Final solutions

2026

(1.) Virial expansion

Dilute classical gas with pair potential $u(r_{ij}) = u(|\vec{r}_i - \vec{r}_j|)$, where $\vec{r}_i$ = position of particle i.

(a) Start with the canonical partition function: (N particles)

$$Z_N = \frac{1}{N!\,\lambda_T^{3N}} \int d^N\vec{r}\; e^{-\beta \mathcal{U}(\vec{r}_1, \dots, \vec{r}_N)},$$

where $\lambda_T = \sqrt{\frac{2\pi\hbar^2}{m k_B T}}$ is the thermal de Broglie wavelength

and $\mathcal{U}(\vec{r}_1, \dots, \vec{r}_N) = \sum_{i<j} u(r_{ij})$.

Introduce $f_{ij} = e^{-\beta u(r_{ij})} - 1$, then

$$f_{ij} \equiv f(r_{ij})$$

$$e^{-\beta \mathcal{U}} = \prod_{i<j} (1 + f_{ij}) .$$

For low density, we expect:

$$\prod_{i<j} (1 + f_{ij}) \simeq 1 + \sum_{i<j} f_{ij}$$ and thus

$$Z_N \simeq Z_N^{(0)} + Z_N^{(1)} .$$

$$Z_N^{(0)} = \frac{V^N}{N!\,\lambda_T^{3N}},$$ whereas

$$Z_N^{(1)} = \frac{1}{N!\,\lambda_T^{3N}} \sum_{i<j} \underbrace{\int d^N\tilde{r}\, f_{ij}}_{V^{N-2}\int d^3r_i\, d^3r_j\, f(r_{ij}) =}$$

$$\underset{\substack{\uparrow \\ \text{transl. inv.}}}{=} V^{N-1} \int d^3r\, f(r).$$

$\sum_{i<j}$ is over $\frac{N(N-1)}{2}$ particle pairs.

Thus, $Z_N^{(1)} = Z_N^{(0)} \frac{1}{V^N} \frac{N(N-1)}{2} V^{N-1} \int d^3r\, f(r) =$

$$= Z_N^{(0)} \frac{N(N-1)}{2V} \int d^3r\, f(r).$$

Next, $F = -k_BT \log Z_N =$

$$\simeq -k_BT \log\left\{ Z_N^{(0)} \left[1 + \underbrace{\frac{N(N-1)}{2V} \int d^3r\, f(r)}_{\text{expect to be small, } \ll 1} \right]\right\} \simeq$$

$$\simeq -k_BT \left[\log Z_N^{(0)} + \frac{N(N-1)}{2V} \int d^3r\, f(r)\right].$$

Finally, $p = k_BT \left(\frac{\partial \log Z_N}{\partial V}\right)_T = -\left(\frac{\partial F}{\partial V}\right)_T$.

$$p = k_B T \, \frac{\cancel{\lambda_T^{3N}}\, \cancel{N!}}{V^N} \, \frac{N V^{N-1}}{\cancel{N!}\, \cancel{\lambda_T^{3N}}} - k_B T \frac{\overset{N \gg 1}{N^2}}{2V^2} \int d^3 r \, f(r) =$$

$$= \frac{k_B T N}{V} \left[1 - \frac{N}{2V} \int d^3 r \, f(r) \right] .$$

This yields $B_2 = - \frac{1}{2} \int d^3 r \, f(r)$, and

$$\frac{p}{n k_B T} \simeq 1 + B_2 n .$$

$\uparrow$ $n = \frac{N}{V}$

(b) Hard spheres:

$$u(r) = \begin{cases} \infty , & r < 2a \\ 0 , & r > 2a \end{cases}$$

Then $$e^{-\beta u(r)} = \begin{cases} 0, & r < 2a \\ 1, & r > 2a \end{cases} \Rightarrow f(r) = \begin{cases} -1, & r < 2a \\ 0, & r > 2a \end{cases}$$

Thus, $$B_2 = - \frac{1}{2} \int_{r<2a} d^3 r \, (-1) = \frac{1}{2} \, \frac{4\pi}{3} (2a)^3 = \frac{16 \pi a^3}{3} .$$

$B_2 \sim$ excluded volume of the particle

Note that $B_2 > 0 \Rightarrow$ pressure is <u>higher</u> than in the ideal gas

(c) If $\underbrace{u(r) < 0}_{\text{attractive interactions}} \Rightarrow e^{-\beta u(r)} > 1 \Rightarrow f(r) > 0 .$

Then $B_2 < 0 \Rightarrow$ the pressure is <u>lowered</u> compared to the ideal gas.

