0}{1-P/P_0} = \frac{aP}{P_0 - P}$$

Problems

1. Mutual information

Consider a probability distribution for two different quantities x and y, $p(x,y)$, with normalization $\sum_{xy} p(x,y) = 1$. The unconditional probability to get a particular value of x is just $p_x(x) = \sum_y p(x,y)$, and there is a completely analogous form for the unconditional probability $p_y(y)$. The mutual information is defined as

$$M = \sum_{xy} p(x,y) \log_2\left(\frac{p(x,y)}{p_x(x)p_y(y)}\right)$$

a. Find a relation among the Shannon entropies associated with $p(x,y)$, $p_x(x)$, and $p_y(y)$, denoted respectively as S_{xy}, S_x, and S_y, and M.

$S_{xy} = -\sum_{xy} p(x,y) \log_2 p(x,y)$

$S_x = -\sum_x p_x(x) \log_2 p_x(x)$

$S_y = -\sum_y p_y(y) \log_2 p_y(y)$

$$M = \sum_{xy} p(x,y) \log_2 p(x,y) - \sum_{xy} p(x,y) \log_2 p_x(x) - \sum_{xy} p(x,y) \log_2 p_y(y)$$
$$= \sum_{xy} p(x,y) \log_2 p(x,y) - \sum_x \sum_y p(x,y) \log_2 p_x(x) - \sum_y \sum_x p(x,y) \log_2 p_y(y)$$
$$= \sum_{xy} p(x,y) \log_2 p(x,y) - \sum_x p_x(x) \log_2 p_x(x) - \sum_y p_y(y) \log_2 p_y(y)$$
$$= -S_{xy} + S_x + S_y$$

b. Recall our example from class involving keys and a wallet, each lost in one of five rooms in an apartment. The rooms in which these are located are denoted by x and y, respectively, so each has five possible values, but no one room is a more likely location than any other for either the keys or the wallet. The probability that the keys and wallet are both in some room x ($x = y$), $\frac{1}{25} + \Delta$, is greater than the probability that they are in separate rooms ($x \neq y$), $\frac{1}{25} - \frac{\Delta}{4}$. Compute the mutual information M for this situation, and show that it obeys the relation you derived in (a). What are the values of M when $\Delta = 0$, and when Δ takes on its maximum possible value?

$$p_x(x) = \sum_y p(x,y) = \frac{1}{25} + \Delta + 4\left(\frac{1}{25} - \frac{\Delta}{4}\right) = 1/5 = p_y(y)$$

$$M = 5\left(\frac{1}{25} + \Delta\right) \log_2\left(25\left(1/25 + \Delta\right)\right) + 20\left(1/25 - \Delta/4\right) \log_2\left(25\left(1/25 - \Delta/4\right)\right)$$
$$= 1/5 \log_2(1 + 25\Delta) + 4/5 \log_2(1 - 25\Delta/4) + 5\Delta \log_2(1 + 25\Delta) - 5\Delta \log_2(1 - 25\Delta/4)$$
$$= (1/5 + 5\Delta) \log_2(1 + 25\Delta) + (4/5 - 5\Delta) \log_2(1 - 25\Delta/4)$$

$$-S_{xy} + S_x + S_y = 5\left(\frac{1}{25} + \Delta\right) \log_2\left(1/25 + \Delta\right) + 20\left(\frac{1}{25} - \frac{\Delta}{4}\right) \log_2\left(\frac{1}{25} - \frac{\Delta}{4}\right) - 2 \log_2(1/5)$$
$$= 1/5 \log_2\left(\frac{1}{25} + \Delta\right) + \frac{4}{5} \log_2\left(\frac{1}{25} - \frac{\Delta}{4}\right) - 2 \log_2(1/5) + 5\Delta \log_2\left(\frac{1}{25} + \Delta\right) - 5\Delta \log_2\left(\frac{1}{25} - \frac{\Delta}{4}\right)$$

