5.5 Statistical thermodynamics

Statistical entropy

Boltzmann formula[a]	$S = k \ln W$	(5.104)	S entropy k Boltzmann constant W number of accessible microstates $g(E)$ density of microstates with energy E
	$\simeq k \ln g(E)$	(5.105)	
Gibbs entropy[b]	$S = -k \sum_i p_i \ln p_i$	(5.106)	$\sum_i$ sum over microstates p_i probability that the system is in microstate i
N two-level systems	$W = \frac{N!}{(N-n)!n!}$	(5.107)	N number of systems n number in upper state
N harmonic oscillators	$W = \frac{(Q+N-1)!}{Q!(N-1)!}$	(5.108)	Q total number of energy quanta available

[a]Sometimes called "configurational entropy." Equation (5.105) is true only for large systems.
[b]Sometimes called "canonical entropy."

Ensemble probabilities

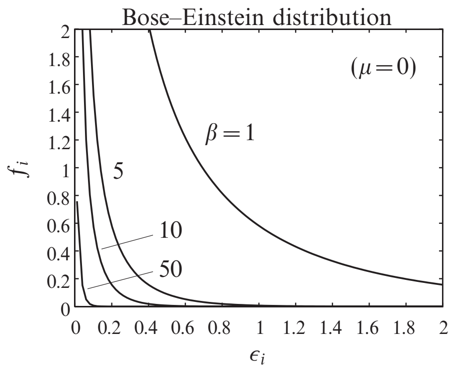
Microcanonical ensemble[a]	$p_i = \frac{1}{W}$	(5.109)	p_i probability that the system is in microstate i W number of accessible microstates
Partition function[b]	$Z = \sum_i e^{-\beta E_i}$	(5.110)	Z partition function $\sum_i$ sum over microstates β $= 1/(kT)$ E_i energy of microstate i
Canonical ensemble (Boltzmann distribution)[c]	$p_i = \frac{1}{Z} e^{-\beta E_i}$	(5.111)	k Boltzmann constant T temperature
Grand partition function	$\Xi = \sum_i e^{-\beta(E_i - \mu N_i)}$	(5.112)	Ξ grand partition function μ chemical potential N_i number of particles in microstate i
Grand canonical ensemble (Gibbs distribution)[d]	$p_i = \frac{1}{\Xi} e^{-\beta(E_i - \mu N_i)}$	(5.113)	

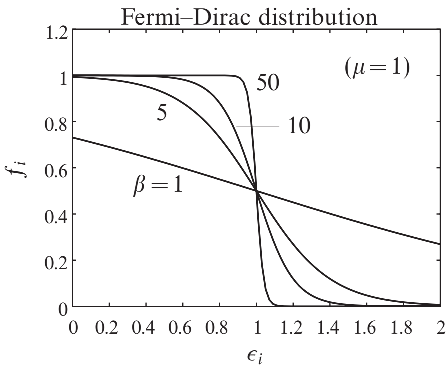
[a]Energy fixed.
[b]Also called "sum over states."
[c]Temperature fixed.
[d]Temperature fixed. Exchange of both heat and particles with a reservoir.

Macroscopic thermodynamic variables

Helmholtz free energy	$F = -kT \ln Z$	(5.114)	F Helmholtz free energy k Boltzmann constant T temperature Z partition function
Grand potential	$\Phi = -kT \ln \Xi$	(5.115)	Φ grand potential Ξ grand partition function
Internal energy	$U = F + TS = -\left.\frac{\partial \ln Z}{\partial \beta}\right\vert_{V,N}$	(5.116)	U internal energy β $= 1/(kT)$
Entropy	$S = -\left.\frac{\partial F}{\partial T}\right\vert_{V,N} = \left.\frac{\partial (kT \ln Z)}{\partial T}\right\vert_{V,N}$	(5.117)	S entropy N number of particles
Pressure	$p = -\left.\frac{\partial F}{\partial V}\right\vert_{T,N} = \left.\frac{\partial (kT \ln Z)}{\partial V}\right\vert_{T,N}$	(5.118)	p pressure
Chemical potential	$\mu = \left.\frac{\partial F}{\partial N}\right\vert_{V,T} = -\left.\frac{\partial (kT \ln Z)}{\partial N}\right\vert_{V,T}$	(5.119)	μ chemical potential