(2.) Blackbody radiation

(a) grand - canonical partition function:

$$Q = \prod_{\vec{k},\vec{\epsilon}} \frac{1}{1-e^{-\beta\hbar\omega_{\vec{k}}}} \quad , \text{ where } \quad \omega_{\vec{k}} = \overset{\text{speed of light}}{c}\underbrace{|\vec{k}|}_{k} .$$

grand potential:

$$\Omega = -k_B T \log Q = k_B T \sum_{\vec{k},\vec{\epsilon}} \log(1-e^{-\beta\hbar\omega_{\vec{k}}}) =$$

$$= \underset{\text{sum over polarizations}}{2} k_B T \sum_{\vec{k}} \log(1-e^{-\beta\hbar\omega_{\vec{k}}}) .$$

Now, use $\sum_{\vec{k}} \rightarrow \frac{V}{(2\pi)^3}\int d^3k$ and standardize the integral:

$$\Omega = 2k_B T \frac{V}{(2\pi)^3} 4\pi \int_0^\infty dk\, k^2 \log(1-e^{-\beta\hbar ck}) \overset{x=\beta\hbar ck}{=}$$

$$= \frac{V k_B T}{\pi^2} \frac{1}{(\beta\hbar c)^3} \underbrace{\int_0^\infty dx\, x^2 \log(1-e^{-x})}_{= -\frac{\pi^4}{45}}$$

Finally, $\Omega = -\frac{V k_B T}{\pi^2(\beta\hbar c)^3}\frac{\pi^4}{45} = -\frac{\pi^2}{45}\frac{V}{\hbar^3 c^3}(k_B T)^4.$

note that $\Omega = A\beta^{-4}$, $A = -\frac{\pi^2}{45}\frac{V}{\hbar^3 c^3}$

(b) $\overset{\text{pressure}}{p} = -\left(\frac{\partial \Omega}{\partial V}\right)_T = -\frac{\Omega}{V}$, since

$\Omega \sim V$ from part (a).

Thus, $p = \frac{\pi^2}{45} \frac{(k_B T)^4}{\hbar^3 c^3} \sim T^4$ — p steeply increases with T

(c) Internal energy
$$\mathcal{U} = + \frac{\partial}{\partial \beta} (\beta \Omega)_V = + \frac{\partial}{\partial \beta} (A \beta^{-3}) =$$

$$= -3 \beta^{-4} A = 3 \underbrace{\frac{\pi^2}{45} \frac{(k_B T)^4}{\hbar^3 c^3}}_{\text{" } p} V \text{, or}$$

$$u = \frac{\mathcal{U}}{V} = 3p \Rightarrow p = \frac{u}{3}.$$

(d) Entropy

$$S = -\left(\frac{\partial \Omega}{\partial T}\right)_V \Rightarrow S = -A k_B^4 \, 4 T^3 =$$

$$= \underbrace{-3A\beta^{-4}}_{\text{" } \mathcal{U}} \times \frac{1}{T} \frac{4}{3} = \frac{4}{3} \frac{\mathcal{U}}{T}.$$

Indeed, $\Omega = \mathcal{U} - TS - \mu N \underset{\substack{\mu = 0 \\ \text{here}}}{\Longrightarrow} S = \frac{\mathcal{U} - \Omega}{T}.$

But $\mathcal{U} = 3pV, \quad \Omega = -pV$:

$$S' = \frac{4pV}{T} \underset{\substack{\uparrow \\ pV = \frac{\mathcal{U}}{3}}}{=} \frac{4}{3}\frac{\mathcal{U}}{T}, \text{ as desired.}$$

3. Mean-field Ising model

(a) Consider $$H = -\frac{2J}{N} \sum_{\substack{i\in A\\ j\in B}} \overset{\swarrow \text{ long-range coupling}}{S_i S_j} - h_A \sum_{i\in A} S_i - h_B \sum_{j\in B} S_j \,, \quad S_i = \pm 1 .$$

a bi-partite lattice with 2 sublattices, with $\frac{N}{2}$ spins each.