$\frac{1}{25} + \Delta = \frac{1 + 25\Delta}{25}$

$\frac{1}{25} - \frac{\Delta}{4} = \frac{1}{25}\left(1 - 25\Delta/4\right)$

$$-S_{xy} + S_x + S_y = \frac{1}{5} \log_2\left(\frac{1 + 25\Delta}{25}\right) + \frac{4}{5} \log_2\left(\frac{1}{25}\left(1 - \frac{25\Delta}{4}\right)\right) - 2 \log_2\left(\frac{1}{5}\right) + 5\Delta \log_2\left(\frac{1 + 25\Delta}{25}\right) - 5\Delta \log_2\left(\frac{1}{25}\left(1 - \frac{25\Delta}{4}\right)\right)$$
$$= \frac{1}{5} \log_2(1 + 25\Delta) + \frac{2}{5} \log_2\left(\frac{1}{5}\right) + \frac{4}{5} \log_2\left(1 - \frac{25\Delta}{4}\right) + \frac{8}{5} \log_2\left(\frac{1}{5}\right)$$
$$+ 5\Delta \log_2(1 + 25\Delta) + 10\Delta \log_2\left(\frac{1}{5}\right) - 5\Delta \log_2\left(1 - \frac{25\Delta}{4}\right) - 10\Delta \log_2\left(\frac{1}{5}\right)$$
$$= \left(\frac{1}{5} + 5\Delta\right) \log_2(1 + 25\Delta) + (4/5 - 5\Delta) \log_2(1 - 25\Delta/4)$$

$\Delta = 0$: $M = \frac{1}{5} \log_2(1) + \frac{4}{5} \log_2(1) = 0$

Δ_{max}: $\frac{1}{25} - \frac{\Delta}{4} = 0$

$\Delta = 4/25$

$$M = \left(\frac{1}{5} + \frac{4}{5}\right) \log_2(1 + 4) + \left(\frac{4}{5} - \frac{4}{5}\right) \log_2(1 - 1)$$
$$= \log_2(5)$$

2. Chemical equilibrium

Consider a system in equilibrium in which particles of different types $\{A_1, A_2, \ldots A_{M_A}\}$ undergo a reaction in which they combine to transform into another set of particles $\{B_1, B_2, \ldots, B_{M_B}\}$ according to

$$m_1 A_1 + m_2 A_2 + \ldots + m_{M_A} A_{M_A} \leftrightarrow n_1 B_1 + n_2 B_2 + \ldots + n_{M_B} B_{M_B}$$

where $\{m_i\}$, $\{n_i\}$ are integers.

a. Show that the chemical potentials for the various species $\{\mu_{A_i}\}$, $\{\mu_{B_j}\}$ obey the relation

$$m_1\mu_{A_1}+m_2\mu_{A_2}+\ldots+m_{n_A}\mu_{A n_A}=n_1\mu_{B_1}+n_2\mu_{B_2}+\ldots+n_{n_B}\mu_{B n_B}$$

We know that at equilibrium $\frac{\partial G}{\partial m_i}=0$ where G is the Gibbs free energy.

$$m_1A_1+m_2A_2+\ldots=n_1B_1+n_2B_2+\ldots$$

$$m_1A_1+m_2A_2+\ldots-n_1B_1-n_2B_2-\ldots=0$$

$$\frac{\partial G}{\partial m_1}=\frac{\partial G}{\partial m_1}+\frac{\partial G}{\partial m_2}\cdot\frac{\partial m_2}{\partial m_1}+\ldots-\frac{\partial G}{\partial n_1}\cdot\frac{\partial n_1}{\partial m_1}-\frac{\partial G}{\partial n_2}\cdot\frac{\partial n_2}{\partial m_1}-\ldots=0$$

$$\mu_i=\frac{\partial G}{\partial N_i}$$

$$0=\mu_{A_1}+\mu_{A_2}\cdot\frac{m_2}{m_1}+\ldots-\mu_{B_1}\cdot\frac{n_1}{m_1}-\mu_{B_2}\cdot\frac{n_2}{m_1}-\ldots$$