Identical particles





Bose–Einstein distribution[a]	$f_i = \frac{1}{e^{\beta(\epsilon_i - \mu)} - 1}$	(5.120)	f_i mean occupation number of ith state β $= 1/(kT)$
Fermi–Dirac distribution[b]	$f_i = \frac{1}{e^{\beta(\epsilon_i - \mu)} + 1}$	(5.121)	ϵ_i energy quantum for ith state μ chemical potential
Fermi energy[c]	$\epsilon_F = \frac{\hbar^2}{2m}\left(\frac{6\pi^2 n}{g}\right)^{2/3}$	(5.122)	ϵ_F Fermi energy $\hbar$ (Planck constant)/(2π) n particle number density m particle mass g spin degeneracy $(= 2s+1)$
Bose condensation temperature	$T_c = \frac{2\pi\hbar^2}{mk}\left[\frac{n}{g\zeta(3/2)}\right]^{2/3}$	(5.123)	ζ Riemann zeta function $\zeta(3/2) \simeq 2.612$ T_c Bose condensation temperature

[a]For bosons. $f_i \geq 0$.
[b]For fermions. $0 \leq f_i \leq 1$.
[c]For noninteracting particles. At low temperatures, $\mu \simeq \epsilon_F$.

Population densities[a]

Boltzmann excitation equation	$$\frac{n_{mj}}{n_{lj}} = \frac{g_{mj}}{g_{lj}} \exp\left[\frac{-(\chi_{mj}-\chi_{lj})}{kT}\right] \quad (5.124)$$ $$= \frac{g_{mj}}{g_{lj}} \exp\left(\frac{-h\nu_{lm}}{kT}\right) \quad (5.125)$$	n_{ij}	number density of atoms in excitation level i of ionisation state j ($j=0$ if not ionised)
		g_{ij}	level degeneracy
		χ_{ij}	excitation energy relative to the ground state
Partition function	$$Z_j(T) = \sum_i g_{ij} \exp\left(\frac{-\chi_{ij}}{kT}\right) \quad (5.126)$$ $$\frac{n_{ij}}{N_j} = \frac{g_{ij}}{Z_j(T)} \exp\left(\frac{-\chi_{ij}}{kT}\right) \quad (5.127)$$	ν_{ij}	photon transition frequency
		h	Planck constant
		k	Boltzmann constant
		T	temperature
Saha equation (general)	$$n_{ij} = n_{0,j+1} n_{\mathrm{e}} \frac{g_{ij}}{g_{0,j+1}} \frac{h^3}{2} (2\pi m_{\mathrm{e}} kT)^{-3/2} \exp\left(\frac{\chi_{Ij}-\chi_{ij}}{kT}\right) \quad (5.128)$$	Z_j	partition function for ionisation state j
		N_j	total number density in ionisation state j
Saha equation (ion populations)	$$\frac{N_j}{N_{j+1}} = n_{\mathrm{e}} \frac{Z_j(T)}{Z_{j+1}(T)} \frac{h^3}{2} (2\pi m_{\mathrm{e}} kT)^{-3/2} \exp\left(\frac{\chi_{Ij}}{kT}\right) \quad (5.129)$$	n_{e}	electron number density
		m_{e}	electron mass
		χ_{Ij}	ionisation energy of atom in ionisation state j

[a] All equations apply only under conditions of local thermodynamic equilibrium (LTE). In atoms with no magnetic splitting, the degeneracy of a level with total angular momentum quantum number J is $g_{ij} = 2J+1$.