Formulas - Statistical Thermodynamics

Reprinted from

Problems in Statistical Thermodynamics
Worked Example Problems
Problems & Solutions
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ISBN-10: 0991153049
ISBN-13: 978-0-9911530-4-6

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Mathematical formulas

formula	example
n!=1*2*3…*n	3!=1*2*3; 0!=1;
$\sum_{j=1}^{3} a_j = a_1 + a_2 + a_3$ $\sum_{j=1}^{N} f(i) = f(1) + f(2) + \ldots + f(n)$ $\sum_{j=1}^{N} c = Nc\,;\ \sum_{i=m}^{n} i = n + i - m$ $\sum_{i=1}^{N} 1 = N + 1 - 1 = N$	Yes, I hope you know that. C and N are constant, i and j are running indicees
$\prod_{j=1}^{3} a_j = a_1 * a_2 * a_3$	
$\lim_{x\to\infty}[1+\frac{a}{x}]^x = e^a$	
$\sum_{j=0}^{\infty} x^j = (1-x)^{-1}$	See PowerPoint class 15, 18 (example problem e.g. 323)
$\overline{(x-\overline{x})^2} = \overline{x^2} - \overline{x}^2$	Used to calculate fluctuations, see problem 75
$\sum_{i=1}^{m}\sum_{j=1}^{n} x_i x_j = (\sum_{i=1}^{m} x_i)(\sum_{j=1}^{n} y_i)$	See problem 27
$e^x = \sum_{n=0}^{\infty}\frac{x^n}{n!}$	Taylor expansion of exponential function, see problem 73
$\frac{\partial g(f(x))}{\partial x} = f'(x)g'(x)$	That chain rule is used very often and can be tricky to apply, see e.g. problems 10, 15, 69
$e^{(\sum_j n_j)} = \prod_j^N e^{n_j}\,;$ $\sum_s^t \ln f(n) = \ln\prod_s^t f(n)$	See FD and BE statistics, see e.g. problem 29, 140

Mathematical formulas

formula	example
ln(1+x)~x for small x	$\ln(\Xi) = \pm\sum_k \ln(1+\lambda e^{-\beta\varepsilon_k}) \to \lambda q$, problem 332
$\lim_{x\to-\infty} e^x = 0$; $\lim_{x\to 0+} \ln(x) = -\infty$	See problem 340, 388
$\lim_{x\to 0\pm} 1/x = \pm\infty$;	
$\int_0^\infty e^{-\alpha x^2} dx = \frac{1}{2}\sqrt{\frac{\pi}{\alpha}}$	Gaussian integral, appears e.g. in treatment of the ideal gas, see problem 356, proof can be found e.g. here http://en.wikipedia.org/wiki/Gauss_Integral
$\ln(x!) \approx x\ln(x) - x$	Stirling's formula

For special integrals see also:
http://en.wikipedia.org/wiki/List_of_integrals_of_exponential_functions
http://en.wikipedia.org/wiki/Debye_function

Boltzmann constant	k = 1.3806488×10^{-23} J/K = 8.6173324×10^{-5} eV/K
Planck's constant	h = 6.62606957×10^{-34} Js = $4.135667516\times10^{-15}$ eV/s
Speed of light	c = 2.99×10^{8} m/s
	hc = 1.98644568×10^{-25} J·m
Avogadro number	$N_A = 6.022\text{x}10^{23}$

Probability theory formulas

$N*(N-1)*(N-2)...2*1 = N!$ Number of permutations of N distinguishable species. The 1st species is selected from N species. The 2nd from (N-1) species, etc.

$\frac{N!}{\prod_{i=1}^{B} n_i}$ Number of permutations of N distinguishable species placed in n_i boxes (i = 1..B). See Boltzmann law, class 5A. For indistinguishable objects, divide by N! (see class 12B, corrected Boltzmann statistics).

$\frac{g_i!}{(g_i - N)!N!}$ Number of permutations of N indistinguishable species placed in g_i numbered boxes with no more than one species per box (g_i = 0 or g_i = 1, see Pauli principle). See Fermi-Dirac statistics, class 13 and class 3b. (For distinguishable species remove 1/N! correction.)

