Solution for Chapter 4

(compiled by Xinkai Wu, revised by Kip Thorne)

A.

Exercise 4.1 Pressure Measuring Device [by Kip Thorne]

We could choose our pressure measuring device (pressure meter) to exchange only volume and not heat with its reservoir, but that leads to some tricky subtleties as we see in Exercise 4.8; so it is better (more straightforward) to let the meter exchange both volume and heat with its reservoir. This is analogous to the meter that Kip discussed in class on Monday, which exchanged particles and heat.

Then the probability for the meter to be in a (quantum) state with volume ΔV and energy $\Delta\tilde{E}$ (probability measured either using an ensemble of meter&reservoir systems or via the fraction of the time the meter spends in a given state) is given by the meter's Gibb's distribution:

$$\rho = K\exp[(-\Delta\tilde{E} - P\Delta V)/kT]\ ;$$

or equivalently

$$\ln\rho = (-\Delta\tilde{E} - P\Delta V)/kT + \text{constant}\ .$$

Here K is the normalization constant and P and T are the reservoir's pressure and temperature.

Suppose that the reservoir plus meter has total energy $\tilde{E}_o$, volume $\tilde{V}_o$, and number of particles N_o; and the meter plus reservoir is a closed system. Then by energy and volume conservation, when the meter has volume ΔV and energy ΔE, the reservoir has volume $V_r = V_o - \Delta V$ and energy $E_r = E_o - \Delta E$. Denote by $\mathcal{N}_r(\tilde{E}_r, V_r)$ the total number of states of the reservoir that have energy E_r, volume V_r and particle number N_r, and similarly $\mathcal{N}_m(\Delta E, \Delta V)$ for the meter. (The meter might not be made of the same kind of particles as the reservoir; it might, for example, just be a mass-spring system that can be heated; the only variables we care about for it are energy and volume.) Then the probability ρ is proportional to the following product of numbers of states for the reservoir and meter:

$$\rho \propto \mathcal{N}_r(E_o - \Delta E, V_o - \Delta V, N_o) \times \mathcal{N}_m(\Delta E, \Delta V)\ .$$

Because the meter is tiny compared to the reservoir, when we take the logarithm of this ρ, the changes in the meter term, as energy and volume flow back and forth, are negligible compared to the changes in the reservoir term, so

$$\ln\rho = \ln[\mathcal{N}_r(E_o - \Delta E, V_o - \Delta V, N_o)] + \text{constant}\ .$$

This logarithm of the number of reservoir states is proportional to the reservoir entropy, so

$$\ln\rho = S_r(E_o - \Delta E, V_o - \Delta V, N_o)/k + \text{constant}\ .$$

Expanding to first order in the meter energy and volume we obtain

$$\ln \rho = -\left(\frac{\partial S_r}{\partial E_r}\right)_{V_r,N_r} \Delta E - \left(\frac{\partial S_r}{\partial V_r}\right)_{E_r,N_r} \Delta V \ .$$

Comparing with our previous expression for $\ln \rho$ we see that the pressure and temperature that appear in the meter's Gibbs distribution are related to the reservoir's entropy by the usual reservoir thermodynamic relations

$$\begin{aligned} \frac{1}{T} &= \left(\frac{\partial S_r}{\partial E_r}\right)_{V_r,N_r} , \\ P &= T\left(\frac{\partial S_r}{\partial V_r}\right)_{\tilde{E}_r,N_r} = \left(\frac{\partial \tilde{E}_r}{\partial S_r}\right)_{N_r,V_r} \left(\frac{\partial S_r}{\partial V_r}\right)_{\tilde{E}_r,N_r} = -\left(\frac{\partial \tilde{E}_r}{\partial V_r}\right)_{N_r,S_r} . \end{aligned}$$

In the last step we have used an obvious analog of Eq. (4) of Box 4.1.

B

Exercise 4.3 Enthalpy Representation of Thermodynamics [by Xinkai Wu]

(a) Combining $H = \tilde{E} + PV$ with the first law $d\tilde{E} = TdS - PdV + \tilde{\mu}dN$ one immediately finds $dH = VdP + TdS + \tilde{\mu}dN$. Having this expression we can compute $V, T, \tilde{\mu}$ by differentiating H w.r.t. P, S, N, respectively, namely H serves as the fundamental potential in this case.

