Review Notes on Thermodynamics and Statistical Mechanics

Dan Elton

May 18, 2011

These are some notes I threw together while preparing for my Statistical Mechanics exam. I make no guraentee of accuracy!

Laws of Thermodynamics

- **Zeroth Law of Thermodynamics**: If T(A) = T(B) and T(B) = T(C), then T(A) = T(C) (def. of thermal equilibrium. T can be replaced with any state variable.)
- **First Law of Thermodynamics**: $dU = \delta W + \delta Q$
- **Second Law of Thermodynamics**: *It is impossible to build a device whose sole effect is to move heat from hot to cold.* (Clausius statement) *It is impossible to build a device whose sole effects are to perform work and extract heat from a reservoir.* (Kelvin-Planck statement). *For a closed system, $\Delta S \geq 0$, with equality only if all processes are reversable.* (Modern statement)
- **Third Law of Thermodynamics**: Entropy goes to zero as temperature goes to zero. (Violated in many systems, including ice)

Work

$$\begin{aligned}
&\textbf{Adiabadic:} \quad Pv^{\gamma} = \text{Const. } \gamma \equiv \frac{C_P}{C_V} \\
&\textbf{Isobaric: } W = P(V_2 - V_1) \\
&\textbf{Isochoric: } W = 0 \\
&\textbf{Isothermal: } W = nRT \ln\left(\frac{V_2}{V_1}\right)
\end{aligned} \tag{1}$$

Heat Engines / The Carnot Cycle

1. Isothermal expansion from V_1 to V_2
2. Adiabatic expansion from V_2 to V_3.
3. Isothermal compression from V_3 to V_4. (at smaller temperature than before)
4. Adiabatic compression from V_4 to V_1.

$$\frac{\Delta Q_1}{T_H} + \frac{\Delta Q_2}{T_C} = 0 \tag{2}$$

Here, Q_1 is the heat exchanged during step 1 and Q_3 is the heat exchanged in step 3. Any cycle can be decomposed into infinitely many tiny Carnot-like steps. Thus we can prove this relation for any cyclic process, and

$$\oint \frac{dQ}{T} = 0 \tag{3}$$

holds for any reversible process. The quantity $S = \frac{dQ}{T}$ is an exact differential and is called the Entropy. The efficiency of the Carnot cycle (or any fully-reversable cycle) is:

$$\epsilon = \frac{|Q_H| - |Q_C|}{|Q_H|} = 1 - \frac{T_C}{T_H} \tag{4}$$

Maxwell Velocity Distribution

$$\begin{aligned}
P(\vec{v}) &= \left(\frac{m}{2\pi kT}\right)^{2/3} e^{\frac{-\beta m\vec{v}^2}{2}} \\
P(v) &= \left(\frac{\beta m}{2\pi}\right)^{3/2} v^2 e^{-\beta m v^2} \\
\bar{v} &= \left(\frac{8kT}{\pi m}\right)^{1/2} \\
v_{\text{rms}} &= \left(\frac{3kT}{m}\right)^{1/2} \\
v_{\max} &= \left(\frac{2kT}{m}\right)^{1/2}
\end{aligned} \tag{5}$$

Response functions

$$\begin{aligned}
&\textbf{Molar Specific heat} & C_v &\equiv \frac{1}{n}\frac{dQ}{dT}\Big|_v \\
&\textbf{Molar Specific heat} & C_p &\equiv \frac{1}{n}\frac{dQ}{dT}\Big|_p \\
&\textbf{Mayer's Equation} & C_p - C_v &= R \\
&\textbf{Coefficient of Thermal Expansion} & \alpha &\equiv \frac{1}{V}\frac{\partial V}{\partial T}\Big|_p \\
&\textbf{Bulk Modulus} & B &\equiv \frac{1}{\kappa_T} \\
&\textbf{Young's Modulus} & E_y &\equiv -\frac{1}{L}\frac{\partial L}{\partial p}\Big|_T \\
&\textbf{Magnetic Susceptibility} & \chi &= \frac{\partial M}{\partial H} \\
&\textbf{Isothermal Compressibility} & \kappa_T &\equiv -\frac{1}{v}\frac{\partial V}{\partial p}_T = -\frac{1}{v}\frac{\partial^2 G}{\partial T^2}
\end{aligned} \tag{6}$$