$\frac{(g_i + N - 1)!}{(g_i - 1)!N!}$ Same as above, but without a restriction on the number of species per box (g_i = 0, 1, …). See Bose-Einstein statistics, class 13 and class 3b.

Plausibility explanations/derivations and more equations can be found e.g. in [May]. [E/R] includes a pedagogical outline about probability theory tailored towards pchem/stat thermo applications.

Thermodynamics formulas

$$H = U + PV$$

$$A = U - TS$$

$$G = H - TS = U + PV - TS$$

Total derivatives

$$dU = TdS - PdV$$

$$dH = TdS - PdV + PdV + VdP = TdS + VdP$$

$$dA = TdS - PdV - TdS - SdT = -SdT - PdV$$

$$dG = TdS + VdP - TdS - SdT = -SdT + VdP$$

Partial derivatives

$$(\frac{\partial G}{\partial T})_P = -S; (\frac{\partial G}{\partial P})_T = V \qquad (\frac{\partial U}{\partial S})_V = T; (\frac{\partial U}{\partial V})_S = -P$$

$$(\frac{\partial A}{\partial T})_V = -S; (\frac{\partial A}{\partial V})_T = -P \qquad (\frac{\partial H}{\partial S})_P = T; (\frac{\partial H}{\partial P})_S = V$$

Maxwell relationships

$$(\frac{\partial S}{\partial V})_T = (\frac{\partial P}{\partial T})_V = \frac{\beta}{\kappa} \qquad -(\frac{\partial T}{\partial P})_S = (\frac{\partial V}{\partial S})_P$$

$$-(\frac{\partial S}{\partial P})_T = (\frac{\partial V}{\partial T})_P = V\beta \qquad (\frac{\partial T}{\partial V})_S = -(\frac{\partial P}{\partial S})_V$$

Here β and κ are materials constants

Other useful equations

SdT – Vdp + Ndμ = 0 (Gibbs-Duhem)

Sign definition in thermodynamics:	
Work done by the system on the surroundings	-
Work done on the system by the surroundings	+
Heat adsorbed by the system from the surroundings	+
Heat adsorbed by the surroundings from the system	-

Stat thermo formulas

Stat thermo postulates *(class 1, problem 126)*

The time average of a mechanical variable in a thermodynamics system equals the ensemble average in the limit of infinite number of systems of the ensemble that replicate the thermodynamic system.

And

The systems of the ensemble are distributed uniformly over the allowed quantum states consistent with N, V, and E.

Stat thermo laws *(class 10, problems 230-252)*

1st $E_t = \sum_j n_j E_j$ (usually not stated as such)

2nd $\Delta S = S_f - S_i = k \ln \frac{\Omega_i}{\Omega_f} > 0$

3rd $\lim_{T \to 0K} [\ln(\Omega)] = \ln(\Omega_0) = 0$

Ensembles (class 7)

Constrains	**Grand canonical ensemble**	**Canonical ensemble**
Energy conservation	$\sum_{j,N} n_j(N) E_j(N,V) = E_t$	$\sum_j n_j E_j = E_t$
Particle # conservation	$\sum_{j,N} n_j(N) N = N_t$	N_t
Sub-system conservation	$\sum_{j,N} n_j(N) = \Pi$	$\sum_j n_j = \Pi$
Lagrange multipliers	α, β, γ	α, β

The wall of the subsystems allow for transfer of

	grand	canonical	micro
Heat	yes	yes	no
Matter	yes	no	no

The subsystems require energy being

Energy	variable	variable	constant

The subsystems are

	open	closed	isolated

We can also summarize this as

All subsystems have the same	μ, V, T	N, V, T	N, V, E

The supersystem (ensemble) is always isolated from the universe.

