Canonical Ensembles

1. *Non-harmonic Gas:* The Hamiltonian for a gas of N non–interacting particles, *in a d–dimensional box*, has the form

$$\mathcal{H} = \sum_{i=1}^{N} A\left|\vec{p}_i\right|^s .$$

(a) The partition function is given by

$$\begin{aligned} Z(N,T,V) &= \frac{1}{N!h^{dN}} \int\cdots\int d^d\vec{q}_1\cdots d^d\vec{q}_N d^d\vec{p}_1\cdots d^d\vec{p}_N \exp\left[-\beta\sum_{i=1}^{N} A\left|\vec{p}_i\right|^s\right] \\ &= \frac{1}{N!h^{dN}}\left[\int\int d^d\vec{q}d^d\vec{p}\exp\left(-\beta A\left|\vec{p}\right|^s\right)\right]^N . \end{aligned}$$

Ignoring hard core exclusion, each atom contributes a d–dimensional volume V to the integral over the spatial degrees of freedom, and

$$Z(N,T,V) = \frac{V^N}{N!h^{dN}}\left[\int d^d\vec{p}\exp\left(-\beta A\left|\vec{p}\right|^s\right)\right]^N .$$

Observing that the integrand depends only on the magnitude $|\vec{p}| = p$, we can evaluate the integral in spherical coordinates using $\int d^d\vec{p} = S_d\int dpp^{d-1}$, where S_d denotes the surface area of a unit sphere in d–dimensions, as

$$Z(N,T,V) = \frac{V^N}{N!h^{dN}}\left[S_d\int_0^\infty dpp^{d-1}\exp\left(-\beta Ap^s\right)\right]^N .$$

Introducing the variable $x \equiv (\beta A)^{1/s}p$, we have

$$\begin{aligned} Z(N,T,V) &= \frac{V^N S_d^N}{N!h^{dN}}\left(\frac{A}{k_BT}\right)^{-dN/s}\left[\int_0^\infty dxx^{d-1}\exp(-x^s)\right]^N \\ &= C^N(d,s)\frac{1}{N!}\left(\frac{VS_d}{h^d}\right)^N\left(\frac{A}{k_BT}\right)^{-dN/s} , \end{aligned}$$

where C denotes the numerical value of the integral. (We assume that A and s are both real and positive. These conditions ensure that energy increases with increasing $|\vec{p}|$.) The integral is in fact equal to

$$C(d,s) = \int_0^\infty dxx^{d-1}\exp(-x^s)dx = \frac{1}{s}\Gamma\left(\frac{d}{s}\right) ,$$

and the partition function is

$$Z=\frac{1}{N!}\left(\frac{VS_d}{h^d s}\right)^N\left(\frac{A}{k_BT}\right)^{-dN/s}\left[\Gamma\left(\frac{d}{s}\right)\right]^N.$$

(b) To calculate the pressure and internal energy, note that the Helmholtz free energy is

$$F=E-TS=-k_BT\ln Z,$$

and that

$$P=-\left.\frac{\partial F}{\partial V}\right|_T,\qquad\text{while}\qquad E=-\left.\frac{\partial\ln Z}{\partial\beta}\right|_V.$$

First calculating the pressure:

$$P=-\left.\frac{\partial F}{\partial V}\right|_T=k_BT\left.\frac{\partial\ln Z}{\partial V}\right|_T=\frac{Nk_BT}{V}.$$

Now calculating the internal energy:

$$E=-\left.\frac{\partial\ln Z}{\partial\beta}\right|_V=-\frac{\partial}{\partial\beta}\left[-\frac{dN}{s}\ln\left(\frac{A}{k_BT}\right)\right]=\frac{d}{s}Nk_BT.$$

Note that for each degree of freedom with energy $A|\vec{p}_i|^s$, we have the average value, $\langle A|\vec{p}_i|^s\rangle=\frac{d}{s}k_BT$. This evaluates to $\frac{3}{2}k_BT$ for the 3–dimensional ideal gas.