(b) In the first law derived in part (a), there's dS, dN but no dV. Thus the only extensive quantities exchanged between the system and the bath are volume and energy; and the energy exchange is fixed completely by the volume exchange, $d\tilde{E} = -PdV$, i.e., it is entirely mechanical energy exchange. There is no exchange of heat and no exchange of particles. A physical situation which could produce this ensemble is: the system is put in a chamber, with a frictionless piston separating the system and the bath, where the walls and the piston are impermeable and heat-insulating.

(c) The equations of state read off from the enthalpy first law and the associated Maxwell relations are:

$$\begin{aligned} V = \left(\frac{\partial H}{\partial P}\right)_{S,N} &, \quad T = \left(\frac{\partial H}{\partial S}\right)_{P,N} , \quad \tilde{\mu} = \left(\frac{\partial H}{\partial N}\right)_{P,S} \\ \frac{\partial^2 H}{\partial P \partial S} &= \left(\frac{\partial V}{\partial S}\right)_{P,N} = \left(\frac{\partial T}{\partial P}\right)_{S,N} = \frac{\partial^2 H}{\partial S \partial P} \\ \frac{\partial^2 H}{\partial S \partial N} &= \left(\frac{\partial T}{\partial N}\right)_{P,S} = \left(\frac{\partial \tilde{\mu}}{\partial S}\right)_{P,N} = \frac{\partial^2 H}{\partial N \partial S} \\ \frac{\partial^2 H}{\partial N \partial P} &= \left(\frac{\partial \tilde{\mu}}{\partial P}\right)_{S,N} = \left(\frac{\partial V}{\partial N}\right)_{P,S} = \frac{\partial^2 H}{\partial P \partial N} \end{aligned}$$

(d) "adding up small subsystems", we get

$$H = TS + \tilde{\mu}N$$

(e) In Exercise 2.4 it is shown that the inertial mass per unit volume is

$$\begin{aligned} \rho^{inert}_{ji} &= T^{00}\delta_{ji} + T_{ji} \\ &for\ isotropic\ system \\ &= \rho\delta_{ji} + P\delta_{ji} = (\rho + P)\delta_{ij} \ . \end{aligned}$$

Thus the total inertial mass is isotropic and is given by $\rho V + PV = \tilde{E} + PV = H$.
(f) To create the sample, we need $\Delta\tilde{E}$, the sample's energy. To inject the sample into the system, we need to perform an amount of work $P\Delta V$ on the system. Thus the total energy required to create the sample and perform the injection is $\Delta\tilde{E} + P\Delta V$, which is just the sample's enthalpy. Thus, enthalpy has the physical interpretation of "energy of injection at fixed volume V".

Exercise 4.2 Energy Representation for a Nonrelativistic Monatomic Gas [by Xinkai Wu]
(a) To derive eqn. (4.18), one only has to substitute the fundamental potential E as given by eqn. (4.15) into eqn. (4.16) and perform the partial differentiation. We assume this is trivial for everyone and omit the details here.
(b) Again, to verify eqn. (4.17) is simple differentiation and we omit the details here.
(c) Expressing $exp\left(\frac{2S}{3kN} - \frac{5}{3}\right)$ in terms of (T, N, V) using the second equation of (4.18), then substituting the resulting expression into the first equation of (4.18), one readily gets $P = \frac{N}{V}kT$.

C

Exercise 4.4 Latent Heat and the Clausius-Clapeyron Equation [by Xinkai Wu]
(a) For fixed temperature and pressure, the change in the Gibbs potential is

$$dG = \tilde{\mu}_a dN_a + \tilde{\mu}_b dN_b = (\tilde{\mu}_a - \tilde{\mu}_b)dN_a$$

