

★ Week 10 reading: Blundell+Blundell, chapters 23, 24, 25, 28.1, 28.2, 28.3.

• Continue where we left off last time, relativistic gases. $E = \sqrt{c^2 p^2 + (mc^2)^2}$. In the ultrarelativistic limit, $E \approx cp$. The single particle partition function is then

$$Z_1 = V \int \frac{d^3 \vec{p}}{(2\pi\hbar)^3} e^{-\beta cp} = \frac{V}{2\pi^2} \left(\frac{k_B T}{\hbar c}\right)^3 \int_0^\infty e^{-x} x^2 dx = \frac{V}{\pi^2} \left(\frac{k_B T}{\hbar c}\right)^3.$$

Recall that in the non-relativistic case we found $Z_1 \propto VT^{3/2}$. Write $Z_1 = V/\Lambda^3$ in the relativistic case, with $\Lambda \sim 1/T$.

For low-density the partition function for N indistinguishable relativistic particles is $Z_N = Z_1^N/N!$ and thus $\ln Z_N \approx N \ln V + 3N \ln T + \text{const}$. So $U = -\frac{d}{d\beta} \ln Z = 3Nk_B T$ (vs $\frac{3}{2}Nk_B T$ in the non-relativistic case) and $C_V = 3Nk_B$ and $F = -k_B T \ln Z_N$ gives $p = -\left(\frac{\partial F}{\partial V}\right)_T = Nk_B T/V$ (same ideal gas law). So we again get $p = u/3$ with $u = U/V$. Find the entropy $S = (U - T)/T = Nk_B(4 - \ln(n\Lambda^3))$.

An adiabatic expansion has constant S and thus constant $n\Lambda^3$ so, taking N constant, VT^3 is a constant. Since $pV \propto T$, write this as $pV^\gamma = \text{const}$ with $\gamma = 4/3$. In the non-relativistic case, recall that $\gamma = 1 + (2/f) = 5/3$.

Consider the expansion of the universe as an adiabatic process, with $V \propto a(t)^3$ the scale factor. So a non-relativistic gas has energy density $\rho \propto a^{-3}$ while a relativistic gas has $\rho \propto u \propto a^{-4}$, and a non-relativistic gas has $VT^{3/2}$ constant so $T \propto a^{-2}$, while a relativistic gas has VT^3 constant so $T \propto a^{-1}$. As the universe expands, it went from radiation dominated at small a to matter dominated.

• Phonons and the Einstein and Debye model for solids. Think of the solid as a lattice of balls (atoms) and springs (restoring forces). Each atom has 3 vibrational d.o.f. and then $Z = \prod_{i=1}^{3N} Z_i$ where each Z_i is treated as a SHO with the approximation that they all have the same frequency ω_E , so $Z_i = e^{-\frac{1}{2}\beta\hbar\omega_E}/(1 - e^{-\beta\hbar\omega_E})$. Gives $\ln Z = 3N \ln Z_i$ and then $U = 3Nk_B \hbar\omega_E \left(\frac{1}{2} + (e^{\beta\hbar\omega_E} - 1)^{-1}\right)$.

The Debye model is an improvement, which replaces the single ω_E of the Einstein model with a distribution $g(\omega)$, with $\int g(\omega)d\omega = 3N$. So the Einstein case is $g_E(\omega) = 3N\delta(\omega - \omega_E)$. The Debye model takes $\omega = v_s k$ and $g(k)dk = \Theta(k - k_D)3V(4\pi)k^2 dk/(2\pi)^3$, which is again counting modes in a box and the 3 is for the polarizations. The constant $k_D = \omega_D/v_s$ is chosen such that $\int_0^{\omega_D} g(\omega)d\omega = 3N$, which gives $\omega_D = (6N\pi^2 v_s^3/V)^{1/3}$. So we can write $g(\omega)d\omega = 9N\omega^2 d\omega/\omega_D^3$. Now the Debye model takes

