

Golden sheet Autumn 2011, ver. 0.1

1 Thermodynamics

- | | |
|---|--|
| 1. law of thermodynamics: | $dU = q + w = q - pdV$ |
| 2. law of thermodynamics (isolated system): | $\Delta S \geq 0, \quad S = k_B \ln \Omega$ |
| 3. law of thermodynamics: | $T \rightarrow 0 \Rightarrow S \rightarrow 0, C_x \rightarrow 0$ |
| Entropy growth by delivering heat: | $dS \geq \frac{q}{T}$ |
| | $dS = \frac{q}{T}$ (Quasistatic, Reversible) |
| Equipartition theorem: | $U = \frac{f}{2} N k_B T, \quad f = \# \text{ degrees of freedom}$ |

Thermodynamic potentials:

Potential	Differential form	Maxwell relation
U	$dU = +TdS - PdV + \mu dN$	$\left(\frac{\partial T}{\partial V}\right)_{S,N} = -\left(\frac{\partial P}{\partial S}\right)_{V,N}$
$H = U + PV$	$dH = +TdS + VdP + \mu dN$	$\left(\frac{\partial T}{\partial P}\right)_{S,N} = +\left(\frac{\partial V}{\partial S}\right)_{P,N}$
$F = U - TS$	$dF = -SdT - PdV + \mu dN$	$\left(\frac{\partial S}{\partial V}\right)_{T,N} = +\left(\frac{\partial P}{\partial T}\right)_{V,N}$
$G = U + PV - TS = \mu N$	$dG = -SdT + VdP + \mu dN$	$\left(\frac{\partial S}{\partial P}\right)_{T,N} = -\left(\frac{\partial V}{\partial T}\right)_{P,N}$

Linear response functions (dN=0):

Specific heat	$C_V = \left(\frac{\partial U}{\partial T}\right)_V = T \left(\frac{\partial S}{\partial T}\right)_V$	$C_P = \left(\frac{\partial H}{\partial T}\right)_P = T \left(\frac{\partial S}{\partial T}\right)_P$
Thermal expansion coefficient	$\alpha_P = +\frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P$	$\alpha_S = -\frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_S$
Compressibility	$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$	$\kappa_S = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_S$
Bulk modulus	$K_T = -V \left(\frac{\partial P}{\partial V}\right)_T = \frac{1}{\kappa_T}$	$K_S = -V \left(\frac{\partial P}{\partial V}\right)_S = \frac{1}{\kappa_S}$
Pressure coefficient	$\beta_V = \left(\frac{\partial P}{\partial T}\right)_V$	$\beta_S = \left(\frac{\partial P}{\partial T}\right)_S$

$dV = 0$: Isochoric; $dP = 0$: Isobaric; $dT = 0$: Isothermal;
 $Q = 0$: Adiabatic; $dS = 0$: Isentropic (Adiabatic + Quasistatic)

2 Statistical mechanics

In thermal equilibrium with the surroundings: $p(s) = \frac{e^{-\beta E(s)}}{Z}, \quad \beta \equiv \frac{1}{k_B T}$

Partition function: $Z = \sum_s e^{-\beta E(s)} \quad (\Rightarrow \sum_s p(s) = 1)$

Average value of variable A : $\langle A \rangle = \sum_s A(s) p(s) = \sum_s A(s) \frac{e^{-\beta E(s)}}{Z}$

Mean energy: $U = \langle E \rangle = -\frac{\partial \ln(Z)}{\partial \beta} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta}$

Helmholtz free energy: $F = -k_B T \ln(Z)$

Distinguishable, independent "particles": $Z = Z_1 \cdot Z_2 \cdot Z_3 \cdot Z_4 \cdot \dots \quad (E = E_1 + E_2 + E_3 + E_4 + \dots)$

Indistinguishable, independent "particles": $Z = Z_1^N / N!$

3 Ideal-gas

Equation of state: $PV = Nk_B T = nRT$

Thermal energy: Only quadratic degrees of freedom; $U = f/2 N k_B T$.