where we've used the fact that $dN_b = -dN_a$.
By the minimum principle for the Gibbs potential, N_a will decrease when $\tilde{\mu}_a > \tilde{\mu}_b$, and increase when $\tilde{\mu}_a < \tilde{\mu}_b$. As a consequence, if phases a and b are in equilibrium with each other, one must have $\tilde{\mu}_a = \tilde{\mu}_b$(subtracting $m_{H_2O}c^2$ from both sides one finds $\mu_a = \mu_b$.) The Gibbs potential G is a function of (T, P, N), so the chemical potential $\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P}$ is also a function of (T, P, N). However, μ is an intensive quantity and consequently can't depend on the extensive quantity N, namely μ is a unique function of T and P. The above reasoning is valid for any phase a. In a two-phase region, we must have $\mu_a(T, P) = \mu_b(T, P)$, which is one equation for two variables T and P, giving a line in the $T - P$ plane. In a three-phase region, $\mu_a(T, P) = \mu_b(T, P),\ and\ \mu_b(T, P) = \mu_c(T, P)$, which are two equations for the two variables T and P, giving a point in the $T - P$ plane.
(b) The melting curve $P = P(T)$ is determined by $\mu_{ice}(T, P) = \mu_{water}(T, P)$. Then taking temperature derivative of the above identity along the melting

curve gives

$$\begin{aligned}
&\left(\frac{\partial\mu_{ice}}{\partial T}\right)_P+\left(\frac{\partial\mu_{ice}}{\partial P}\right)_T\left(\frac{dP}{dT}\right)_{melt}=\left(\frac{\partial\mu_{water}}{\partial T}\right)_P+\left(\frac{\partial\mu_{water}}{\partial P}\right)_T\left(\frac{dP}{dT}\right)_{melt}\\
&\quad\Rightarrow\left(\frac{dP}{dT}\right)_{melt}=\left[\left(\frac{\partial\mu_{water}}{\partial T}\right)_P-\left(\frac{\partial\mu_{ice}}{\partial T}\right)_P\right]/\left[\left(\frac{\partial\mu_{ice}}{\partial P}\right)_T-\left(\frac{\partial\mu_{water}}{\partial P}\right)_T\right]
\end{aligned}$$

Using the Maxwell relations that one reads off of $dG=-SdT+VdP+\mu dN$, we find

$$\begin{aligned}
\left(\frac{\partial\mu_I}{\partial T}\right)_P&=-\left(\frac{\partial S_I}{\partial N_I}\right)_{T,P}=-m_{H_2O}s_I\\
\left(\frac{\partial\mu_I}{\partial P}\right)_T&=\left(\frac{\partial V_I}{\partial N_I}\right)_{T,P}=m_{H_2O}/\rho_I
\end{aligned}$$

where I denotes either phase(ice or water), $s_I,\ \rho_I$ are the entropy per unit mass and density for phase I, respectively. Thus

$$\begin{aligned}
\left(\frac{dP}{dT}\right)_{melt}&=\frac{-m_{H_2O}(s_{water}-s_{ice})}{\frac{m_{H_2O}}{\rho_{ice}}-\frac{m_{H_2O}}{\rho_{water}}}\\
&=(s_{water}-s_{ice})\frac{\rho_{ice}\rho_{water}}{\rho_{ice}-\rho_{water}}\\
&=\frac{\Delta q_{melt}}{T}\left(\frac{\rho_{ice}\rho_{water}}{\rho_{ice}-\rho_{water}}\right)
\end{aligned}$$

(c) In equilibrium we still have $\mu_{water}(T,P_{water})=\mu_{vapor}(T,P_{vapor})$. However, now P_{water} is no longer equal to P_{vapor}. Instead, $P_{water}=P_{total}=P_{vapor}+P_{gas}$. So we have $\mu_{water}(T,P_{total})=\mu_{vapor}(T,P_{vapor})$. Fixing T and differentiating the above identity w.r.t. P_{total}, we have

$$\begin{aligned}
\left(\frac{\partial\mu_{water}}{\partial P_{total}}\right)_T&=\left(\frac{\partial\mu_{vapor}}{\partial P_{vapor}}\right)_T\left(\frac{dP_{vapor}}{dP_{total}}\right)_T\\
\Rightarrow\left(\frac{dP_{vapor}}{dP_{total}}\right)_T&=\left(\frac{\partial\mu_{water}}{\partial P_{total}}\right)_T/\left(\frac{\partial\mu_{vapor}}{\partial P_{vapor}}\right)_T\\
&=\frac{m_{H_2O}}{\rho_{water}}/\frac{m_{H_2O}}{\rho_{vapor}}\\
&=\rho_{vapor}/\rho_{water}
\end{aligned}$$

Exercise 4.5 Electron-Positron Equilibrium at "Low" Temperatures [by Xinkai Wu]

(a) The reaction equation $e^-+p\longrightarrow e^-+p+e^-+e^+$ gives $\tilde\mu_{e^-}+\tilde\mu_p=2\tilde\mu_{e^-}+\tilde\mu_p+\tilde\mu_{e^+}$, which implies $\tilde\mu_{e^-}+\tilde\mu_{e^+}=0$, i.e. $\tilde\mu_{e^-}=-\tilde\mu_{e^+}$.