(c) Now consider N diatomic molecules, with

$$\mathcal{H}=\sum_{i=1}^N\mathcal{H}_i,\qquad\text{where}\qquad\mathcal{H}_i=A\left(\left|\vec{p}_i^{\,(1)}\right|^s+\left|\vec{p}_i^{\,(2)}\right|^s\right)+K\left|\vec{q}_i^{\,(1)}-\vec{q}_i^{\,(2)}\right|^t.$$

The expectation value

$$\left\langle\left|\vec{q}_i^{\,(1)}-\vec{q}_i^{\,(2)}\right|^t\right\rangle=\frac{\frac{1}{N!}\int\prod_{i=1}^N d^d\vec{q}_i^{\,(1)}d^d\vec{q}_i^{\,(2)}d^d\vec{p}_i^{\,(1)}d^d\vec{p}_i^{\,(2)}\left|\vec{q}_i^{\,(1)}-\vec{q}_i^{\,(2)}\right|^t\exp\left[-\beta\sum_i\mathcal{H}_i\right]}{\frac{1}{N!}\int\prod_{i=1}^N d^d\vec{q}_i^{\,(1)}d^d\vec{q}_i^{\,(2)}d^d\vec{p}_i^{\,(1)}d^d\vec{p}_i^{\,(2)}\exp\left[-\beta\sum_i\mathcal{H}_i\right]},$$

is easily calculated by changing variables to

$$\vec{x}\equiv\vec{q}^{\,(1)}-\vec{q}^{\,(2)},\qquad\text{and}\qquad\vec{y}\equiv\frac{\vec{q}^{\,(1)}+\vec{q}^{\,(2)}}{2},$$

as (note that the Jacobian of the transformation is unity)

$$\begin{aligned}\left\langle\left|\vec{q}^{\,(1)}-\vec{q}^{\,(2)}\right|^t\right\rangle&=\frac{\int d^d\vec{x}d^d\vec{y}\cdot|\vec{x}\,|^t\cdot\exp\left[-\beta K|\vec{x}\,|^t\right]}{\int d^d\vec{x}d^d\vec{y}\cdot\exp\left[-\beta K|\vec{x}\,|^t\right]}\\&=\frac{\int d^d\vec{x}\cdot|\vec{x}\,|^t\cdot\exp\left[-\beta K|\vec{x}\,|^t\right]}{\int d^d\vec{x}\cdot\exp\left[-\beta K|\vec{x}\,|^t\right]}.\end{aligned}$$

Further simplifying the algebra by introducing the variable $\vec{z} \equiv (\beta K)^{1/t}\vec{x}$, leads to

$$\left\langle \left| \vec{q}^{\,(1)} - \vec{q}^{\,(2)} \right|^t \right\rangle = \frac{(\beta K)^{-t/t} \int d^d\vec{z} \cdot |\vec{z}\,|^t \cdot \exp\left[-|\vec{z}\,|^t\right]}{\int d^d\vec{z} \cdot \exp\left[-|\vec{z}\,|^t\right]} = \frac{d}{t} \cdot \frac{k_B T}{K}.$$

Here we have assumed that the volume is large enough, so that the range of integration over the relative coordinate can be extended from 0 to ∞.

Alternatively, note that for the degree of freedom $\vec{x} = \vec{q}^{\,(1)} - \vec{q}^{\,(2)}$, the energy is $K|\vec{x}\,|^t$. Thus, from part (b) we know that

$$\left\langle K|\vec{x}\,|^t \right\rangle = \frac{d}{t} \cdot \frac{k_B T}{K},$$

i.e.

$$\left\langle |\vec{x}\,|^t \right\rangle = \left\langle \left| \vec{q}^{\,(1)} - \vec{q}^{\,(2)} \right|^t \right\rangle = \frac{d}{t} \cdot \frac{k_B T}{K}.$$

And yet another way of calculating the expectation value is from

$$\sum_{i=1}^{N} \left\langle \left| \vec{q}_i^{\,(1)} - \vec{q}_i^{\,(2)} \right|^t \right\rangle = -\frac{1}{\beta}\frac{\partial \ln Z}{\partial K} = \frac{Nd}{t} \cdot \frac{k_B T}{K},$$

(note that the relevant part of Z is calculated in part (d) below).