4 Math

Binomial-coefficient: $\binom{N}{n} = \frac{N!}{n!(N-n)!}$

Stirling's approximation: $\ln(N!) \approx N \ln(N) - N$ ($N \gg 1$)

Taylor expansion: $f(x) = f(a) + f'(a)(x-a) + \frac{f''(a)}{2!}(x-a)^2 + \frac{f'''(a)}{3!}(x-a)^3 + \dots$

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \frac{x^4}{4!} + \dots$$

$$\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \dots$$

$$\sin(x) = x - \frac{x^3}{3!} + \frac{x^5}{5!} - \dots$$

$$\cos(x) = 1 - \frac{x^2}{2!} + \frac{x^4}{4!} - \dots$$

$$\frac{1}{1-x} = 1 + x + x^2 + x^3 + x^4 + \dots$$

$$(1+x)^\alpha = \sum_{n=0}^{\infty} \binom{\alpha}{n} x^n, \text{ hvor } \binom{\alpha}{n} = \frac{\alpha(\alpha-1)(\alpha-2)\dots(\alpha-n+1)}{n!}$$

$$\int_0^{\infty} x^n \exp(-ax^2) dx = I(n, a), \quad \frac{\partial I(n, a)}{\partial a} = -I(n+2, a)$$

$$\begin{array}{lll} I(0, a) = \frac{1}{2}\sqrt{\pi}a^{-1/2} & I(2, a) = \frac{1}{4}\sqrt{\pi}a^{-3/2} & I(4, a) = \frac{3}{8}\sqrt{\pi}a^{-5/2} \\ I(1, a) = \frac{1}{2}a^{-1} & I(3, a) = \frac{1}{2}a^{-2} & I(5, a) = a^{-3} \end{array}$$

Z is a function of X and Y ($Z = Z(X, Y)$),

Y is a function of X and Q ($Y = Y(X, Q)$):

$$dZ = \left(\frac{\partial Z}{\partial X}\right)_Y dX + \left(\frac{\partial Z}{\partial Y}\right)_X dY \quad \text{[Total differential]}$$

$$\left(\frac{\partial Z}{\partial X}\right)_Y = \left[\left(\frac{\partial Z}{\partial X}\right)_Y\right]^{-1} \quad \text{[The inverse of the derivative]}$$

$$\left(\frac{\partial Z}{\partial X}\right)_Y = \left(\frac{\partial Z}{\partial Q}\right)_Y \left(\frac{\partial Q}{\partial X}\right)_Y \quad \text{[The chain rule]}$$

$$-1 = \left(\frac{\partial Z}{\partial X}\right)_Y \left(\frac{\partial X}{\partial Y}\right)_Z \left(\frac{\partial Y}{\partial Z}\right)_X \quad \text{[“The fake chain rule”]}$$

$$\left(\frac{\partial}{\partial X} \left(\frac{\partial Z}{\partial Y}\right)_X\right)_Y = \left(\frac{\partial}{\partial Y} \left(\frac{\partial Z}{\partial X}\right)_Y\right)_X \quad \text{[Exchange of order of differentiation]}$$

$$\left(\frac{\partial Z}{\partial X}\right)_Q = \left(\frac{\partial Z}{\partial X}\right)_Y + \left(\frac{\partial Z}{\partial Y}\right)_X \left(\frac{\partial Y}{\partial X}\right)_Q \quad \text{[Exchange of fixed variable]}$$

5 Constants

$$k_B = 1.381 \cdot 10^{-23} \text{ J/K} = 8.617 \cdot 10^{-5} \text{ eV/K} \quad R = 8.315 \text{ J/(mol K)}$$

$$N_A = 6.022 \cdot 10^{23}$$

$$h = 6.626 \cdot 10^{-34} \text{ J s} = 4.136 \cdot 10^{-15} \text{ eV s}$$

$$1 \text{ atm} = 1.013 \text{ bar} = 1.013 \cdot 10^5 \text{ N/m}^2 = 1.013 \cdot 10^5 \text{ Pa}$$

$$1 \text{ eV} = 1.602 \cdot 10^{-19} \text{ J}$$

$$1 \text{ u} = 1.661 \cdot 10^{-27} \text{ kg}$$