Heat Conduction

$$\begin{aligned} \frac{dQ}{dT} &= kA\frac{dT}{dx} \\ k &= \text{ thermal conductivity} \end{aligned} \tag{7}$$

Thermodynamics Potentials & Differentials

$$\begin{aligned} dU &= TdS - pdV + \mu dN & & \\ H &= E = U + pV & dH &= TdS + VdP \\ G &= H - TS & dG &= Vdp - SdT \\ A &= U - TS & dAh &= -SdT - pdV \end{aligned} \tag{8}$$

The "Maxwell relations" can be derived from these using the fact that for non-singular functions, $\partial_x \partial_y f(x,y) = \partial_y \partial_x f(x,y)$. If we are describing a magnetic system, we simply make the replacements $V \to -M$ and $p \to H$.

Blackbody radiation

Planck's Law

$$I(\nu, T) = \frac{2h\nu^3}{c^2}\frac{1}{e^{\frac{h\nu}{kT}} - 1} \tag{9}$$

Wein's Law

$$\lambda_{\text{max}}T = 2.91 \times 10^{-3} \text{ mK} \tag{10}$$

Stefan-Boltzmann Law

$$\begin{aligned} P &= \sigma T^4 \\ \sigma &= 5.67 \times 10^8 \text{ Wm}^{-2}\text{K}^{-4} \end{aligned} \tag{11}$$

The Partition Function

$$Z \equiv \sum_{\text{states}} e^{-\beta \mathcal{H}} \tag{12}$$

$$\begin{array}{lr} \textbf{The Partition Function:} & Z = \sum_i g_i e^{-\beta \epsilon_i} \\ \textbf{Internal Energy:} & U = NkT^2 \frac{\partial \ln(Z)}{\partial T}_V = -\frac{\partial \ln(Z)}{\partial \beta} \\ \textbf{Gibb's Free Energy:} & G = -k_B T \ln(Z) \\ \textbf{Reduced Gibb's FE:} & f = \ln(Z) \\ \textbf{Entropy} & S = k_B(\beta U + f) \\ \textbf{Specific Heat:} & C = -k_B \beta^2 \frac{\partial U}{\partial \beta} \end{array} \tag{13}$$

For systems with an enormous number of degrees of freedom (ideal gas, etc) we treat the state-space as continuous. We must use the notion of the **Density of States**:

$$\begin{aligned} Z &= \int_0^\infty g(\epsilon) e^{-\beta\epsilon} d\epsilon \\ g(\epsilon) &= \frac{dn(\epsilon)}{d\epsilon} \end{aligned} \tag{14}$$

The Grand Canonical Ensemble

$$Z_G = \sum_{\text{states}} e^{-\beta(E-\mu N)} \tag{15}$$

Distribution Functions

Boltzmann & Maxwell-Boltzmann

$$N_j = g_j \frac{N}{Z} e^{-\beta\epsilon_j} \tag{16}$$

Fermi-Dirac

$$\langle n\rangle = \sum_{k,\sigma} \frac{1}{e^{\beta(E_{k,\sigma}-\mu)}+1} \tag{17}$$

Bose-Einstein

$$\langle n\rangle = \sum_{k,\sigma} \frac{1}{e^{\beta(E_{k,\sigma}-\mu)}-1} \tag{18}$$