Boltzmann law *(class 5A, problems 130-153)*

$$\frac{n_i}{n_j} = e^{-(E_i - E_j)/kT}; \quad \Omega_t(n) = \frac{N!}{\prod_j n_j!}; \; P_j = \frac{\overline{n}_j}{\Pi} = \frac{\sum_j \Omega(n) n_j(n)}{\sum_j \Omega(n)}$$

Boltzmann distribution *(class 5B, problems 130-153)*

$n_j^* = \Pi e^{-\alpha - \beta E_j}$ (most like population numbers); $e^{-\alpha} = \sum_j e^{-\beta E_j}; \beta = \frac{1}{kT}$

(see also canonical ensemble and Boltzmann law)

Partition functions of ensembles *(class 12C, problems 284-304)*

I♥Eq.

Distinguishable particles $Q = q_a q_b q_c$; $q_a = \sum_j e^{-\varepsilon_j^a/kT}$; $Q = q_a q_b q_c = q^N$;

$$q = q_a = q_b = \ldots = \sum_j e^{-\varepsilon_j/kT}$$

Indistinguishable particles $Q = \dfrac{q^N}{N!}$

$$Q(N,V,T) = \sum_j e^{-E_j(N,V)/kT} \quad \text{(Boltzmann)}$$

$$\Xi = \prod_k \sum_{n_k=0}^{n_k^{\max}} (\lambda e^{-\beta\varepsilon_k})^{n_k} \text{ (General case)}; \ \lambda = e^{\beta\mu}; \ \beta = 1/kT$$

$$\Xi_{FD} = \prod_k [1 + (\lambda e^{-\beta\varepsilon_k})^1] \text{ (Fermi-Dirac)}$$

$$\Xi_{BE} = \prod_k (1 - \lambda e^{-\beta\varepsilon_k})^{-1} \text{ (Bose-Einstein)}$$

$$\Xi_{\substack{FD \\ BE}} = \prod_k (1 \pm \lambda e^{-\beta\varepsilon_k})^{\pm 1} \text{ (FD/BE)}$$

Partition functions for model systems

Diatomic/polyatomic $q = q_{trans} q_{vib} q_{rot} q_{electronic} q_{nuclear}$ (class 18)

$$q_{electronic} = \sum_i \Omega_i e^{-\varepsilon_i/kT} \ ; \ q_{nuclear} = 1;$$

Translations $q_{kinetic} = (\dfrac{2\pi m}{h^2} kT)^{3/2} V = q_t$ (particle-in-a-box, class 14)

Vibrations $q = \dfrac{e^{-\Theta/2T}}{1 - e^{-\Theta/T}}$ (harmonic oscillator, Einstein crystal, class 15)

Diatomic $q_{vibrations}^{T\to\infty} = \dfrac{kT}{h\nu} = \dfrac{T}{\Theta_v}$; $q_{rot} = \dfrac{T}{\Theta_r} = \dfrac{8\pi^2 IkT}{h^2}$; *(class 18A-C, problems 426-473)*

$$q_{total}^{diatomic} = (\frac{2\pi mkT}{h^2})^{3/2} V \frac{8\pi^2 IkT}{\sigma h^2} \frac{e^{-\beta h\nu/2}}{(1 - e^{-\beta h\nu})} \omega_{e_1} e^{D_e/kT}$$

Canonical ensemble $Q(N,V,T)$ *(class 5A/B, problems 130-153)*

Characteristic function dA = -SdT – pdV + μdN

Probability $$P_j = \frac{\bar{n}_j}{\Pi} = \frac{\sum_j \Omega(n) n_j(n)}{\sum_j \Omega(n)}$$

$$\Omega_t(n) = \frac{\Pi!}{\prod_j n_j!}$$

$$P_j(N,V,T) = \frac{e^{-E_j(N,V)/kT}}{Q(N,V,T)}$$

$$Q(N,V,T) = \sum_j e^{-E_j(N,V)/kT}$$

Helmholtz free energy $A = -kT\ln(Q)$

Entropy $S = k\ln(Q) + kT\frac{\partial \ln(Q)}{\partial T}|_{N,V}$

Pressure $p = -\frac{\partial A}{\partial V}|_{T,N} = kT\frac{\partial \ln(Q)}{\partial V}|_{N,T}$

Chemical potential $\mu = \frac{\partial A}{\partial N_i}|_{T,V,N\neq N_i} = -kT\frac{\partial \ln(Q)}{\partial V}|_{V,T}$