$$0=m_1\mu_{A_1}+m_2\mu_{A_2}+\ldots-\mu_{B_1}n_1-\mu_{B_2}n_2-\ldots$$

$$m_1\mu_{A_1}+m_2\mu_{A_2}+\ldots=n_1\mu_{B_1}+n_2\mu_{B_2}+\ldots$$

b. In the sun's corona, protons and electrons constantly combine into hydrogen atoms, which then later dissociate. Assume that after forming the hydrogen atoms are always in a 1s state with energy Δ when the atom is at rest. Treating all three constituents as ideal gases, show that the densities obey the relation $\rho_p\rho_e=\rho_H\left(\frac{m_e k_B T}{2\pi\hbar^2}\right)^{3/2}\exp(\Delta/k_BT)$, where ρ_p, ρ_e, and ρ_H are respectively the densities of the protons, electrons, and hydrogen atoms. (Note in writing this relation one assumes the mass of a proton is the same as the mass of a hydrogen atom, i.e. the mass of an electron m_e is negligible compared to the other two masses). This relation is an example of the law of mass action.

$$n_e\mu_e+n_p\mu_p=n_H\mu_H$$

$$Z_G=\sum_i\exp\left(\frac{N_i\mu-E_i}{k_BT}\right)$$

$$=\exp(\beta n_e\mu_e)+\exp(\beta n_p\mu_p)+\exp(\beta(n_H\mu_H-\Delta))$$

$$\langle N_p\rangle=\frac{1}{\beta}\cdot\frac{1}{Z_G}\beta n_p\exp(\beta n_p\mu_p)$$

$$=\frac{n_p}{Z_G}\exp(\beta n_p\mu_p)$$

$$Z_p=\frac{V}{\lambda_p^3}\exp(\beta\mu_p)$$

$$\rho_p\rho_e=\frac{Z_pZ_e}{V^2Z_G^2}=\exp(\beta\mu_p+\beta\mu_e)/\lambda_p^3\lambda_e^3Z_G^2$$

$$=\frac{\rho_H}{\lambda_e^3}\exp(\beta\Delta)=\rho_H\left(\frac{m_ek_BT}{2\pi\hbar^2}\right)^{3/2}\exp(\beta/k_BT)$$

3. Lattice gas

A fluid of particles with a repulsive interparticle interaction can be modeled as a "lattice gas" as follows. Consider the container to be divided into N cells, each of volume v, comparable with the volume of a particle. An unoccupied cell and a cell occupied by one particle have zero energy. A cell occupied by two particles has an energy of ε, and no cell may be occupied by more than two particles.

a. Use the grand canonical ensemble to find the average energy per cell, the concentration c of particles (c is the total number of particles divided by N) and the pressure P in terms of temperature and chemical potential.

$$Z_G=\sum\exp(-\beta[E\{n_i\}-\mu N])$$

$$=(1+\exp(\beta\mu)+\exp(2\beta\mu-\beta\varepsilon))^N$$

$$\langle E\rangle=-\frac{\partial}{\partial\beta}\ln Z_G=\frac{\varepsilon\exp(2\beta\mu-\beta\varepsilon)}{1+\exp(\beta\mu)+\exp(2\beta\mu-\beta\varepsilon)}$$

$$\langle c\rangle=\frac{\langle N\rangle}{V}=\frac{-1}{V}\frac{\partial}{\partial\alpha}\ln Z_G=\frac{\exp(\beta\mu)+2\exp(2\beta\mu-\beta\varepsilon)}{V(1+\exp(\beta\mu)+\exp(2\beta\mu-\beta\varepsilon))}$$

$PV = k_B T \ln Z_G$

$= k_B T N \ln(1 + \exp(\beta\mu) + \exp(2\beta\mu - \beta\varepsilon))$

$P = \frac{k_B T N}{V} (1 + \exp(\beta\mu) + \exp(2\beta\mu - \beta\varepsilon))$

b. Find approximate expressions for the average energy per cell and for the pressure in terms of T and c in the limits that c is very small and that c is close to its maximum value.

$c \sim z$

$\frac{E}{N} \approx z^2 \varepsilon e^{-\beta\varepsilon} \approx c^2 \varepsilon e^{-\beta\varepsilon}$

$P = \frac{k_B T}{V} \ln(1+z) \approx \frac{k_B T}{V} z \approx \frac{k_B T}{V} c$

$c \approx 2$ at its max

$\frac{E}{N} \approx \varepsilon(c-1)$

$P \approx -2 \frac{k_B T}{V} \ln(2-c)$