The Ising Model

Ising Model

$$\begin{aligned} \mathcal{H} &= J\sum_{i=1}^{N} \sigma_i\sigma_{i+1} - H\sum_i \sigma_i \\ Z &= \sum_{\sigma_1=\pm 1} \cdots \sum_{\sigma_N=\pm 1} e^{\beta J\sum_{i=1}^{N}\sigma_i\sigma_{i+1} - H\sum_i \sigma_i} \end{aligned} \tag{19}$$

The analysis is simplified if we ignore end effects and put the spins of a circle, since in the thermodynamic limit the end spin contributions don't matter. We also define $K \equiv \beta J$ and $h = \beta H$. For 2 spins,

$$Z_2 = \sum_{\sigma_1=\pm 1}\sum_{\sigma_2=\pm 1} e^{\beta J\sigma_1\sigma_2} = 2(e^K + e^{-K}) = 4\cosh K \tag{20}$$

for N spins in a line:

$$Z_N = 2^N(\cosh K)^{N-1} \tag{21}$$

for N spins on a circle:

$$Z_N = 2^N(\cosh K)^N \tag{22}$$

1D Transfer Matrix Method

The transfer matrix is defined as

$$T = \begin{pmatrix} e^{K+h} & e^{-K} \\ e^{-K} & e^{K-h} \end{pmatrix} \tag{23}$$

$$Z = \mathrm{tr}(T^N) = \lambda_1^N + \lambda_2^N \tag{24}$$

The Pott's Model

The Classical Spin Model

The van der Waals equation

The vdW Equation

$$\left(p + \frac{aN^2}{V^2}\right)(V - bN) = Nk_BT \tag{25}$$

Law of Corresponding States

$$\bar{p} \equiv \frac{p}{p_C} \qquad \bar{v} \equiv \frac{v}{v_C} \qquad \bar{T} \equiv \frac{T}{T_C} \tag{26}$$

$$\left(\bar{p} + \frac{3}{\bar{v}}\right)(3\bar{v} - 1) = 8\bar{T} \tag{27}$$

The Leonard-Jones Potential

Due to dipole-dipole interactions

$$U = U_0\left[\left(\frac{r_0}{r}\right)^{12} - 2\left(\frac{r_0}{r}\right)^{6}\right] \tag{28}$$

for Argon, $r_0 = 3.8$ angstroms, and $U_0 = 11 \times 10^{-2}$ eV.

Virial (low-density) expansion

$$\beta p = \sum_{l=1}^{\infty} B_l \rho^l \tag{29}$$

The Clausius-Claperon Equation

Recall

$$dG = -SdT + vdP \tag{30}$$

On a given coexistance curve, $dG_1 = dG_2$, thus

$$\begin{aligned} -S_2dT + v_2dP &= -S_1dT + v_1dP \\ (S_2 - S_1)dT &= (v_2 - v_1)dP \\ \frac{dP}{dT} &= \frac{\Delta S}{\Delta V} \text{ (The C.C. Equation)} \end{aligned} \tag{31}$$

Here, $\Delta S = \frac{L_v}{T}$

$$\begin{aligned} \frac{1}{P}\frac{dP}{dT} &= \frac{L_v}{TP\Delta V} = \frac{L_v}{nRT^2} \\ &\rightarrow P = P_0 e^{-\frac{L_v}{nRT}} \end{aligned} \tag{32}$$

Phase Transitions

- **First order phase transition**: Has discontinuous change in entropy. The (Gibbs) free energy must be have a discontinous derivative with respect to one of the externally applied variables (eg. temperature, pressure, magnetic field).
- **Second order phase transition**: Has continuous change in entropy, free energy is smooth and continous. Has discontinuity or divergence in it's second derivatives (ie, quantities like specific heat or susceptability). (famous example: superfluidity in He-4.. there are many other examples though. Also, at the critical point of the liquid-vapor co-existance curve, the first order transition becomes second order at that point.)
- **nth order phase transition**: Has a discontinuity or divergence in the nth derivative of the free energy.

–Glass must be considered a liquid - it undergoes no phase change during melting – the degree of order does not change.