(b) In what follows we shall use $\tilde\mu_-$ to denote $\tilde\mu_{e^-}$, and $\tilde\mu_+$ to denote $\tilde\mu_{e^+}$. The distribution function(density in phase space) for positrons and electrons (both having $g_s = 2$) is given by

$$\begin{aligned}
&\mathcal{N}_\pm = \frac{2}{h^3}\eta_\pm = \frac{2}{h^3}\frac{1}{e^{(\tilde{E}-\tilde{\mu}_\pm)/kT}+1} \\
&\tilde{E} \approx mc^2 + \mathbf{p}^2/2m \\
&\Rightarrow \mathcal{N}_\pm = \frac{2}{h^3}\frac{1}{e^{(\frac{\mathbf{p}^2}{2m}+mc^2-\tilde{\mu}_\pm)/kT}+1}
\end{aligned}$$

The density in coordinate space $n_\pm$ is given by $\int d^3\mathbf{p}\mathcal{N}_\pm$. We know that $n_- > n_+$ because while positrons and electrons are created in pairs we also have ionization electrons from hydrogen atoms. Thus we must have $\tilde{\mu}_- > \tilde{\mu}_+$. This inequality combined with $\tilde{\mu}_- + \tilde{\mu}_+ = 0$ gives $\tilde{\mu}_- > 0,\ \tilde{\mu}_+ < 0$.

(c) In the dilute-gas regime, $\eta_\pm \approx exp\left[-(\frac{\mathbf{p}^2}{2m} + mc^2 - \tilde{\mu}_\pm)/kT\right]$. It's trivial to perform the momentum-space integral and find

$$n_\pm = \frac{2}{h^3}(2\pi mkT)^{3/2} exp\left(\frac{\tilde{\mu}_\pm - mc^2}{kT}\right)$$

$\eta << 1$ means $(\tilde{\mu}_\pm - mc^2) << -kT$ (see Chapter 2), i.e.

$$n_\pm << \frac{2}{h^3}(2\pi mkT)^{3/2} = 4.8\times 10^{27}\left(\frac{T}{10^8K}\right)^{3/2} cm^{-3}$$

The hydrogen mass density is $\rho \approx n_- m_p$ (because $m_e << m_p$ and also electron-positron pair generation is negligible.) Thus the dilute-gas region is given by

$$\rho << 8\times 10^3\left(\frac{T}{10^8K}\right)^{3/2} g\cdot cm^{-3}$$

(d) Define $x \equiv e^{\tilde{\mu}_-/kT}$, then $e^{\tilde{\mu}_+/kT} = 1/x$. And using the expression for $n_\pm$ we found in part (c), we get

$$\begin{aligned}
&n = n_- - n_+ = \frac{2}{h^3}(2\pi mkT)^{3/2}e^{-mc^2/kT}(x - 1/x) \\
&define\ y \equiv \frac{1}{4}n\lambda^3 e^{mc^2/kT}, \quad where\ \lambda \equiv \frac{h}{\sqrt{2\pi mkT}} \\
&\Rightarrow 2y = (x - 1/x) \\
&\Rightarrow x = y + (1+y^2)^{1/2} \\
&Thus\ \frac{n_+}{n} = \frac{1/x}{x - 1/x} = \frac{1}{2y\left[y + (1+y^2)^{1/2}\right]}
\end{aligned}$$

(e) [this part by Kip Thorne] The amount of phase space available to the ionization electrons, per ionization electron, is of order $V_{phase} \sim (2\pi mkT)^{3/2}\frac{m_p}{\rho}$. If one pair forms per ionization electron (our criterion for significant pair formation), then each positron will also have available to it the phase volume V_{phase}.

