Statistical Mechanics

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Here are some of the formulas I use the most in statistical mechanics

1 Microcanonical

The independent variables are E, V and N

1.1 Classical Statistics

Number of microstates

$$\Sigma \equiv \frac{1}{N!h^{3N}} \int d^{3N}q \; d^{3N}p \; \delta(E - \mathscr{H}[q_\nu, p_\nu]) \tag{1}$$

$$= \frac{1}{N!h^{3N}} \int\limits_{E<\mathscr{H}<E+\delta E} d^{3N}q \; d^{3N}p \tag{2}$$

Probability Density

$$\rho[q_\nu, p_\nu] \equiv \frac{1}{\Sigma}\delta(E - \mathscr{H}[q_\nu, p_\nu]) \tag{3}$$

$$= \begin{cases} \frac{1}{\Sigma} & E < \mathscr{H}[q_\nu, p_\nu] < E + \delta E \\ 0 & \sim \end{cases} \tag{4}$$

1.2 Quantum Statistics

Number of microstates

$$\Sigma \equiv \sum_{\substack{l \\ E<E_l<E+\delta E}} 1 \tag{5}$$

Probability of the state l

$$P_l \equiv \begin{cases} \frac{1}{\Sigma} & E < E_l < E + \delta E \\ 0 & \sim \end{cases} \tag{6}$$

Partial probability

$$P(y) \equiv \sum_{\substack{l \\ y_l = y}} P_l = \frac{1}{\Sigma} \underbrace{\sum_{\substack{l \\ y_l = y}} 1}_{\equiv w[y]} = \frac{w[y]}{\Sigma} \tag{7}$$

where $\Sigma = \sum_l 1 = \sum_y w[y]$. If we define the partial entropy as $S[y] \equiv k \ln w[y]$, then the partial probability can be written as $P[y] \propto e^{\frac{1}{k}S[y]}$

2 Canonical

The independent variables are T, V and N

2.1 Classical Statistics

Probability density

$$\rho[q_\nu, p_\nu] \equiv \frac{e^{-\beta \mathscr{H}[q_\nu, p_\nu]}}{Z} \tag{8}$$

where $Z \equiv \frac{1}{N! h^{3N}} \int d^{3N}q \; d^{3N}p \; e^{-\beta \mathscr{H}[q_\nu, p_\nu]}$

2.2 Quantum Statistics

Probability of the state l

$$P_l \equiv \frac{e^{-\beta E_l}}{Z} \qquad \text{where} \quad Z \equiv \sum_l e^{-\beta E_l} \tag{9}$$

Partial Probability

$$P[y] \equiv \sum_{\substack{l \\ y_l = y}} \frac{e^{-\beta E_l}}{Z} = \frac{1}{Z} \underbrace{\sum_{\substack{l \\ y_l = y}} e^{-\beta E_l}}_{\equiv Z[y]} = \frac{Z[y]}{Z} \tag{10}$$

If we define the partial Helmholtz Free Energy as $F[y] = -k_B T \ln Z[y]$, then the partial probability can be written as $P[y] \propto e^{-\beta F[y]}$

3 Grand Canonical

The independent variables are T, V and μ

3.1 Classical Statistics

Probability density

$$\rho[N, q_\nu, p_\nu] \equiv \frac{e^{-\beta(\mathscr{H}[q_\nu, p_\nu] - \mu N)}}{\Xi} \tag{11}$$

where $\Xi \equiv \sum_{N=0}^{\infty} \frac{1}{h^{3N}} \int d^{3N}q \; d^{3N}p \; e^{-\beta(\mathscr{H}[q_\nu, p_\nu] - \mu N)}$

3.2 Quantum Statistics

Probability of the state l

$$P_l \equiv \frac{e^{-\beta(E_l - \mu N_l)}}{\Xi} \qquad \text{where} \quad \Xi \equiv \sum_l e^{-\beta(E_l - \mu N)} \tag{12}$$

4 Thermodynamics

4.1 Microcanonical

Entropy: $S = S[E, V, N] = k_B \ln \Sigma$

$$\frac{1}{T} = \frac{\partial S}{\partial E} \qquad \frac{p}{T} = \frac{\partial S}{\partial V} \qquad -\frac{\mu}{T} = \frac{\partial S}{\partial N} \tag{13}$$

4.2 Canonical

Helmholtz Free Energy: $F = F[T, V, N] \equiv -k_B T \ln Z = E - TS$

$$p = -\frac{\partial F}{\partial V} \qquad \mu = \frac{\partial F}{\partial N} \qquad S = -\frac{\partial F}{\partial T} \qquad \bar{E} = -\frac{\partial \ln Z}{\partial \beta} \tag{14}$$

4.3 Grand Canonical

Grand canonical potential: $\Omega = \Omega[T, V, \mu] \equiv -k_B T \ln \Xi = F - \mu N = E - TS - \mu N$

$$p = -\frac{\partial \Omega}{\partial V} \qquad S = -\frac{\partial \Omega}{\partial T} \qquad \bar{N} = -\frac{\partial \Omega}{\partial \mu} \qquad \bar{E} - \mu \bar{N} = -\frac{\partial \ln \Xi}{\partial \beta} \tag{15}$$

References

[1] Diu, “Physique Statistique”

[2] Greiner, “Thermodynamics and statistical mechanics”

[3] Sears, “Thermodynamics, kinetic theory, and statistical thermodynamics”

[4] Kubo, “Statistical Mechanics”