Critical Exponents Order Parameter: $\psi = \rho_l - \rho_g$ As $T \rightarrow T_C$, the order parameter vanishes as:

$$\begin{aligned}
\epsilon &\equiv \frac{T - T_c}{T_c} = \frac{T}{T_c} - 1 \\
\psi &\sim (-\epsilon)^{\beta} \text{ for } \epsilon > 0 \\
C_V &\sim (-\epsilon)^{-\alpha]} \text{ for } \epsilon < 0 \\
C_V &\sim \epsilon^{-\alpha} \text{ for } \epsilon > 0 \\
\kappa_T &\sim (-\epsilon)^{-\gamma'} \text{ for } \epsilon < 0 \\
\kappa_T &\sim \epsilon^{-\gamma} \text{ for } \epsilon > 0 \\
P - P_C &\sim |\rho_L - \rho_G|^{\delta} \text{sgn}(\rho_L - \rho_G) \quad \text{(Critical Isotherm)} \\
\xi &\sim (-\epsilon)^{-\nu'} \text{ for } \epsilon < 0 \quad \text{(Correlation length)} \\
\xi &\sim \epsilon^{-\nu} \text{ for } \epsilon > 0
\end{aligned}$$

$$\chi \propto \left|1 - \frac{T}{T_C}\right|^{-\gamma} \text{for} \quad T \geq T_C \tag{34}$$

β **Brass**

Magnetism

- **Ferromagnetism** The transition from magnetic to non-magnetic occurs at the **Curie Temperature**
- **Paramagnetism**
- **Anti-ferromagnetism** at the **Néel temperature** there is a phase transition to paramagnetism.

- **Ferrimagnetism** - is similiar to ferromagnetism, accept nearby atoms actually have opposing mangetic moments. One atomic species dominates, creating a net magnetic field.

Currie'slaw: (Valid at high temperature)

$$\vec{M} = \chi \vec{H} = C\frac{\vec{H}}{T} \tag{35}$$

C= the Curie Constant
Curie-Weiss Law

$$\xi \propto \frac{1}{T - T_C} \tag{36}$$

Analysis of a Paramagnet:
Let B be in the z direction. The spin angular momentum of an electron can take on $2j+1$ possible values. We restric our attention to a single spin. The energies of those states are:

$$\begin{aligned} E_m &= -gm\mu_B B \\ \mu_B &= \frac{e\hbar}{2m} \end{aligned} \tag{37}$$

The relative probabilities of these states is given by the Boltzmann factor:

$$\begin{aligned} P(m) &= \frac{1}{Z}e^{\beta E_m} \\ Z &= \sum_{-s}^{s} e^{\beta g\mu_B sH} \end{aligned} \tag{38}$$

We make the change of variables $x = e^{\beta g\mu_B H} = e^Y$ and use the fact that

$$\sum_{k=0}^{n} r^k = \frac{(1 - r^{n+1})}{1 - r} \tag{39}$$

to find

$$Z = \frac{\sinh{(s + \frac{1}{2})y}}{\sinh\frac{y}{2}} \tag{40}$$

The average magnetic moment is

$$\bar{\mu} = \frac{1}{\beta}\frac{\partial\ln(Z)}{\partial H} \tag{41}$$

It can be shown that if Z_1 is the partition function for 1 spin, for N non-interacting *dinstinguishable* spins, the partition function is

$$Z_N = (Z_1)^N \tag{42}$$

Stuff I should have studied

- Mean field theory
- Landau-Ginsberg approach to phase transitions
- Universality classes of phase transitions
- How to calculate critical exponents, etc.

Misc

Stirling's Approximation

$$\ln(N!) \approx N\ln(N) - N \tag{43}$$

1 cal = 3.186 J

$$T_F = \frac{9}{5}T_C + 32$$
$$T_C = \frac{5}{9}(T_F - 32)$$