When this V_{phase} is very large (i.e. when ρ is very small, at fixed $T \sim 10^8 K$), then the positron is almost completely unaware of the presence of the electrons, so the probability of its meeting an electron and annihilating is very small. This means that, although pair production occurs only very rarely (because of the very few number of photons with sufficient energy to produce a pair), once it has occured, on average the positron lives for a very long time. It is this balancing of the long life, due to the huge phase space per particle, against the rarity of pair production, that enables significant pairs to form at T as low as $\sim 10^8 K$.

D

Exercise 4.7 Fluctuations and Phase Transitions in a Van der Waals Gas [by Xinkai Wu]

(a)

$$P = -\left(\frac{\partial E}{\partial V}\right)_{S,N} = \frac{h^2}{2\pi m}\left(\frac{V}{N} - b\right)^{-5/3} exp\left(\frac{2S}{3kN} - \frac{5}{3}\right) - \frac{aN^2}{V^2}$$

$$T = \left(\frac{\partial E}{\partial S}\right)_{N,V} = \frac{h^2}{2\pi mk}\left(\frac{V}{N} - b\right)^{-2/3} exp\left(\frac{2S}{3kN} - \frac{5}{3}\right)$$

$$use\ the\ second\ equation\ to\ eliminate\ S\ in\ favor\ of\ N, V, T$$

$$P(N,V,T) = \frac{kT}{V/N - b} - \frac{a}{(V/N)^2} = \frac{kT}{v-b} - \frac{a}{v^2} \quad where\ v \equiv V/N$$

$$while\ for\ an\ ideal\ gas$$

$$P(N,V,T) = \frac{NkT}{V} = \frac{kT}{v}$$

One needs to solve the equation $\left(\frac{\partial P}{\partial v}\right)_T = 0$ for v. One finds that for $T < T_{crit}$, there are two solutions v_1, v_2 (namely there's a local maximum and a local minimum); when $T = T_{crit}$, v_1 and v_2 merge into a single v_{crit}; and when $T > T_{crit}$, there's no solution. Now let's determine T_{crit} and v_{crit}. At T_{crit}, v_{crit}, we have

$$0 = \left(\frac{\partial P}{\partial v}\right)_T = \frac{-kT}{(v-b)^2} + \frac{2a}{v^3}$$

$$0 = \left(\frac{\partial^2 P}{\partial^2 v}\right)_T = \frac{2kT}{(v-b)^3} - \frac{6a}{v^4}$$

Combining the above two equations, we find $T_{crit} = \frac{8a}{27bk} = \frac{8}{27}T_0$, and $v_{crit} = 3b$.

(b) For the system to be stable against volume fluctuations under isothermal conditions, we must have $\left(\frac{\partial P}{\partial v}\right)_T < 0$ (the arguement for this is: suppose initially our system is in equilibrium under the external pressure, namely $P_{system} = P_{external}$. If by statistical fluctuation the system's volume decreases by a small amount $\Delta v > 0$, P_{system} will correspondingly change by $\Delta P_{system} = -\Delta v \left(\frac{\partial P}{\partial v}\right)_T$. If $\left(\frac{\partial P}{\partial v}\right)_T > 0$, then $\Delta P_{system} < 0$, namely P_{system} will drop below $P_{external}$ and the system will keep collapsing. A similar reasoning can be carried out when the volume increases a little bit by fluctuation. Thus we conclude

$\left(\frac{\partial P}{\partial v}\right)_T > 0$ would lead to instability against volume fluctuations.)
So we can look at the slope of the curves in Fig. 4.7(a) and conclude that: when $T > T_{crit}$, the gas is stable all along the curve; when $T = T_{crit}$, the gas is stable except at the one particular point $v = v_{crit}$; when $T < T_{crit}$, the gas is stable in two regions (and these are the two different phases that are both stable against volume fluctuations) $b < v < v_{min}$ and $v > v_{max}$, where v_{min} and v_{max} are the locations of the local minimum and the local maximum, respectively, and the gas is unstable in the region $v_{min} < v < v_{max}$.
(c) By the principle of minimum Gibbs potential, the chemical potential at point A must be equal to that at point B (see Exercise 4.4). Recall that being on the same isothermal curve A and B have the same temperature. Thus $\mu(T, P_A) = \mu(T, P_B)$ gives $P_A = P_B$, i.e. the straight line from A to B is horizontal.
We have the following differential equation

$$\begin{aligned}
&dG = d(\mu N) = -SdT + VdP + \mu dN \\
&\Rightarrow Nd\mu = -SdT + VdP \\
&\Rightarrow d\mu = -sdT + vdP, \quad where\ s \equiv S/N, \quad v \equiv V/N
\end{aligned}$$