Internal energy $U = E = \bar{E} = kT^2(\frac{\partial \ln(Q)}{\partial T})_{N,V}$

Fluctuations $\sigma_E^2 = kT^2C_p$; $\sigma_p^2 = kT[\frac{\partial \bar{p}_i}{\partial V} - \frac{\partial p_i}{\partial V}]$

Energy $\bar{E} = kT^2\frac{\partial \ln(Q)}{\partial T}$ (Problem 141a)

Grand Canonical ensemble $\Xi(V, T, \mu)$ *(class 6A/B, problems 154-187)*

Characteristic function $d(pV) = SdT + Nd\mu + pdV$

Partition function
$$\Xi(V,T,\mu) = \sum_{j,N} e^{-E_j(N,V)/kT} e^{-N\mu/kT} = \sum_N [e^{-E_j(N,V)/kT} \sum_j e^{-N\mu/kT}]$$
$$= \sum_N Q e^{-N\mu/kT}$$

Probability $P_j = \dfrac{\overline{n}_j(N)}{\Pi} = \dfrac{n_j^*(N)}{\Pi} = \dfrac{e^{-\beta E_j(N,V)} e^{-\gamma N}}{\sum_{i,N'} e^{-\beta E_i(N',V)} e^{-\gamma N'}} = \dfrac{e^{-\beta E_j(N,V)} e^{-\gamma N}}{\Xi}$ $\gamma = -\mu\beta = -\dfrac{\mu}{kT}$

Number of possible states $\Omega_t(n) = \dfrac{\sum_{j,N} n_j(N)!}{\prod_{j,N} n_j(N)!}$

Pressure $pV = kT\ln(\Xi)\,;\; p = kT(\dfrac{\partial \ln(\Xi)}{\partial V})\Big|_{\mu,T}$

Entropy $S = k\ln(\Xi) + kT\dfrac{\partial \ln(\Xi)}{\partial T}|_{\mu,T} = -k\sum_j P_j(N)\ln[P_j(N)]$

Fluctuations $\sigma_N^2 = kT(\dfrac{\partial \overline{N}}{\partial \mu})_{V,T} = \dfrac{\overline{N}^2 kT\kappa}{V}$

Micro Canonical ensemble $\Omega(N,V,E)$ *(class 7, problems 188-204)*

Entropy	$dS = \frac{1}{T}dE + \frac{p}{T}dV - \frac{\mu}{T}dN$
Pressure	$\frac{p}{kT} = \frac{\partial \ln(\Omega)}{\partial E}\vert_{N,E}\,;\frac{1}{kT} = \frac{\partial \ln(\Omega)}{\partial E}\vert_{N,V}$
Chemical potential	$\frac{\mu}{kT} = -\frac{\partial \ln(\Omega)}{\partial N}\vert_{V,E}$
Boltzmann equation	$S = k\ln(\Omega)$

“Gibbs” ensemble $\Delta(N,T,P)$ *(problems 222, 223, 227, 229)*

Characteristic function G = E – TS + pV; dG = -SdT + Vdp + μdN; $G = -kT\ln(\Delta)$

Partition function $\Delta = \sum_V \sum_j e^{-E_j/kT - pV/kT}$; $\Delta = [\frac{(kT)^{5/2}(2\pi m)^{3/2}}{ph^3}]^N = X^N$ (for ideal gas)

Fluctuations $\sigma_H^2 = kT^2 C_p$

Fluctuations (class 8A/B, problems 205-229)

Canonical ensemble energy $\sigma_E^2 = kT^2 C_p$

Grand canonical ensemble energy $\sigma_E^2 = kT(\frac{\partial \overline{N}}{\partial \mu})_{V,T} = \frac{\overline{N}^2 kT\kappa}{V}$

Average of a distribution function

$\overline{g}(x) = \frac{\sum_i \mathrm{g_i} f_i}{\sum_i f_i}$ for example $P_j = \frac{\overline{\mathrm{n}}_\mathrm{j}}{N} = \frac{1}{N} \frac{\sum_j w_j n_j}{\sum_j w_j} = \frac{1}{N} \frac{\sum_j w_j(n) n_j(n)}{\sum_j w_j(n)}$

