Statistical Physics (A1) – A. Schekochihin

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§§ 12-13. Grand Canonical Ensemble & Multispecies Systems.

SUMMARY

Open systems: can exchange energy and particles with the world

Microstates: $\alpha \leftrightarrow E_\alpha, N_\alpha$ (energy; number of particles)

Equilibrium: $S = -k_B \sum_\alpha p_\alpha \ln p_\alpha \to \max$

subject to $\langle E_\alpha \rangle = U$ and $\langle N_\alpha \rangle = \bar{N}$

$\Downarrow$

$$\boxed{p_\alpha = \frac{e^{-\beta(E_\alpha - \mu N_\alpha)}}{\mathcal{Z}}}$$

grand canonical distribution

$$\boxed{\mathcal{Z} = \sum_\alpha e^{-\beta(E_\alpha - \mu N_\alpha)}}$$

grand canonical partition f-n

$\beta = \frac{1}{k_B T}$ temperature

μ chemical potential

T and μ constant across system in equilibrium

$$\mu = \left(\frac{\partial U}{\partial \bar{N}}\right)_{S,V} = \frac{G}{\bar{N}}$$

energy per added particle; Gibbs free energy per particle

$\mu = \mu(P, T)$ intensive function

$\Downarrow$

$$\Phi = -k_B T \ln \mathcal{Z}$$ grand potential

$$= U - TS - \mu \bar{N}$$

$$= -PV$$ ← equation of state

$\Downarrow$

$$d\Phi = -S\,dT - p\,dV - \bar{N}\,d\mu$$
$$dU = T\,dS - p\,dV + \mu\,d\bar{N}$$
$$dF = -S\,dT - p\,dV + \mu\,d\bar{N}$$
$$dG = -S\,dT + V\,dP + \mu\,d\bar{N}$$

and the rest of thermodynamic calculus follows

Classical ideal gas: $\mathcal{Z} = e^{Z_1 e^{\beta\mu}}$ ← single-particle partition function

Chemical potential:

$$\boxed{\mu = -k_B T \ln \frac{Z_1}{\bar{N}} = k_B T \ln (n \lambda_{th}^3) = k_B T \ln p - k_B T \ln \frac{k_B T}{\lambda_{th}^3}}$$

$$\lambda_{th} = \hbar \sqrt{\frac{2\pi}{m k_B T}}$$

Multispecies/multicomponent systems:

Each species has its own $\bar{N}_i$ and μ_i

All of the above generalites by replacing

$$\mu N \to \sum_i \mu_i N_i \quad \text{and} \quad \mu d\bar{N} \to \sum_i \mu_i d\bar{N}_i,$$

in particular, $\boxed{G = \sum_i \mu_i \bar{N}_i}$

Equilibrium:
$\mu_i = \text{const}$
$\mu_i \neq \mu_j \quad i \neq j$

$$\mu_i = \mu_i(P, T, c_1, \ldots, c_m), \quad c_i = \frac{\bar{N}_i}{\bar{N}}, \quad \bar{N} = \sum_{i=1}^{m} \bar{N}_i$$

Concentrations

Chemical equilibrium:

Reaction: $\sum_i \nu_i A_i = 0$ (weights ν_i, components A_i) $\Rightarrow$ minimise G (@const P, T)

$$\boxed{\sum_i \nu_i \mu_i = 0}$$ equation of chemical equilibrium

⇓

relationship between concentrations, p and T

For a mixture of ideal gases, equation of chemical equilibrium becomes

Law of mass action

$$\boxed{\prod_i c_i^{\nu_i} = P^{-\sum_i \nu_i} \prod_i \left[\frac{k_B T}{\lambda_{th_i}^3} Z_{1\,\text{internal}}^{(i)}\right]^{\nu_i} \equiv K(P, T)}$$

$Z_{1\,\text{internal}}^{(i)}$: s.p. partition function containing the internal degrees of freedom

$K(P,T)$: chemical equilibrium constant

Applications: chemical reations
ionization-recombination (plasmas)
pair production etc. etc.

also multiphase systems; solutions