Along the isothermal curve, $dT = 0$, so $d\mu = vdP$. Thus

$$\mu|_B - \mu|_A = \int_A^B d\mu = \int_A^B \ vdP$$

Easily seen, $\int_A^B \ vdP$ is just the difference between the areas of the two stippled regions. Thus $\mu|_A = \mu|_B$ tells us that these two areas are equal.
(d) The fractional volume fluctuation is given by

$$\frac{\sigma_V}{V} = \frac{\sqrt{kT\kappa}}{V} = \sqrt{\frac{kT}{-\left(\frac{\partial P}{\partial V}\right)_{T,N} V^2}}\ ;$$

see Eq. (4.80) and the paragraph that follows it. We see that small values of $-\left(\frac{\partial P}{\partial V}\right)_{T,N}$ correspond to large volume fluctuations. Thus near the "critical point" (with $T_{crit} = \frac{8a}{27kb}, V_{crit} = 3Nb, P_{crit} = \frac{a}{27b^2}$), $-\left(\frac{\partial P}{\partial V}\right)_{T,N}$ is very small and the gas exhibit huge volume fluctuations. (For $T < T_{crit}$, near the the local minimum and maximum on the $P - V$ plot, we also have small $-\left(\frac{\partial P}{\partial V}\right)_{T,N}$. However, as argued in part (b) and (c), these regions are not physical and in general don't exist in nature. Also, $-\left(\frac{\partial P}{\partial V}\right)_{T,N}$ gets small when V gets large. But σ_V/V actually doesn't get huge, because $-\left(\frac{\partial P}{\partial V}\right)_{T,N} \sim NkT/V^2$ for large V, and σ_V/V remains $\sim 1/\sqrt{N}$.)

Exercise 4.8 Fluctuations of Systems in Contact with a Volume Bath [by Xinkai Wu]
(a) No matter whether the ensemble is in equilibrium or not, the (very general) energy conservation law always holds. Since there's no heat or particle

exchange between the system and the bath, the change in the system's energy is completely due to the work performed on the system by the bath, namely $d\tilde{E} = -P_b dV$. (Note that since the bath is huge compared to the system, the bath's pressure P_b remains fixed, so $\Delta\tilde{E} = -P_b \Delta V$ for finite volume change.) This implies that $\Delta H = \Delta\tilde{E} + P_b \Delta V = 0$, i.e. the system's enthalpy is conserved.

(b) Since the system is very small compared to the bath, the bath is always in equilibrium. Then we can use the first law for the bath $\Delta\tilde{E}_b = T_b \Delta S_b - P_b \Delta V_b + \tilde{\mu}_b \Delta N_b$. Since there's no particle exchange, $\Delta N_b = 0$. Also by energy and volume conservation, $\Delta\tilde{E}_b = -\Delta\tilde{E} = P_b \Delta V = -P_b \Delta V_b$. These combined with the first law tells us $T_b \Delta S_b = 0$, i.e. $\Delta S_b = 0$. So we conclude that interaction with a system cannot change the bath's entropy.

(c) The bath and the system form a closed supersystem with a total entropy $S_{total} = S_b + S$. This supersystem, like any closed system, must evolve toward increasing S_{total}. This combined with the fact that S_b doesn't change (proved in part (b)) tells us S always increases. When the supersystem reaches statistical equilibrium, it is in the microcanonical ensemble with $\rho_{total} = e^{-S_{total}/k} = e^{(-S_b - S)/k} = const$. This, combined with $S_b = const$, gives us $\rho = e^{-S/k} = const$ for the regions of phase space that have enthalpy H in the small range δH.

(d) For fluctuations away from equilibrium, the probability $\propto e^{S_{total}/k} \propto e^{S/k}$. Note that the enthalpy H is a function of (P, S, N) (see Exercise 4.3). Inverting this relation we get $S = S(H, P, N)$. So we still have equations (4.65), (4.66) but with E replaced by H, V replaced by P.