PHY452 Problem Set 1

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Problem 1

(a) Consider the ideal gas law (non-interacting gas particles) $PV = Nk_BT$. The first law of thermodynamics states that energy is determined via heat and work contributions,

$$dE = TdS - PdV. \tag{1.1}$$

Now consider the gas law for a gas at constant volume V. An infinitessimal change in pressure must then be proportional to a change in temperature:

$$VdP = Nk_BdT \tag{1.2}$$

which implies that

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{Nk_B}{V} \tag{1.3}$$

If we invoke the Maxwell relation

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \tag{1.4}$$

then we also find that

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{Nk_B}{V}. \tag{1.5}$$

In (1.5), temperature is held fixed, but V can vary again according to (1.4). This then implies that

$$dS = \frac{Nk_B}{V}dV \tag{1.6}$$

which, when placed into the first law (1.1), we find

$$dE = \left(T\frac{Nk_B}{V} - P\right)dV \tag{1.7}$$

$$= (0)\,dV. \tag{1.8}$$

(1.8) follows from the ideal gas law, and is only true for fixed temperature T while P and V can still vary. The total derivative of energy takes all three of these thermodynamic variables into account, and since $dE = 0$, E can not be a function of V or P and hence can only be a function of temperature T.

(b) If E is a function of only T, then $dE = 0$ at fixed temperature, as shown above. If temperature is fixed, the only (and most simple) equation of state relating P, V, and T altogether is that of a direct proportionality:

$$PV = aT. \tag{1.9}$$

As it turns out, the proportionality constant a is the gas constant nR where n is the number of moles of the gas in the volume. Equivalently, we can write Nk_B. Regardless of the choice of a, the equation relating the thermodynamic variables together is the ideal gas law. It can be shown that (1.8) can also be obtained if one were to start with (1.9) and the Maxwell relation given in (1.4).

Problem 2

In this problem, we consider two heat capacities for two phase transitions of a substance A going to a lower temperature B:

$$C_A(T) = Vc_aT^3 \tag{2.1}$$

$$C_B(T) = V[c_2T^3 + c_3T] \tag{2.2}$$

where V is the volume, and c_1, c_2, c_3 are constants with $c_1 > c_2$. We assume that there is no appreciable change in V for this transition.

(a) We begin by determining the entropies $S_A(T), S_B(T)$. The first law of thermodynamics states that $dS = C_X(T)\dfrac{dT}{T}$, and thus finding the entropies just involves integration in T:

$$\int_0^T dS = S(T) - \cancelto{0}{S(0)} = \int_0^T C_X(T')\frac{dT'}{T'} \tag{2.2}$$

$$\implies S_A(T) = Vc_1\int_0^T dT'\,(T')^2 \tag{2.3}$$

$$= \frac{1}{3}Vc_1T^3 \tag{2.4}$$

$$\implies S_B(T) = Vc_2\int_0^T dT'(T')^2 + Vc_3\int_0^T dT' \tag{2.5}$$

$$= \frac{1}{3}Vc_2T^3 + Vc_3T. \tag{2.6}$$

Thus $S_A(T) = \dfrac{1}{3}Vc_1T^3$ and $S_B(T) = \dfrac{1}{3}Vc_2T^3 + Vc_3T$.

(b) The transition temperature is given as T_c, the temperature when the substance changes phase. If there is no latent heat during the transition, then there is no external heat exchange between the system and the environment, which implies that over a cycle,

$$\oint \frac{dQ}{T} = 0. \tag{2.7}$$

Furthermore, by the first law (2.2) with $dQ = C_X(T)dT$, the heat exchange with the environment is actually just the differences between phase entropies:

$$0 = \int_A^B \frac{dQ}{T} = S_B(T_c) - S_A(T_c). \tag{2.8}$$

Thus T_c is given by solving $S_B(T_c) - S_A(T_c) = 0$:

$$0 = V\left[\frac{1}{3}c_2T_c^3 + c_3T_c - \frac{1}{3}c_1T_c^3\right] \tag{2.9}$$

$$\implies 0 = T_c\left[\frac{1}{3}(c_2 - c_1)T_c^2 + c_3\right]. \tag{2.10}$$

Solving the cubic equation (2.10) implies that either $T_c = 0, \pm\sqrt{\dfrac{3c_3}{c_1 - c_2}}$. However, $T_c > 0$ for a system since $T_c = 0$ implies that entropy is zero, and negative Kelvin does not make sense. Thus we find the transition temperature of the substance with zero latent heat exchange to be

$$T_c = \sqrt{\frac{3c_3}{c_1 - c_2}} \tag{2.11}$$

which also is reasonable, since $c_1 > c_2$ so $c_1 - c_2 > 0$.

