9. (Statistical Mechanics)

A gas that deviates slightly from ideal behavior exhibits an equation of state given by

$$p\nu = RT - \frac{a}{\nu}$$

where p is the pressure, T is the absolute temperature, R is the gas constant, "a" is a small constant coefficient, and ν is the volume per unit mole, i.e., $\nu = V/N_m$. The system consists of N particles corresponding to N_m moles.

(a) Deduce the dependence of the partition function Z on volume for this gas.

(b) Use your knowledge of the perfect ideal gas to identify the fully normalized partition function for this system. The answer should include the proper quantum normalization for phase-space and account for indistinguishability. The particle mass is m.

(c) If the average energy for this system is given by $\overline{E} = \frac{3}{2}N_m RT + a\frac{N_m^3}{V}$, find the specific heat at constant pressure, i.e., c_p. Give your answer in terms of T and ν.

The above expression for the average energy of the system is inconsistent with the equation of state. The expression for the average energy of the system was probably meant to be given as $\overline{E} = \frac{3}{2}N_m RT - a\frac{N_m^2}{V}$.

Solution: *Solution by Jonah Hyman (jthyman@g.ucla.edu)*

(a) The equation of state relates the pressure of the gas p to the volume of the gas V, the number of particles in the gas N, and the temperature of the gas T:

$$\begin{aligned} p\nu &= RT - \frac{a}{\nu} \\ p &= \frac{RT}{\nu} - \frac{a}{\nu^2} \\ p &= \frac{N_m RT}{V} - \frac{aN_m^2}{V^2} \quad \text{since } \nu \equiv \frac{V}{N_m} \end{aligned} \tag{1}$$

We don't know anything about the microstates of this non-ideal gas, so the typical definition of the partition function $Z = \sum_{\text{microstates } r} e^{-\beta E_r}$ doesn't work here. Instead, we need to relate the partition function to a macroscopic quantity. The appropriate macroscopic quantity to use is the free energy F, defined by

$$F = -kT \ln Z \tag{2}$$

How does the free energy relate pressure, volume, and temperature? To answer this question, we need to find dF. Recall that by the first law of thermodynamics, the differential of the energy E (in the canonical ensemble) is given by

$$dE = T\,dS - p\,dV \tag{3}$$

To get from the energy E to the free energy F, we perform a Legendre transform to swap the roles of the varables T and S:

$$dF = d(E - TS) = -S\,dT - p\,dV \tag{4}$$

This equation tells us that F depends on T and V. For any function of T and V, we can break up its differential into partial derivatives:

$$dF = \left.\frac{\partial F}{\partial T}\right|_V dT + \left.\frac{\partial F}{\partial V}\right|_T dV \tag{5}$$

Comparing (4) with (5), we get

$$-S = \left.\frac{\partial F}{\partial T}\right|_V \quad \text{and} \quad -p = \left.\frac{\partial F}{\partial V}\right|_T \tag{6}$$

The second equation here tells us that the pressure p, when expressed in terms of V and T, is a partial derivative of the free energy. Using (1) to write p in terms of V and T, we can write this partial differential equation as

$$\left.\frac{\partial F}{\partial V}\right|_T = -p = -\frac{N_m RT}{V} + \frac{aN_m^2}{V^2} \tag{7}$$

Taking the antiderivative with respect to V, we get that the free energy is

$$F(T, V) = -N_m RT \ln V - \frac{aN_m^2}{V} + f(T) \tag{8}$$

where $f(T)$ is a (possibly T-dependent) constant of integration. Using (2), we can find the partition function from the free energy:

$$F = -kT \ln Z \qquad \Longrightarrow \qquad Z = e^{-F/(kT)} \tag{9}$$

Plugging in the free energy from (8), we can find Z:

$$Z = \exp\left[-\frac{1}{kT}\left(-N_m RT\ln V - \frac{aN_m^2}{V} + f(T)\right)\right] \tag{10}$$

Before simplifying further, we should take a moment to relate the Boltzmann constant k to the ideal gas constant R. The ideal gas law is

$$pV = NkT = N_m RT \quad \text{where } N_m \text{ is the number of moles} \tag{11}$$