$$\ln Z = \int_0^{\omega_D} d\omega g(\omega) \ln \left(\frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} \right).$$

$$U = -\frac{\partial}{\partial \beta} \ln Z = \frac{9}{8} N \beta \hbar \omega + \frac{9N\hbar}{\omega_D^3} \int_0^{\omega_D} \frac{\omega^3 d\omega}{e^{\beta \hbar \omega} - 1}.$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{9Nk_B}{x_D^3} \int_0^{x_D} x^4 e^x (e^x - 1)^{-2} dx$$

with $x_D = \beta \hbar \omega_D$. For low temperature, $x_D \rightarrow \infty$ and $C \propto T^3$. For high temperature, $x \rightarrow 0$ and $C \rightarrow 3Nk_B$ as expected from the equipartition theorem.

- Euler equation in thermodynamics: the fact that U , S , V , and N are extensive means that $U(\lambda S, \lambda V, \lambda N_i) = \lambda U(S, V, N)$. Taking the derivative with respect to λ and setting $\lambda = 1$ gives $U = TS - pV + \sum_i \mu_i N_i$. Since $G = U - TS + pV$, this shows that $G = \sum_i \mu_i N_i$.

- Now compare $U = TS - pV + \sum_i \mu_i N_i$ with $dU = TdS - pdV + \sum_i \mu_i dN_i$ to get the Gibbs-Duhem relation: $SdT - Vdp + \sum_i N_i d\mu_i = 0$. For a single-component system this gives $Nd\mu = Vdp - SdT$.

- Chemical potential and phase changes: consider two phases of a substance (e.g. H_2O) at constant pressure. Suppose that there are N_1 particles of phase 1 (e.g. steam) and N_2 particles of phase 2 (e.g. water or ice). Because P and T are fixed, the useful quantity is G . The correct phase is the one which minimizes $G = \mu_1 N_1 + \mu_2 N_2$. If the two phases are in equilibrium it means that $dG = dN_1 \mu_1 + dN_2 \mu_2 = 0$. Since $dN_1 = -dN_2$, this requires $\mu_1 = \mu_2$. So the equilibrium phase boundary is when $\mu_1(T, P) = \mu_2(T, P)$. If we move along the phase boundary by varying dp and dT , then this relation must be preserved, so $\mu_1(p + dp, T + dT) = \mu_2(p + dp, T + dT)$. Now recall that $dG = -SdT + Vdp$ and $G = \mu N$ to obtain $-s_1 dT + v_1 dp = -s_2 dT + v_2 dp$ where $s_1 = S_1/N$ is the entropy per particle, v_1 is the volume per particle in phase 1, etc. So then get

$$\frac{dp}{dT} = \frac{s_2 - s_1}{v_2 - v_1} = \frac{\ell}{T(v_2 - v_1)},$$

where $\ell = T\delta s$ is the latent heat per particle.

This is called the ‘‘Clausius-Clapeyron’’ equation.

Example: suppose $v_2 \gg v_1$, and $Pv_2 = RT$, then the above equation becomes

$$\frac{dP}{P} = \frac{\ell dT}{RT^2},$$

which integrates to $P = P_0 \exp(-\ell/RT)$. This is the vapor pressure, which rapidly increases with T .

• $(\partial\mu/\partial p)_T = v > 0$ and $(\partial\mu/\partial T)_p = -s < 0$. If we plot μ_{liq} and μ_{vap} as a function of temperature, find that $\mu_{liq}(T < T_*) < \mu_{vap}(T < T_*)$ but $\mu_{liq}(T > T_*) > \mu_{vap}(T > T_*)$, where T_* is the temperature where the liquid boils. Recall that the correct phase minimizes G or maximizes S . If you quickly continue from one phase you can end up with superheated liquid or supercooled vapor, where the wrong phase is temporarily obtained, before the system has time to realize its mistake and change phase. Will try to do a demo in class of supercooled water.