(c) We now consider the internal energies of the system $E_A(T)$ and $E_B(T)$. We set the zero-temperature energies of the phases to be

$$E_A(0) = E_0 \tag{2.12}$$
$$E_B(0) = E_0 - V\Phi \tag{2.13}$$

for a constant Φ (and volume V, as before). To determine the energies for temperatures greater than zero, we can again apply the first law of thermodynamics, which gives

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_V \tag{2.14}$$

for a fixed volume V. Hence $TdS = dE$, from which integration in temperaure yields

$$\int_0^T dE = \int_0^T dST' \tag{2.15}$$
$$\implies E(T) = E(T=0) + \int_0^T dT' \, \frac{\partial S}{\partial T'} T'. \tag{2.16}$$

We can now compute $E(T)$ for both phases independently given $S_A(T)$ and $S_B(T)$ in (2.4) and (2.6) respectively:

$$E_A(T) = E_0 + \int_0^T dT' \, V c_1 (T')^3 \tag{2.17}$$
$$= E_0 + \frac{1}{4} V c_1 T^4 \tag{2.18}$$
$$E_B(T) = E_0 - V\Phi + \int_0^T dT' \, [V c_2 (T')^3 + V c_3 T'] \tag{2.19}$$
$$= E_0 + V\left[\frac{1}{4} c_2 T^4 + \frac{1}{2} c_3 T^2 - \Phi\right] \tag{2.20}$$

from which the $T \to 0$ limit is satisfied in both cases.

(d) We now determine Φ in terms of c_1, c_2, and c_3 by invoking the Helmholtz free energy relation, $F = E - TS$. Note that, at the phase transition temperature T_c, the Helmholtz energies are the same, so $F_A = F_B$ at $T = T_c$. We have

$$F_A = E_A(T_c) - TS_A(T_c) \tag{2.21}$$
$$= E_0 + \frac{1}{4} V c_1 T_c^4 - \frac{1}{3} V c_1 T_c^4 \tag{2.22}$$
$$= E_0 - \frac{1}{12} V c_1 T_c^4 \tag{2.23}$$
$$F_B = E_B(T_c) - TS_B(T_c) \tag{2.24}$$
$$= E_0 - V\Phi + \frac{1}{4} V c_2 T_c^4 + \frac{1}{2} V c_3 T_c^2 - \frac{1}{3} V c_2 T_c^4 - V c_3 T_c^2 \tag{2.25}$$
$$= E_0 - V\Phi - \frac{1}{12} V c_2 T_c^4 - \frac{1}{2} V c_3 T_c^2 \tag{2.26}$$

From which, at T_c, we obtain

$$E_0 - \frac{1}{12}Vc_1T_c^4 = E_0 - V\Phi - \frac{1}{12}Vc_2T_c^4 - \frac{1}{2}Vc_3T_c^2 \tag{2.27}$$

$$\implies V\Phi = \frac{1}{12}V(c_1 - c_2)T_c^4 - \frac{1}{2}Vc_3T_c^2 \tag{2.28}$$

$$\implies \Phi = \frac{1}{12}(c_1 - c_2)\left[\frac{9c_3^2}{(c_1 - c_2)^2}\right] - \frac{1}{2}c_3\left[\frac{3c_3}{c_1 - c_2}\right] \tag{2.29}$$

$$= \frac{3}{4}\frac{c_3^2}{c_1 - c_2} - \frac{3}{2}\frac{c_3^2}{c_1 - c_2} \tag{2.30}$$

$$= -\frac{3}{4}\frac{c_3^2}{c_1 - c_2}, \tag{2.31}$$

so $\Phi = -\frac{3}{4}\frac{c_3^2}{c_1 - c_2} < 0$, which makes sense as then $E_B(T) = E_0 - V\Phi$ is positive.

Problem 3

(a) We wish to find the one-body density $\rho_1(\mathbf{p}, \mathbf{q})$ which minimizes the functional

$$H[\rho_1] = N \int dV\, \rho_1(\mathbf{p}, \mathbf{q}) \log \rho_1(\mathbf{p}, \mathbf{q}), \tag{3.1}$$

where $dV = \prod_{i=1}^{N} d^3p\, d^3q$. From here on I will refer to $\rho_1(\mathbf{p}, \mathbf{q})$ as just ρ_1. There are two ways this problem can be approached, via the method of variation of the function and integrating by parts, or by invoking the method of Lagrange multipliers and taking derivatives in ρ_1. I will choose the latter.