Pressure $\overline{p} = \sum_i \mathrm{p_i} P_i = \sum_i (\frac{\partial \mathrm{E_j}}{\partial \mathrm{V}}) P_i =_i \frac{\sum_i (\frac{\partial \mathrm{E_j}}{\partial \mathrm{V}}) f_i}{\sum_i f_i} = \frac{\sum_i (\frac{\partial \mathrm{E_j}}{\partial \mathrm{V}}) e^{-E_i/kT}}{\sum_i e^{-E_i/kT}}$ with $P_i = \frac{f_i}{\sum_i f_i} = \frac{e^{-E_i/kT}}{\sum_i e^{-E_i/kT}}$

Energy $\overline{E} = \sum_i E_i P_i = \frac{\sum_i \mathrm{E_i} e^{-E_i/kT}}{\sum_i e^{-E_i/kT}}$

Density of states for 3D particle in box

For an electron/photon gas multiply by factor of two for degeneracy of electron spin/polarization of wave.

$$\omega(\varepsilon)d\varepsilon = \frac{\pi}{4}(\frac{8m}{h^2})^{3/2}V\varepsilon^{1/2}d\varepsilon = 2\pi(\frac{2m}{h^2})^{3/2}V\varepsilon^{1/2}d\varepsilon =$$

$$2\pi(\frac{1}{\pi\hbar^2})^3 V(2m)^{3/2}\varepsilon^{1/2}d\varepsilon$$ *(class 4, problems 110-111)*

$$g(\nu)d\nu = \frac{4\pi}{c^3}V\nu^2 d\nu$$

Monoatomic ideal gas (particle-in-box) *(class 14A/B, problems 354-375)*

Partition function $q_{kinetic} = (\frac{2\pi m}{h^2} kT)^{3/2} V$

Thermal de Broglie wavelength $\Lambda = \frac{h}{p} = \frac{h}{(2\pi mkT)^{1/2}}$

Helmholtz energy $A(N,V,T) = -kT \ln(Q) = -NkT \ln\{(\frac{2\pi mkT}{h^2})^{3/2} \frac{Ve}{N}\}$

Gibbs energy $G = -kT \ln(Q) + NkT = -kTN \ln(\frac{q}{N}); G_m = -RT \ln(\frac{q_m}{L})$

Pressure $p = NkT(\frac{\partial \ln(q)}{\partial V})_T = NkT \frac{1}{V} = \frac{2}{3}\rho ;(\rho = U/V)$

Energy $E = NkT^2(\frac{\partial \ln(q)}{\partial T})_V = \frac{3}{2} NkT$

Heat capacity $C_V = (\frac{\partial E}{\partial T})_{V,N} = \frac{3}{2} Nk$

Entropy $S = Nk\{\ln[(\frac{2\pi mkT}{h^2})^{3/2} \frac{Ve^{5/2}}{N}]\}$

Chemical potential $\mu = -kT \ln\{(\frac{2\pi mkT}{h^2})^{3/2} \frac{V}{N}\}$

Diatomic ideal gas *(class 18A-C, problems 426-473)*

Key $X_{total} : X_{translations} ; X_{rotations} ; X_{vibrations} ; X_{electronic}$

Partition function $q_{total} = (\frac{2\pi mkT}{h^2})^{3/2} V \frac{8\pi^2 IkT}{\sigma h^2} \frac{e^{-\beta h\nu/2}}{(1-e^{-\beta h\nu})} \omega_{e_1} e^{D_e/kT}$

Partition function- high temperature limit $q_V = e^{-\beta h\nu/2} \sum_{n=0}^{\infty} e^{-\beta h\nu_n/2} \rightarrow e^{-\beta h\nu/2} \int_0^{\infty} e^{-\beta h\nu_n/2} = \frac{kT}{h\nu} = \frac{T}{\Theta_v};$