This implies that $k = \frac{N_m}{N}R$. The number of particles N is related to the number of moles by Avogadro's number N_A, using the equation $N = N_A N_m$. In other words,

$$k = \frac{N_m}{N}R = \frac{R}{N_A} \tag{12}$$

Plugging this into (10), we get

$$\begin{aligned}
Z &= \exp\left[-\frac{1}{RT/N_A}\left(-N_m RT\ln V - \frac{aN_m^2}{V} + f(T)\right)\right]\\
&= \exp\left[N_A N_m \ln V + \frac{aN_A N_m^2}{VRT} - \frac{N_A}{RT}f(T)\right]\\
&= \exp\left[N_A N_m \ln V + \frac{aN_A N_m}{\nu RT} - \frac{N_A}{RT}f(T)\right] \quad \text{since } N = N_A N_m\\
&= \exp\left[N \ln V + \frac{aN}{\nu RT} - \frac{N_A}{RT}f(T)\right] \quad \text{since } \nu \equiv \frac{V}{N_m}\\
&= V^N \exp\left(\frac{aN}{\nu RT}\right)\exp\left(-\frac{N_A}{RT}f(T)\right)\\
Z &= g(T)V^N \exp\left(\frac{aN}{\nu RT}\right) \quad \text{where } g(T) \equiv \exp\left(-\frac{N_A}{RT}f(T)\right)
\end{aligned} \tag{13}$$

Therefore, the volume dependence of the partition function for this gas is

$$\boxed{Z = g(T)V^N \exp\left(\frac{aN}{\nu RT}\right)} \tag{14}$$

where $g(T)$ is a function of T, N_A is Avogadro's number, and $\nu \equiv \frac{V}{N_m}$.

(b) We will assume that the gas is made of classical point particles, since we are not given an information about its quantum statistics or any extra degrees of freedom. When $a = 0$, the equation of state for this gas is just $pV = N_m RT$, meaning that this is an ideal monatomic classical gas.

Using the phase-space formalism for classical noninteracting point particles, the partition function for a single particle in a monatomic ideal gas is

$$Z_1 = \int \frac{d^3p\, d^3x}{h^3} e^{-\beta E} \quad \text{where } \beta \equiv \frac{1}{kT} \tag{15}$$

The energy of a single particle is its nonrelativistic kinetic energy:

$$E = \frac{p^2}{2m} \tag{16}$$

Plugging this in and carrying out the spatial integral for the partition function, we get

$$\begin{aligned} Z_1 &= \int \frac{d^3p\, d^3x}{h^3} e^{-\beta\left(\frac{p^2}{2m}\right)} \\ &= \int \frac{d^3p\, d^3x}{h^3} e^{-\beta p^2/(2m)} \\ &= \frac{V}{h^3} \int d^3p\, e^{-\beta p^2/(2m)} \quad \text{since} \int d^3x = V \\ &= \frac{V}{h^3} \int_{-\infty}^{\infty} dp_x \int_{-\infty}^{\infty} dp_y \int_{-\infty}^{\infty} dp_z\, e^{-\beta(p_x^2+p_y^2+p_z^2)/(2m)}] \\ &= \frac{V}{h^3} \left[\int_{-\infty}^{\infty} dp_x\, e^{-\beta p_x^2/(2m)}\right] \left[\int_{-\infty}^{\infty} dp_y\, e^{-\beta p_y^2/(2m)}\right] \left[\int_{-\infty}^{\infty} dp_z\, e^{-\beta p_z^2/(2m)}\right] \end{aligned} \tag{17}$$

Each of these three integrals is the same Gaussian integral, which can be calculated by a change of coordinates $u \equiv (\beta/(2m))^{1/2}\, p = (2mkT)^{-1/2}\, p$:

$$\begin{aligned} \int_{-\infty}^{\infty} dp\, e^{-\beta p^2/(2m)} &= (2mkT)^{1/2} \int_{-\infty}^{\infty} du\, e^{-u^2} \\ &= (2\pi mkT)^{1/2} \quad \text{using the result} \int_{-\infty}^{\infty} du\, e^{-u^2} = \pi^{1/2} \end{aligned} \tag{18}$$

Plugging this back into (17), we get

$$\begin{aligned} Z_1 &= \frac{V}{h^3} (2mkT)^{3/2} \\ &= V \left(\frac{2\pi mkT}{h^2}\right)^{3/2} \\ Z_1 &= \frac{V}{\lambda^3} \quad \text{for} \quad \lambda \equiv \left(\frac{h^2}{2\pi mkT}\right)^{1/2} \end{aligned} \tag{19}$$

The quantity λ is called the thermal wavelength.