As in multivariable calculus, we take spatial gradients to determine coordinates which optimize the function subject to a certain boundary,

$$\nabla f = \lambda \nabla g, \tag{3.2}$$

$$c = g(\mathbf{x}). \tag{3.3}$$

In this case, we optimize a functional, so instead of taking spatial gradients we take derivatives in ρ_1 subject to the constraint that total energy is constant. Since total energy is the complete sum of energy per particle over all space for N particles, we find that the most probable system energy is

$$E = N \int dV \mathcal{H} \rho_1 \tag{3.4}$$

where $\mathcal{H} = \frac{\mathbf{p}^2}{2m} + U(\mathbf{q})$ is the Hamiltonian of the i-th particle. Since the volume integration dV is independent of ρ, Feynman's integration rule implies the following system of equations:

$$\frac{\partial H}{\partial \rho_1} = N \int dV \frac{\partial}{\partial \rho_1} [\rho_1 \log \rho_1] \tag{3.5}$$

$$= N \int dV [\log \rho_1 + 1] \tag{3.5}$$

$$= \lambda \frac{\partial E}{\partial \rho_1} \tag{3.6}$$

$$= \lambda N \int dV \mathcal{H} \tag{3.7}$$

hence

$$N \int dV [\log \rho_1 + 1] = N\lambda \int dV \mathcal{H} \tag{3.8}$$

by (3.2). Matching integrands gives an expression for ρ_1 as a function of λ (which we will need to find) and $\mathcal{H}$:

$$(\log \rho_1 + 1) = \lambda \mathcal{H} \tag{3.9}$$

$$\implies \rho_1 = \exp\left[\lambda \mathcal{H} - 1\right]. \tag{3.10}$$

From here we impose the constraint that E must be constant in order to determine λ. Since E contains the product $\rho\mathcal{H}$, we can observe that the integrand is proportional to a derivative in λ:

$$\frac{\partial}{\partial \lambda} \rho_1 = \mathcal{H} \rho_1, \tag{3.11}$$

which therein implies that

$$E = N \int dV \rho_1 \mathcal{H} = N \frac{\partial}{\partial \lambda} \int dV \rho_1, \tag{3.12}$$

but since probability is normalized, $\int dV \rho_1 = 1$, we have that

$$E = N \frac{\partial}{\partial \lambda}(1). \tag{3.13}$$

Now integrating both sides of (3.13) with respect to λ yields

$$\lambda E = N \implies \lambda = \frac{N}{E} \tag{3.14}$$

and therefore the functional form which minimizes H is

$$\rho_1 = \exp\left[\frac{N\mathcal{H}}{E} - 1\right]. \tag{3.15}$$

It can then be shown that the ρ_1 found above also satisfied Liouville's theorem, as one can observe directly because ρ_1 is a function of the Hamiltonian and is time-independent.

$$\begin{aligned}
\frac{\partial \rho_1}{\partial t} &= -\{\rho_1, \mathcal{H}\} && (3.16)\\
&= \frac{\partial \rho_1}{\partial q_i}\frac{\partial \mathcal{H}}{\partial p_i} - \frac{\partial \rho_1}{\partial p_i}\frac{\partial \mathcal{H}}{\partial q_i} && (3.17)\\
&= \frac{\partial \rho_1}{\partial \mathcal{H}}\left[\frac{\partial \mathcal{H}}{\partial q_i}\frac{\partial \mathcal{H}}{\partial p_i} - \frac{\partial \mathcal{H}}{\partial p_i}\frac{\partial \mathcal{H}}{\partial q_i}\right] && (3.18)\\
&= \frac{\partial \rho_1}{\partial \mathcal{H}}\{\mathcal{H}, \mathcal{H}\} && (3.19)\\
&= 0 && (1)
\end{aligned}$$

and so ρ_1 in (3.10) takes the functional form $\rho_1 \propto \exp[-\beta\mathcal{H}]$ hence the same result is obtained via Liouville's theorem. Note that ρ_1 here is normalizeable and convergent because $\mathcal{H} < E$, so $\frac{\mathcal{H}}{E} - 1 < 0$.