$q_{rot} = \frac{T}{\Theta_r} = \frac{8\pi^2 IkT}{h^2}$

Heat capacity $C_{total} = \frac{3}{2} nR + nR + nR(\frac{\Theta_v}{T})^2 \frac{e^{\Theta_v/T}}{(e^{\Theta_v/T} - 1)^2}$

Helmholtz energy

$$A_{total} = -NkT\{\ln[\frac{2\pi(m_1+m_2)kT}{h^2}]^{3/2} \frac{Ve}{N} + \ln[\frac{8\pi^2 IkT}{\sigma h^2}] - \frac{h\nu}{2kT}$$
$$-\ln[1-e^{h\nu/kT}] + \frac{D_e}{kT} + \ln[\omega_{e_1}]\}$$

Internal energy $E_{total} = NkT\{\frac{3}{2} + \frac{2}{2} + \frac{h\nu}{2kT} + \frac{h\nu/kT}{e^{h\nu/kT}-1} - \frac{D_e}{kT}\}$

Entropy

$$S_{total} = NkT\{\ln[\frac{2\pi(m_1+m_2)kT}{h^2}]^{3/2} \frac{Ve^{5/2}}{N} + \ln[\frac{8\pi^2 IkTe}{\sigma h^2}]$$
$$+\frac{h\nu/kT}{e^{h\nu/kT}-1} - \ln[1-e^{h\nu/kT}] + \ln[\omega_{e_1}]\}$$

Pressure $p = NkT(\frac{\partial \ln(q)}{\partial V})_T = NkT\frac{1}{V}$

Chemical potential $F = NkT\{\frac{\mu^0}{kT} + \ln p\}$

$$\mu^0 = kT\{-\ln[\frac{2\pi(m_1+m_2)kT}{h^2}]^{3/2} kT - \ln[\frac{8\pi^2 IkT}{\sigma h^2}] +$$
$$+\frac{h\nu}{2kT} + \ln[1-e^{h\nu/kT}] - \frac{D_e}{kT} - \ln[\omega_{e_1}]\}$$

Polyatomic ideal gas *(class 19, problems 474-492)*

	Vibrations $x = 3n - 5$ (linear) $x = 3n - 6$ (non-linear)	Rotations linear	Rotations nonlinear
Partition function	$q = \prod_{i=1}^{x} \frac{e^{-\Theta_i/2T}}{1 - e^{-\Theta_i/T}}$	$q_{rot} = \frac{T}{\sigma\Theta_r} = \frac{8\pi^2 IkT}{\sigma h^2}$	$q_{rot} = \frac{\pi^{1/2}}{\sigma}\left(\frac{T^3}{\Theta_A\Theta_B\Theta_C}\right)^{1/2} = \frac{\pi^{1/2}}{\sigma}\left(\frac{8\pi^2 I_A kT}{h^2}\right)^{1/2} \left(\frac{8\pi^2 I_B kT}{h^2}\right)^{1/2} \left(\frac{8\pi^2 I_C kT}{h^2}\right)^{1/2}$
Heat capacity	$C_V = Nk\sum_{i=1}^{x}\{(\frac{\Theta_i}{T})^2 \frac{e^{\Theta_i/T}}{(e^{\Theta_i/T}-1)^2}\}$	$C_{rot} = \frac{\partial E}{\partial T} = Nk$	$C_{rot} = \frac{\partial E}{\partial T} = \frac{3}{2}Nk$
Energy	$E = Nk\sum_{i=1}^{x}(\frac{\Theta_i}{2} + \frac{\Theta_i}{e^{\Theta_i/T}-1})$; $\Theta_i = \frac{h\nu_i}{k}$	$E_{rot} = NkT^2 \frac{\partial \ln q_{rot}}{\partial T} = NkT$	$E_{rot} = NkT^2 \frac{\partial \ln q_{rot}}{\partial T} = \frac{3}{2}NkT$

An extended list of equations for polyatomic molecules can also be found in [McQ, chapter 8-3].

