Ensembles in Statistical Mechanics

Microcanonical ensemble:

Variables: U, N, V. Potential: S [maximized at equilibrium]

$$\begin{aligned}
g(U,N,V) &= \text{number of microstates} \\
S(U,N,V) &= k_B \log g(U,N,V) \\
\frac{1}{T(U,N,V)} &= k_B \frac{\partial}{\partial U} \log g(U,N,V) = \left(\frac{\partial S}{\partial U}\right)_{N,V} \\
\mu(U,N,V) &= -k_B T \frac{\partial}{\partial N} \log g(U,N,V) = -T\left(\frac{\partial S}{\partial N}\right)_{U,V} \\
P(U,N,V) &= k_B T \frac{\partial}{\partial V} \log g(U,N,V) = T\left(\frac{\partial S}{\partial V}\right)_{U,N}
\end{aligned} \tag{1}$$

Canonical ensemble:

Variables: T, N, V. Potential: F [minimized at equilibrium]

$$\begin{aligned}
Z(T,N,V) &= \sum_U e^{-U/(k_B T)} g(U,N,V) \\
F(T,N,V) &= -k_B T \log Z(T,N,V) = -TS + U \\
S(T,N,V) &= -\left(\frac{\partial F}{\partial T}\right)_{N,V} \\
U(T,N,V) &= k_B T^2 \frac{\partial}{\partial T} \log Z(T,N,V) \\
\mu(T,N,V) &= -k_B T \frac{\partial}{\partial N} \log Z(T,N,V) = \left(\frac{\partial F}{\partial N}\right)_{T,V} \\
P(T,N,V) &= k_B T \frac{\partial}{\partial V} \log Z(T,N,V) = -\left(\frac{\partial F}{\partial V}\right)_{T,N}
\end{aligned} \tag{2}$$

Grand canonical ensemble:

Variables: T, μ, V. Potential: $\mathfrak{G}$ [minimized at equilibrium]

$$\begin{aligned}
\mathfrak{Z}(T,\mu,V) &= \sum_N e^{\mu N/(k_B T)} Z(T,N,V) \\
\mathfrak{G}(T,\mu,V) &= -k_B T \log \mathfrak{Z}(T,\mu,V) = -TS + U - \mu N = -PV \\
S(T,\mu,V) &= -\left(\frac{\partial \mathfrak{G}}{\partial T}\right)_{\mu,V} \\
U(T,\mu,V) &= k_B T^2 \frac{\partial}{\partial T} \log \mathfrak{Z}(T,\mu,V) + N\mu \\
N(T,\mu,V) &= k_B T \frac{\partial}{\partial \mu} \log \mathfrak{Z}(T,\mu,V) = -\left(\frac{\partial \mathfrak{G}}{\partial \mu}\right)_{T,V} \\
P(T,\mu,V) &= k_B T \frac{\partial}{\partial V} \log \mathfrak{Z}(T,\mu,V) = -\left(\frac{\partial \mathfrak{G}}{\partial V}\right)_{T,\mu}
\end{aligned} \tag{3}$$

Canonical ensemble, fixed pressure:

Variables: T, N, P. Potential: $\mathcal{G}$ [minimized at equilibrium]

$$\begin{aligned}
\mathcal{Z}(T,N,P) &= \frac{P}{k_B T}\int_0^\infty e^{-PV/(k_B T)} Z(T,N,V)dV \\
\mathcal{G}(T,N,P) &= -k_B T \log \mathcal{Z}(T,N,P) = -TS + U + PV = -TS + H = \mu N \\
S(T,N,P) &= -\left(\frac{\partial \mathcal{G}}{\partial T}\right)_{N,P} \\
U(T,N,P) &= k_B T^2 \frac{\partial}{\partial T}\log \mathcal{Z}(T,N,P) - PV = H - PV \\
\mu(T,N,P) &= -k_B T \frac{\partial}{\partial N}\log \mathcal{Z}(T,N,P) = \left(\frac{\partial \mathcal{G}}{\partial N}\right)_{T,P} \\
V(T,N,P) &= -k_B T \frac{\partial}{\partial P}\log \mathcal{Z}(T,N,P) = \left(\frac{\partial \mathcal{G}}{\partial P}\right)_{T,N}
\end{aligned} \qquad (4)$$

Nomenclature:

symbol	meaning
F	Helmholtz free energy
g	multiplicity
$\mathcal{G}$	Gibbs free energy
$\mathfrak{G}$	grand potential
H	enthalpy
k_B	Boltzmann's constant
μ	chemical potential
N	# of particles
P	pressure
S	entropy
T	temperature
U	energy
V	volume
Z	partition function (canonical)
$\mathcal{Z}$	partition function (fixed P)
$\mathfrak{Z}$	grand partition function