(d) For the ideal gas, the internal energy depends only on temperature T. The gas in part (c) is ideal in the sense that there are no molecule–molecule interactions. Therefore,

$$C_V = \left.\frac{đQ}{dT}\right|_V = \left.\frac{dE + PdV}{dT}\right|_V = \frac{dE(T)}{dT},$$

and

$$C_P = \left.\frac{đQ}{dT}\right|_P = \left.\frac{dE + PdV}{dT}\right|_P = \frac{dE(T)}{dT} + P\left.\frac{\partial V(T)}{\partial T}\right|_P.$$

Since $PV = Nk_BT$,

$$C_P = \frac{dE(T)}{dT} + Nk_B.$$

We now calculate the partition function

$$\begin{aligned} Z &= \frac{1}{N!h^{dN}} \int \prod_{i=1}^{N} d^d\vec{q}_i^{\,(1)} d^d\vec{q}_i^{\,(2)} d^d\vec{p}_i^{\,(1)} d^d\vec{p}_i^{\,(2)} \exp\left[-\beta \sum_i \mathcal{H}_i\right] \\ &= \frac{1}{N!h^{dN}} z_1^N, \end{aligned}$$

where

$$\begin{aligned}
z_1 &= \int d^d\vec{q}^{\,(1)} d^d\vec{q}^{\,(2)} d^d\vec{p}^{\,(1)} d^d\vec{p}^{\,(2)} \exp\left[-\beta\cdot\left(A\left|\vec{p}^{\,(1)}\right|^s + A\left|\vec{p}^{\,(2)}\right|^s + K\left|\vec{q}^{\,(1)}-\vec{q}^{\,(2)}\right|^t\right)\right] \\
&= \left[\int d^d\vec{q}^{\,(1)} d^d\vec{q}^{\,(2)} \exp\left(-\beta K\left|\vec{q}^{\,(1)}-\vec{q}^{\,(2)}\right|^t\right)\right]\cdot\left[\int d^d\vec{p}^{\,(1)}\exp\left(-\beta A\left|\vec{p}^{\,(1)}\right|^s\right)\right]^2 .
\end{aligned}$$

Introducing the variables, $\vec{x}$, $\vec{y}$, and $\vec{z}$, as in part (c),

$$\begin{aligned}
Z &\propto \frac{V^N}{N!}\left[(\beta K)^{-d/t}\int_0^\infty z^{d-1}\exp(-z^t)dz\right]^N\cdot\left[\int_0^\infty p^{d-1}\exp(-\beta A p^s)dp\right]^{2N} \\
&= \frac{V^N}{N!}\left[(\beta K)^{-d/t}\frac{1}{t}\Gamma\left(\frac{d}{t}\right)\right]^N\cdot\left[\frac{1}{s}(\beta A)^{-d/s}\Gamma\left(\frac{d}{s}\right)\right]^{2N} \\
&\propto \frac{V^N}{N!}\left(\beta K\right)^{-dN/t}\left(\beta A\right)^{-2Nd/s} .
\end{aligned}$$

Now we can calculate the internal energy as

$$\langle E\rangle = -\frac{\partial \ln Z}{\partial\beta} = \frac{d}{t}Nk_BT + \frac{2d}{s}Nk_BT = dNk_BT\left(\frac{1}{t}+\frac{2}{s}\right).$$

From this result, the heat capacities are obtained as

$$\begin{aligned}
C_P &= \left.\frac{\partial E}{\partial T}\right|_P + P\left.\frac{\partial V}{\partial T}\right|_P = Nk_B\left(\frac{2d}{s}+\frac{d}{t}+1\right), \\
C_V &= \left.\frac{\partial E}{\partial T}\right|_V = dNk_B\left(\frac{2}{s}+\frac{1}{t}\right).
\end{aligned}$$

resulting in the ratio

$$\gamma = \frac{C_P}{C_V} = \frac{2d/s+d/t+1}{2d/s+d/t} = 1+\frac{st}{d(2t+s)}.$$