Define $\begin{cases} m_A = \langle S_i \rangle_{i\in A} \\ m_B = \langle S_j \rangle_{j\in B} \end{cases}$ per-spin magnetization

Mean-field: each spin in A feels

$$\sum_{j\in B} S_j \Rightarrow \underbrace{\frac{N}{2} m_B}_{\text{on average}}$$

Likewise, each spin in B feels

$$\sum_{i\in A} S_i \Rightarrow \underbrace{\frac{N}{2} m_A}_{\text{on average}} .$$

Then $$H_{MF} = -\frac{J}{N} \sum_{i\in A} S_i \left(\frac{N}{2} m_B\right) - h_A \sum_{i\in A} S_i - \frac{J}{N} \sum_{j\in B} S_j \left(\frac{N}{2} m_A\right) - h_B \sum_{j\in B} S_j =$$

$$= -\underbrace{\left(\frac{J}{2} m_B + h_A\right)}_{\text{"} h_A^{eff}} \sum_{i\in A} S_i - \underbrace{\left(\frac{J}{2} m_A + h_B\right)}_{\text{"} h_B^{eff}} \sum_{j\in B} S_j$$

Thus, we have:

$$\begin{cases} m_A = \tanh\left[\beta\left(\frac{J}{2} m_B + h_A\right)\right], \\ m_B = \tanh\left[\beta\left(\frac{J}{2} m_A + h_B\right)\right]. \end{cases} \quad (*)$$

(b) Now, consider $h_A = 0$, $h_B = 0$:

$$\begin{cases} m_A = \tanh\left[\frac{\beta J}{2} m_B\right], \\ m_B = \tanh\left[\frac{\beta J}{2} m_A\right]. \end{cases}$$

Expand near T_c:

$$\begin{cases} m_A \simeq \frac{\beta J}{2} m_B, \\ m_B \simeq \frac{\beta J}{2} m_A \end{cases} \Rightarrow m_A = \underbrace{\left(\frac{\beta J}{2}\right)^2}_{\text{have to have this } = 1, \text{ otherwise only } m_A = 0 \text{ works}} m_A$$

similar for m_B

Then $\beta_c = \frac{2}{J} \Rightarrow \underline{\underline{T_c = \frac{J}{2k_B}}}$. ferromagnetic transition

We can also do: $\begin{pmatrix} m_A \\ m_B \end{pmatrix} = \begin{pmatrix} 0 & \frac{\beta J}{2} \\ \frac{\beta J}{2} & 0 \end{pmatrix} \begin{pmatrix} m_A \\ m_B \end{pmatrix}$, or

$$\begin{pmatrix} 1 & -\frac{\beta J}{2} \\ -\frac{\beta J}{2} & 1 \end{pmatrix} \begin{pmatrix} m_A \\ m_B \end{pmatrix} = 0.$$

To have non-trivial solutions, need

$\det(\dots) = 0 \Rightarrow \left(\frac{\beta J}{2}\right)^2 = 1$, as before.

(c) Now, set $h_A = h$, $h_B = -h$
(staggered fields)

Eq. (*) becomes:
$$\begin{cases} m_A = \tanh\left[\beta\left(\frac{J}{2} m_B + h\right)\right], \\ m_B = \tanh\left[\beta\left(\frac{J}{2} m_A - h\right)\right]. \end{cases}$$

Linearize and solve for $m_s = \frac{m_A - m_B}{2}$:

$$m_A - m_B \approx \beta \frac{J}{2}(m_B - m_A) + 2\beta h, \text{ or}$$

$$\underline{\underline{m_s = \frac{\beta h}{1 + \beta \frac{J}{2}}}} \quad \text{staggered magnetization}$$

(d) Staggered susceptibility:
$$\chi_s = \left(\frac{\partial m_s}{\partial h}\right)_T = \frac{\beta}{1 + \beta \frac{J}{2}}.$$

at $T = T_c$, $\underbrace{\chi_c = \frac{\beta}{2}}$ no divergence at T_c, stable anti-ferromagnetic mode