$q_{electronic} = \sum_i \Omega_i e^{-\varepsilon_i/kT}$; $\Omega_i = 1$; $q_{nuclear} = 1$; $q_{kinetic} = (\frac{2\pi(m_1 + m_2)}{h^2}kT)^{3/2}V$ are the same equations as for diatomic molecules. The complete partition function would be given by

$q = q_{trans} q_{vib} q_{rot} q_{electronic} q_{nuclear}$, for example.

Maxwell-Boltzmann speed distribution *(class 17, problems 420-425)*

$$N(\varepsilon)d\varepsilon = 4\pi N(\frac{m}{2\pi kT})^{3/2} v^2 e^{-\frac{1}{2}mv/kT} dv$$

$$f(V_x) = \sqrt{\frac{m}{2\pi kT}} e^{-mV_x^2/2kT} dV_x ;\ f(c) = 4\pi c^2 (\frac{m}{2\pi kT})^{3/2} e^{-mc^2/2kT} dc$$

Classical limit *(problems 416-419)*

Quantum mechanics $n \to \infty; h \to 0; a \to \infty; m \to \infty\ E_n \to E; \psi_n \to \psi;\ ZPE \to E_0 = 0$

Stat thermo $q = \sum e^{-\varepsilon_i/kT} \to \frac{kT}{h\nu}; h \sum_{\substack{quantum\\states}} e^{-\varepsilon_i/kT} \to \int_{\substack{phase\\space}} \int e^{-\varepsilon_i/kT}$

Harmonic oscillator (Einstein/Debye model of crystals) *(class 15/16, problems 376-415)*

	Einstein	Debye
Partition function	$Q = e^{-\varphi(0)/2kT} q^{3N}$; $q = \frac{e^{-\Theta/2T}}{1-e^{-\Theta/T}}$	Density of states $g(\nu)d\nu = \frac{4\pi}{c^3} V\nu^2 d\nu$
Heat capacity	$C_V = 3Nk(\frac{\Theta}{T})^2 \frac{e^{\Theta/T}}{(e^{\Theta/T}-1)^2}$	$C_V = 3Nk[4D(u) - \frac{3u}{e^u - 1}]$ $D(u) = \frac{3}{u^3}\int_0^u \frac{x^3 du}{e^x - 1}$
	$C_V = \frac{12\pi^4}{5}(\frac{T}{\Theta_D})^3 + \eta R \frac{\pi^2}{2}(\frac{T}{\Theta_F}) \approx T^3 + T$	
$T \to \infty$	$C = 3Nk$	$C = 3Nk$
$T \to 0$	$C = 3Nk(\frac{\Theta}{T})^2 e^{-\Theta/T}$	$C \approx (\frac{T}{\Theta_D})^3$

Chemical equilibrium *(class 20, problems 493-506)*

$$S \underset{\text{isolated system}}{\longrightarrow} \max \Rightarrow A \underset{\text{V,T,N const}}{\longrightarrow} \min \Rightarrow Q \rightarrow \max$$

$$\nu_A A + \nu_B B \Leftrightarrow \nu_C C + \nu_D D$$

Equilibrium constant $K(T) = \dfrac{\rho_C^{\nu_C} \rho_D^{\nu_D}}{\rho_A^{\nu_A} \rho_B^{\nu_B}}$; $K(P) = \dfrac{p_C^{\nu_C}\, p_D^{\nu_D}}{p_A^{\nu_A}\, p_B^{\nu_B}} = (kT)^{(\nu_C+\nu_D-\nu_A-\nu_B)} K(T)$

The equilibrium constant is the ratio of partition functions per volume. This is of some direct practical use in the transition state theory.

Quantum statistics: Fermi-Dirac gas, electron gas *(class 23A, problems 520-534)*

Fermi function (Fermi distribution) $f_{FD} = f(\varepsilon) = \frac{1}{1+e^{(\varepsilon_k - \mu)/kT}}$

Population numbers $n_i^* = \frac{g_i}{e^{\alpha+\beta\varepsilon_i}+1}; \beta = \frac{1}{kT}; \alpha = -\frac{\mu}{kT}$ (g_i degeneracy)

Average number of Fermions (with energy ε_i) $\overline{n}_i = g_i n_i$ or using density of states $dN = \omega(\varepsilon) f(\varepsilon)$