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2. *Curie Susceptibility:* The net magnetization of the N quantum spins is

$$M_z = \mu\sum_{i=1}^N m_i, \qquad \text{with} \qquad m_i = -s, -(s-1), \cdots, (s-1), s.$$

(a) The Gibbs partition function is

$$\mathcal{Z} = \sum_{\{m_i\}}\exp\left(\beta\vec{B}\cdot\vec{M}\right) = \sum_{\{m_i\}}\exp\left(\beta B\mu\sum_{i=1}^N m_i\right) = \left[\sum_{m_i=-s}^{m_i=s}\exp(\beta\mu B\cdot m_i)\right]^N .$$

Thus we obtain the series

$$\mathcal{Z} = \left[\exp(-\beta B\mu s) + \exp(-\beta B\mu(s-1)) + \cdots + \exp(\beta B\mu(s-1)) + \exp(\beta B\mu s)\right]^N .$$

In general, to evaluate a geometrical series of the form

$$S = x^{-s} + x^{-(s-1)} + \cdots + x^{s-1} + x^{s},$$

increase the order of the series by one,

$$Sx = x^{-s+1} + \cdots + x^{s} + x^{s+1},$$

and subtract from the original series:

$$(1-x)S = x^{-s} - x^{s+1}, \quad \Longrightarrow \quad S = \frac{x^{-s} - x^{s+1}}{1-x}.$$

(Note that the same result is obtained whether s is an integer or half–integer quantity.) Using this expression, we get

$$\begin{aligned} \mathcal{Z} &= \left(\frac{\exp(-\beta B\mu s) - \exp(\beta B\mu(s+1))}{1-\exp(\beta B\mu)}\right)^N \\ &= \left(\frac{\exp(-\beta B\mu(s+1/2)) - \exp(-\beta B\mu(s+1/2))}{\exp(-\beta B\mu/2) - \exp(-\beta B\mu/2)}\right)^N . \end{aligned}$$

Substituting in the proper trigonometric identity,

$$\mathcal{Z} = \left[\frac{\sinh\left(\beta\mu B(s+1/2)\right)}{\sinh(\beta\mu B/2)}\right]^N .$$

(b) The Gibbs free energy is

$$\begin{aligned} G &= E - BM = -k_BT\ln\mathcal{Z} \\ &= -Nk_BT\ln[\sinh(\beta\mu B(s+1/2))] + Nk_BT\ln[\sinh(\beta\mu B/2)]. \end{aligned}$$

Using an approximation of $\sinh\theta$ for small θ,

$$\sinh\theta = \frac{1}{2}\left(e^{\theta} - e^{-\theta}\right) \approx \frac{1}{2}\left(2\theta + 2\frac{\theta^3}{3!}\right) + \mathcal{O}(\theta^5), \qquad \text{for} \qquad \theta \ll 1,$$

we find (setting $\alpha = \beta\mu B$),

$$G \approx -Nk_BT\left\{\ln\left[\alpha\left(s+\frac{1}{2}\right)\left(1+\frac{\alpha^2}{6}\left(s+\frac{1}{2}\right)^2\right)\right] - \ln\left[\frac{\alpha}{2}\left(1+\frac{\alpha^2}{24}\right)\right] + \mathcal{O}(\alpha^4)\right\}.$$

Using the expansion $\ln(1+x) = x - x^2/2 + x^3/3 - \cdots$, we find

$$\begin{aligned} G &\approx -Nk_BT\left[\ln(2s+1) + \frac{1}{6}\left(\alpha(s+1/2)\right)^2 - \frac{1}{6}\left(\alpha/2\right)^2 + \mathcal{O}(\alpha^4)\right] \\ &\approx -Nk_BT\ln(2s+1) - Nk_BT\alpha^2\frac{(s^2+s)}{6} \\ &= G_0 - \frac{N\mu^2B^2s(s+1)}{6k_BT} + \mathcal{O}(B^4). \end{aligned}$$

(c) The magnetic susceptibility, $\chi = \partial M_z/\partial B$, is obtained by noting that the average magnetization is

$$\langle M_z \rangle = k_BT\frac{\partial \ln \mathcal{Z}}{\partial B} = -\frac{\partial G}{\partial B}.$$

Thus

$$\chi = \frac{\partial \langle M_z \rangle}{\partial B} = -\frac{\partial}{\partial B}\frac{\partial G}{\partial B} = \frac{N\mu^2ts(s+1)}{3k_BT},$$

which obeys *Curie's law*, $\chi = c/T$, with $c = N\mu^2s(s+1)/3k_B$.