(b) We now consider a gas mixture (N_a, ρ_a, H_a, E_a) and (N_b, ρ_b, H_b, E_b) where the ρ_i's are still regarded as one-body densities. We now wish to find these densities which minimize the total H function, $H = H_a + H_b$ subject to the constraint again that total energy remains constant. We can take this out using Lagrange multipliers again for the functional $H[\rho_a, \rho_b]$ but now working in a basis of (ρ_a, ρ_b) (two-dimensional gradient operator $\left(\frac{\partial}{\partial \rho_a}, \frac{\partial}{\partial \rho_b}\right)$). As in (3.2) and (3.5), we have

$$(\log \rho_a + 1) = \lambda \mathcal{H}_a \tag{3.20}$$

$$(\log \rho_b + 1) = \lambda \mathcal{H}_b \tag{3.21}$$

$$\int dV [N_a \rho_a \mathcal{H}_a + N_b \rho_b \mathcal{H}_b] = E. \tag{3.22}$$

We then obtain two functional forms for ρ_a and ρ_b as functions of the Hamiltonian and λ, as we previously derived in part (a):

$$\rho_a = \exp[\lambda \mathcal{H}_a - 1] \tag{3.23}$$

$$\rho_b = \exp\left[\lambda \mathcal{H}_b - 1\right]. \tag{3.24}$$

Taking derivatives in λ give

$$E = \frac{\partial}{\partial \lambda}\left[N_a \int dV \rho_a + N_b \int dV \rho_b\right] \tag{3.25}$$

$$= \frac{\partial}{\partial \lambda}(N_a + N_b) \tag{3.26}$$

where we have used normalization of both density functions in the last line. Just as before, integrating with respect to λ implies that $\lambda = \dfrac{N_a + N_b}{E}$, and therefore the functional forms which minimize (total) H are

$$\rho_a = \exp\left[\frac{N_a + N_b}{E}\mathcal{H}_a - 1\right] \tag{3.27}$$

$$\rho_b = \exp\left[\frac{N_a + N_b}{E}\mathcal{H}_b - 1\right]. \tag{3.28}$$

These two functions also satisfy Liouville's theorem, as both are functions of $\mathcal{H}$. We observe that the total average energy per particle is the same for both densities, given $\dfrac{E}{N_a + N_b}$. This can be explicitly shown as since the total energy is given as derivatives in $\lambda = \dfrac{N_a + N_b}{E}$, the energy for gas A is

$$E_a = \frac{E}{N_a + N_b} \cdot N_a \tag{3.29}$$

and

$$E_b = \frac{E}{N_a + N_b} \cdot N_b \tag{3.30}$$

from (3.26), hence the average energies for both particles are the same.
We can next consider the canonical ensemble $\rho(E) = \dfrac{1}{\Omega(E)}$, since $\mathbf{p}$ and $\mathbf{q}$ determine E with respect to the kinetic and potential energy. Then, by the definition of statistical entropy, we have that

$$S = k_B \log \Omega(E) \tag{3.31}$$

so, for ρ_a, ρ_b, we have (since $\Omega(E) = \Omega_A(E_a)\Omega_b(E_b)$)

$$S_a + S_b = k_B\left(1 - \frac{N_a + N_b}{E}\mathcal{H}_a\right) + k_B\left(1 - \frac{N_a + N_b}{E}\mathcal{H}_b\right) \tag{3.32}$$

$$= k_B\left(2 - \frac{N_a + N_b}{E}(\mathcal{H}_a + \mathcal{H}_b)\right). \tag{3.33}$$

The empirical temperature is obtained via $\dfrac{1}{T} = \dfrac{\partial S}{\partial E}$, from which implies that

$$\frac{1}{T} = k_B(\mathcal{H}_a + \mathcal{H}_b)\frac{N_a + N_b}{E^2} \tag{3.34}$$

$$\implies k_B T = \frac{E^2}{(N_a + N_b)(\mathcal{H}_a + \mathcal{H}_b)}. \tag{3.35}$$

Since the microstate exists under the condition that energy be partitioned equivalently under the equipartition theorem, assuming the potential goes to zero and $\mathcal{H}_a = E_a$, $\mathcal{H}_b = E_b$, we find

$$E = (N_a + N_b)k_B T \tag{3.36}$$

which serves as empirical temperature. Note that this appears familiar to $E = \frac{3}{2}k_B T$ for an ideal gas in three dimensions.