Stat Mech Bible

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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 $\mathcal{Z}$ will denote the Grand Canonical partition function. The qual equation sheet does it differently (z for fugacity, $\mathcal{Z}$ for the partition function, and $\mathcal{Q}$ 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

$$\mathrm{d}f(x, y) = \left(\frac{\partial f}{\partial x}\right)\mathrm{d}x + \left(\frac{\partial f}{\partial y}\right)\mathrm{d}y \tag{1}$$

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

$$\langle a \rangle = \int a\, P_a \,\mathrm{d}a \quad \textbf{OR} \quad \langle a \rangle = \sum_a a\, P_a \tag{3}$$

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

$$\Omega(E): \text{ Number of states for a given energy} \tag{6}$$

$$Z = \sum_n e^{-\beta H_n} : \text{ For a quantized phase space} \tag{7}$$

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

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

$$g(E) = \sum_i \delta(E - E_i) : \text{ For discrete energies} \tag{10}$$

$$Z = \int g(E) \, e^{-\beta E} \, \mathrm{d}E \tag{11}$$

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

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

$$S = -k \sum_i \rho_i \ln \rho_i = -k \sum_i P_i \ln P_i = k \ln \Omega(E) = -\frac{\partial F}{\partial T} \tag{14}$$

$$T = \left(\frac{\partial U}{\partial S} \right)_{V,N} \tag{15}$$

$$p = -\frac{\partial F}{\partial V} \tag{16}$$

$$\mu = \frac{\partial F}{\partial N} \tag{17}$$

$$M = -kT \frac{\partial}{\partial B} \ln Z \tag{18}$$

$$\chi = \frac{\partial M}{\partial B} \approx \frac{C}{T} : \text{ where C is the Curie constant} \tag{19}$$

$$c_V = \frac{\partial U}{\partial T} = k\beta^2 \frac{\partial^2}{\partial \beta^2} \ln Z \tag{20}$$

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

$$P(U, N) = \frac{1}{\mathcal{Z}} e^{-\beta(U - \mu N)} \tag{21}$$

$$\mathcal{Z} = \sum_U \sum_N e^{-\beta(U - \mu N)} = \sum_N e^{\beta \mu N} Z_N = \sum_N Z_N z^N \tag{22}$$

$$\Phi_G = -kT \ln \mathcal{Z} \tag{23}$$

$$U = -\frac{\partial}{\partial \beta} \ln \mathcal{Z} \bigg|_z \tag{24}$$

$$N = z \frac{\partial}{\partial z} \ln \mathcal{Z} = -\frac{\partial \Phi_G}{\partial \mu} \tag{25}$$

$$p = \frac{\Phi_G}{V} \tag{26}$$

3 Energies

Thermodynamic Potential:
$$U(S, V, N) \tag{27}$$

Helmholtz Free Energy:
$$F(T, V, N) = U - TS \tag{28}$$

Gibbs Free Energy:
$$G(T, p, N) = U - TS - pV \tag{29}$$

Grand Potential:
$$\Phi_G(T, V, \mu) = U - TS - \mu N \tag{30}$$