Density of states of a free electron gas $\omega(\varepsilon)d\varepsilon = 2\frac{\pi}{4}(\frac{8m}{h^2})^{3/2} V\varepsilon^{1/2} d\varepsilon$; $N = \int_0^\infty \omega(\varepsilon) f_{FD} d\varepsilon$

Fermi energy, chemical potential (T = 0K) $\mu_0 = (\frac{3N}{8\pi V})^{2/3}\frac{h^2}{2m}$; $\mu_0 = \varepsilon_F = kT_F$;

$$\mu(T) \approx \mu_0[1 - \frac{\pi^2}{12}(\frac{kT}{\mu})^2 \pm \ldots]$$

Internal energy $U = \int_0^\infty \varepsilon N(\varepsilon) d\varepsilon z = \frac{3}{5} N\varepsilon_F [1 + \frac{5\pi^2}{12}(\frac{T}{T_F})^2 - \frac{\pi^4}{16}(\frac{T}{T_F})^4 + \ldots]$

Heat capacity $C = \frac{dU}{dT} = \frac{1}{2}\pi^2 Nk \frac{T}{T_F} \pm \ldots$; $C_{total} = C_{electrons} + C_{bulk} \approx T + T^3$

Helmholtz energy $A = U - TS = nkT_F[\frac{3}{5} - \frac{\pi^2}{4}(\frac{T}{T_F})^2 + \ldots]$

Pressure $p = -\frac{\partial A}{\partial V} = \frac{2}{3}\overline{E} = \frac{2}{3}\frac{U}{V}$

Entropy $S = \int \frac{C}{T} dT = \frac{\pi^2}{2} Nk[(\frac{T}{T_F}) - \frac{\pi^2}{10}(\frac{T}{T_F})^3 + \ldots]$

Quantum statistics: Bose-Einstein gas, photon gas *(class 23B, problems 535-555)*

BE distribution for photons $f_{Ph} = \frac{1}{e^{h\nu/kT} - 1}$

Population numbers $n_i = \frac{g_i}{e^{\alpha+\beta\varepsilon_i} - 1}$; $\beta = \frac{1}{kT}$; $\alpha = -\frac{\mu}{kT}$ (g_i degeneracy)

Average number of Fermions (with energy ε_i) $\overline{n}_i = g_i n_i$ or using density of states $dN = \omega(\varepsilon) f(\varepsilon)$

Density of states of a free electron gas $\omega(\nu) d\nu = 2\frac{4\pi \mathrm{V}}{\mathrm{c}^3}\nu^2 d\nu$

Chemical potential $\mu = 0$

Internal energy $u(\nu)d\nu = \frac{8\pi \mathrm{hV}}{\mathrm{c}^3}[\frac{\nu^3}{e^{h\nu/kT} - 1}]d\nu$; $u(\lambda)d\lambda = 8\pi \mathrm{hVc}\frac{1}{e^{hc/\lambda kT} - 1}d\lambda$ (Blackbody equation)

Total energy $\rho = \Diamond T^4$ (Stefan Boltzmann law); $T\lambda_{\max} = \mathrm{constant}$ (Wien's displacement law)

Heat capacity $C_{Photons} = 4\Diamond VT^3$; $\Diamond = \frac{8}{15}\pi^5 \frac{1}{h^2}\frac{1}{c^3}k^4$

Helmholtz energy $A = -\frac{1}{3}\Diamond VT^3$

Pressure $P = \frac{1}{3}\Diamond T^4 = \frac{1}{3}\rho$ (energy density $\delta = \frac{U}{V}$)

Entropy $S_{Photons} = \frac{4}{3}\Diamond VT^3$

Quantum statistics: Bose-Einstein condensation *(class 23C, problems 556-569)*

Ground state/excited state population $\frac{N_0}{N} = 1 - \frac{N_{ext}}{N} = 1 - (\frac{T}{T_B})^{3/2}$

Condensation temperature $T_{BEC} = (\frac{N_{ext}}{2.612V})^{2/3} \frac{h^2}{2\pi mk}$

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