Stat Mech Bible

Garrett Van Dyke gvandyke@uab.edu

UAB — Last compiled: Thursday 5th March, 2020 at 10:58am

This is my attempt to catalog everything not included on the Statistical Mechanics qualifying exam equation sheets. Here we go.

Let it be hereby known now and forevermore: z will denote fugacity, Z will denote the canonical partition function, and Z will denote the Grand Canonical partition function. The qual equation sheet does it differently (z for fugacity, Z for the partition function, and Q for the Grand Canonical partition function), but this is written to match in-class notes.

Let it also hereby be known now and forevermore: Don't forget to add a factor of $\frac{1}{N!}$ on partition functions when your particles are indistinguishable.

1 General Math

$$df(x,y) = \left(\frac{\partial f}{\partial x}\right) dx + \left(\frac{\partial f}{\partial y}\right) dy \tag{1}$$

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x + \left(\frac{\partial x}{\partial z}\right)_y = 0 \tag{2}$$

2 Formulas

2.1 Canonical Ensemble: Exchange of energy

2.1.1 Specific to Ideal Gas

$$\Omega(E) = \frac{1}{N!} \alpha^N \frac{E}{N} V^N \tag{4}$$

$$Z_N = \left(\frac{V}{\lambda^3}\right)^N \tag{5}$$

2.1.2 In General

$$\Omega(E)$$
: Number of states for a given energy (6)

$$Z = \sum_{n} e^{-\beta H_n}$$
: For a quantized phase space (7)

$$Z = \int \cdots \int_{p_N, q_N} e^{-\beta H_N} \frac{\mathrm{d}p_N \, \mathrm{d}q_N}{h^{3N}} : \text{ For a continuous phase space}$$
 (8)

$$P(E_i) = \frac{1}{Z}e^{-\beta E_i} \tag{9}$$

$$g(E) = \sum_{i} \delta(E - E_i)$$
: For discrete energies (10)

$$Z = \int g(E) e^{-\beta E} dE$$
 (11)

$$F = -kT \ln Z \tag{12}$$

$$U = -\frac{\partial}{\partial \beta} \ln Z \tag{13}$$

$$S = -k \sum_{i} \rho_{i} \ln \rho_{i} = -k \sum_{i} P_{i} \ln P_{i} = k \ln \Omega(E) = -\frac{\partial F}{\partial T}$$
(14)

$$p = -\frac{\partial F}{\partial V} \tag{15}$$

$$\mu = \frac{\partial F}{\partial N} \tag{16}$$

$$M = -kT \frac{\partial}{\partial B} \ln Z \tag{17}$$

$$\chi = \frac{\partial M}{\partial B} \approx \frac{C}{T}$$
: where C is the Curie constant (18)

$$c_V = \frac{\partial U}{\partial T} = k\beta^2 \frac{\partial^2}{\partial \beta^2} \ln Z \tag{19}$$

2.2 Grand Canonical Ensemble: Exchange of energy and number of particles

$$P(U,N) = \frac{1}{\mathcal{Z}}e^{-\beta(U-\mu N)}$$
(20)

$$\mathcal{Z} = \sum_{U} \sum_{N} e^{-\beta(U - \mu N)} = \sum_{N} e^{\beta \mu N} Z_{N} = \sum_{N} Z_{N} z^{N}$$
 (21)

$$\Phi_G = -kT \ln \mathcal{Z} \tag{22}$$

$$U = -\frac{\partial}{\partial \beta} \ln \mathcal{Z} \bigg|_{z} \tag{23}$$

$$N = z \frac{\partial}{\partial z} \ln \mathcal{Z} = -\frac{\partial \Phi_G}{\partial \mu}$$
 (24)

$$p = \frac{\Phi_G}{V} \tag{25}$$

3 Energies

Thermodynamic Potential:

$$U(S, V, N) \tag{26}$$

Helmholtz Free Energy:

$$F(T, V, N) = U - TS \tag{27}$$

Gibbs Free Energy:

$$G(T, p, N) = U - TS - pV \tag{28}$$

Grand Potential:

$$\Phi_G(T, V, \mu) = U - TS - \mu N \tag{29}$$