The partition function Z for a set of N noninteracting, indistinguishable classical particles can be derived from the partition function for a single particle Z_1 using the formula

$$Z = \frac{Z_1^N}{N!} \tag{20}$$

The extra factor of $1/N!$ is to account for the indistinguishability of the particles. In this case, we therefore have

$$Z_{\text{ideal gas}} = \frac{1}{N!} \frac{V^N}{\lambda^{3N}} \quad \text{for} \quad \lambda \equiv \left(\frac{h^2}{2\pi mkT}\right)^{1/2} \tag{21}$$

Our answer from part (a) (14) must reduce to the partition function for an ideal gas, $Z_{\text{ideal gas}}$, when $a = 0$:

$$Z|_{a=0} = g(T) V^N \exp\left(\frac{aN}{\nu RT}\right)\bigg|_{a=0} = g(T) V^N \tag{22}$$

Comparing to (21), we get that

$$g(T) = \frac{1}{N!} \frac{1}{\lambda^{3N}} \quad \text{for} \quad \lambda \equiv \left(\frac{h^2}{2\pi mkT}\right)^{1/2} \tag{23}$$

Plugging this in, we get the full partition function

$$\boxed{Z = \frac{1}{N!} \frac{V^N}{\lambda^{3N}} \exp\left(\frac{aN}{\nu RT}\right) \quad \text{for} \quad \lambda \equiv \left(\frac{h^2}{2\pi mkT}\right)^{1/2}} \tag{24}$$

(c) To begin, note the definition of the heat capacity for a constant variable X

$$C_X \equiv \left.\frac{đQ}{dT}\right|_X = T\left.\frac{\partial S}{\partial T}\right|_X \tag{25}$$

The problem gives us the energy, so to get closer to this formula, let's write dS in terms of dE and dV. Starting with the first law of thermodynamics, we get

$$dE = T\,dS - p\,dV \qquad \Longrightarrow \qquad dS = \frac{1}{T}\,dE + \frac{p}{T}\,dV \tag{26}$$

We need to find the heat capacity at constant pressure

$$C_p \equiv T\left.\frac{\partial S}{\partial T}\right|_p \tag{27}$$

First, we need to find a general expression for C_p. There are two equivalent ways to do this, and we will present both:

Finding the heat capacity using energy:
We are given an expression for E in terms of T and V, so we should expand dE in terms of dT and dV.

$$dE = \left.\frac{\partial E}{\partial T}\right|_V dT + \left.\frac{\partial E}{\partial V}\right|_T dV \tag{28}$$

Plugging into (26), we get

$$\begin{aligned} dS &= \frac{1}{T}\left(\left.\frac{\partial E}{\partial T}\right|_V dT + \left.\frac{\partial E}{\partial V}\right|_T dV\right) + \frac{p}{T}\,dV \\ dS &= \frac{1}{T}\left.\frac{\partial E}{\partial T}\right|_V dT + \frac{1}{T}\left(\left.\frac{\partial E}{\partial V}\right|_T + p\right) dV \end{aligned} \tag{29}$$

To find the heat capacity at constant pressure, we need to first find $\left.\frac{\partial S}{\partial T}\right|_p$. This means we want to find dS in terms of dT and dp. The equation of state relates V to T and p, so we can use it to write dV in terms of dT and dp:

$$dV = \left.\frac{\partial V}{\partial T}\right|_p dT + \left.\frac{\partial V}{\partial p}\right|_T dp \tag{30}$$

Plugging this into (29), we get

$$\begin{aligned} dS &= \frac{1}{T}\left.\frac{\partial E}{\partial T}\right|_V dT + \frac{1}{T}\left(\left.\frac{\partial E}{\partial V}\right|_T + p\right)\left(\left.\frac{\partial V}{\partial T}\right|_p dT + \left.\frac{\partial V}{\partial p}\right|_T dp\right) \\ dS &= \frac{1}{T}\left[\left.\frac{\partial E}{\partial T}\right|_V + \left(\left.\frac{\partial E}{\partial V}\right|_T + p\right)\left.\frac{\partial V}{\partial T}\right|_p\right] dT + [\ldots]\; dp \end{aligned} \tag{31}$$

