

5.5 Statistical thermodynamics

Statistical entropy

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

^aSometimes called “configurational entropy.” Equation (5.105) is true only for large systems.

^bSometimes called “canonical entropy.”

Ensemble probabilities

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

^aEnergy fixed.

^bAlso called “sum over states.”

^cTemperature fixed.

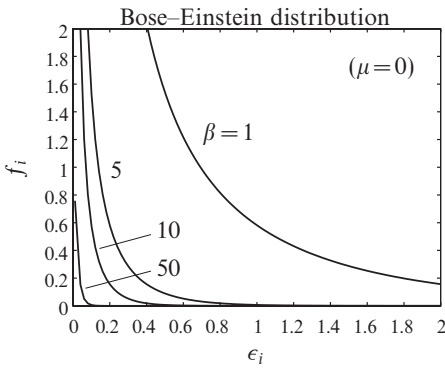
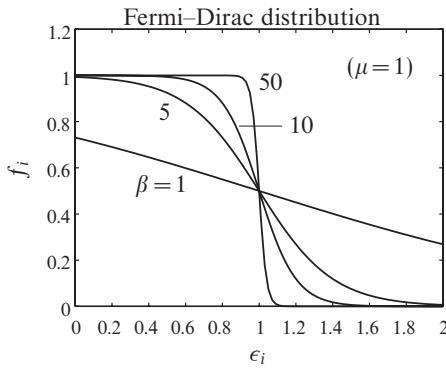
^dTemperature fixed. Exchange of both heat and particles with a reservoir.



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	$U = F + TS = -\frac{\partial \ln Z}{\partial \beta} \Big _{V,N}$	(5.116)	U internal energy $\beta = 1/(kT)$
Entropy	$S = -\frac{\partial F}{\partial T} \Big _{V,N} = \frac{\partial (kT \ln Z)}{\partial T} \Big _{V,N}$	(5.117)	S entropy N number of particles
Pressure	$p = -\frac{\partial F}{\partial V} \Big _{T,N} = \frac{\partial (kT \ln Z)}{\partial V} \Big _{T,N}$	(5.118)	p pressure
Chemical potential	$\mu = \frac{\partial F}{\partial N} \Big _{V,T} = -\frac{\partial (kT \ln Z)}{\partial N} \Big _{V,T}$	(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 i th state $\beta = 1/(kT)$
Fermi-Dirac distribution ^b	$f_i = \frac{1}{e^{\beta(\epsilon_i - \mu)} + 1}$	(5.121)	ϵ_i energy quantum for i th 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

^aFor bosons. $f_i \geq 0$.

^bFor fermions. $0 \leq f_i \leq 1$.

^cFor noninteracting particles. At low temperatures, $\mu \simeq \epsilon_F$.

Population densities^a

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

^aAll 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 $g_{ij} = 2J + 1$.