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3. *Surfactant Adsorption:*

(a) The partition function of a d-dimensional ideal gas is given by

$$\begin{aligned} Z_d &= \frac{1}{N_d!h^{dN_d}}\int\cdots\int\prod_{i=1}^{N_d} d^d\vec{q}_i d^d\vec{p}_i \exp\left\{-\beta\left[N_d\varepsilon_d + \sum_{i=1}^{N_d}\left(\frac{\vec{p}_i^{\,2}}{2m}\right)\right]\right\} \\ &= \frac{1}{N_d!}\left(\frac{V_d}{\lambda^d}\right)^{N_d} e^{-\beta N_d\varepsilon_d}, \end{aligned}$$

where

$$\lambda \equiv \frac{h}{\sqrt{2\pi mk_BT}}.$$

The chemical potential is calculated from the Helmholtz free energy as

$$\begin{aligned} \mu_d = \left.\frac{\partial F}{\partial N}\right|_{V,T} &= -k_BT\left.\frac{\partial \ln Z_d}{\partial N_d}\right|_{V,T} \\ &= -\varepsilon_d + k_BT\ln\left(\frac{V_d}{N_d\lambda^d}\right). \end{aligned}$$

(b) The density of particles can also be calculated from the grand canonical partition function, which for particles in a d–dimensional space is

$$\begin{aligned} \Xi(\mu, V_d, T) &= \sum_{N_d=0}^{\infty} Z(N_d, V_d, T)e^{\beta N_d\mu} \\ &= \sum_{N_d=0}^{\infty}\frac{1}{N_d!}\left(\frac{V_d}{\lambda^d}\right)^{N_d} e^{-\beta N_d\varepsilon_d}e^{\beta N_d\mu} = \exp\left[\left(\frac{V_d}{\lambda^d}\right)\cdot e^{\beta(\mu-\varepsilon_d)}\right]. \end{aligned}$$

The average number of particles absorbed in the space is

$$\langle N_d \rangle = \frac{1}{\beta}\frac{\partial}{\partial \mu}\ln \Xi = \frac{1}{\beta}\frac{\partial}{\partial \mu}\left[\left(\frac{V_d}{\lambda^d}\right)\cdot e^{\beta(\mu-\varepsilon_d)}\right] = \left(\frac{V_d}{\lambda^d}\right)\cdot e^{\beta(\mu-\varepsilon_d)}.$$

We are interested in the coexistence of surfactants between a $d = 3$ dimensional solution, and its $d = 2$ dimensional surface. Dividing the expressions for $\langle N_3 \rangle$ and $\langle N_2 \rangle$, and taking into account $\varepsilon_0 = \varepsilon_3 - \varepsilon_2$, gives

$$\frac{\langle N_2 \rangle}{\langle N_3 \rangle} = \frac{A\lambda}{V} e^{\beta\varepsilon_0},$$

which implies that

$$n_2 = \frac{\langle N_2 \rangle}{A} = n\lambda e^{\beta\varepsilon_0}.$$

(c) It has been suggested that a porous gel should be regarded as fractal, and the surfactants adsorbed on its surface treated as a gas in d_f–dimensional space, with a non–integer d_f. Using the result found in part (b), but regarding the gel as a d_f–dimensional container, the adsorbed particle density is

$$\langle n_{\text{gel}} \rangle = n\lambda^{3-d_f} \exp\left[\beta(\varepsilon_3 - \varepsilon_{\text{gel}})\right].$$

Thus by studying the adsorption of particles as a function of temperature one can determine the fractal dimensionality, d_f, of the surface. The largest contribution comes from the difference in energies. If this leading part is accurately determined, there is a subleading dependence via λ^{3-d_f} which depends on d_f.

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