We have written the second term of dS with ellipses because this term isn't important for our purposes. What we want is $\left.\frac{\partial S}{\partial T}\right|_p$, which is given by the first term:

$$\left.\frac{\partial S}{\partial T}\right|_p = \frac{1}{T}\left[\left.\frac{\partial E}{\partial T}\right|_V + \left(\left.\frac{\partial E}{\partial V}\right|_T + p\right)\left.\frac{\partial V}{\partial T}\right|_p\right] \tag{32}$$

Therefore, the heat capacity at constant pressure is

$$\begin{aligned} C_p &= T\left.\frac{\partial S}{\partial T}\right|_p \\ C_p &= \left.\frac{\partial E}{\partial T}\right|_V + \left(\left.\frac{\partial E}{\partial V}\right|_T + p\right)\left.\frac{\partial V}{\partial T}\right|_p \end{aligned} \tag{33}$$

We have a closed-form expression for E in terms of T and V (the internal energy given in part (c)), as well as a closed-form expression for p in terms of T and V (the equation of state). But we don't have a nice closed-form expression for V in terms of p and T, since the equation of state is quadratic in V. Therefore, it would be nice to rewrite $\frac{\partial V}{\partial T}\big|_p$ in terms of derivatives of p.

We can do this by using a standard stat mech trick for finding the chain rule for partial derivatives (sometimes called a "cyclic relation"). Writing p in terms of T and V, we have

$$dp = \frac{\partial p}{\partial T}\bigg|_V dT + \frac{\partial p}{\partial V}\bigg|_T dV \tag{34}$$

If p is constant, $dp = 0$ and we can solve for $\frac{\partial V}{\partial T}$:

$$\begin{aligned} 0 &= \frac{\partial p}{\partial T}\bigg|_V dT + \frac{\partial p}{\partial V}\bigg|_T dV \quad \text{if } p \text{ is constant} \\ \frac{\partial p}{\partial V}\bigg|_T dV &= -\frac{\partial p}{\partial T}\bigg|_V dT \quad \text{if } p \text{ is constant} \\ \implies \qquad \frac{\partial V}{\partial T}\bigg|_p &= -\frac{\partial p/\partial T\big|_V}{\partial p/\partial V\big|_T} \end{aligned} \tag{35}$$

Plugging this into (33), we get

$$C_p = \frac{\partial E}{\partial T}\bigg|_V - \left(\frac{\partial E}{\partial V}\bigg|_T + p\right)\frac{\partial p/\partial T\big|_V}{\partial p/\partial V\big|_T} \tag{36}$$

Finding the heat capacity using entropy and a Maxwell relation:
An alternative method for finding a general expression for the heat capacity at constant pressure starts with the differential entropy, not the energy, in terms of T and V:

$$dS = \frac{\partial S}{\partial T}\bigg|_V dT + \frac{\partial S}{\partial V}\bigg|_T dV \tag{37}$$

As before, we want to find $\frac{\partial S}{\partial T}\big|_p$. The first step is to expand dV in terms of dp and dT:

$$dV = \frac{\partial V}{\partial T}\bigg|_p dT + \frac{\partial V}{\partial p}\bigg|_T dp \tag{38}$$

Plugging this into (37), we get

$$\begin{aligned} dS &= \frac{\partial S}{\partial T}\bigg|_V dT + \frac{\partial S}{\partial V}\bigg|_T \left[\frac{\partial V}{\partial T}\bigg|_p dT + \frac{\partial V}{\partial p}\bigg|_T dp\right] \\ &= \left[\frac{\partial S}{\partial T}\bigg|_V + \frac{\partial S}{\partial V}\bigg|_T \frac{\partial V}{\partial T}\bigg|_p\right] dT + [\ldots]\, dp \end{aligned} \tag{39}$$

We have written the second term of dS with ellipses because this term isn't important for our purposes. What we want is $\frac{\partial S}{\partial T}\big|_p$, which is given by the first term:

$$\frac{\partial S}{\partial T}\bigg|_p = \frac{\partial S}{\partial T}\bigg|_V + \frac{\partial S}{\partial V}\bigg|_T \frac{\partial V}{\partial T}\bigg|_p \tag{40}$$

We have a closed-form expression for E in terms of T and V (the internal energy given in part (c)), as well as a closed-form expression for p in terms of T and V (the equation of state). But we don't have any expression for the entropy S. And we also don't have a nice closed-form expression for the volume V in terms of p and T, since the equation of state is quadratic in V.

To find $\frac{\partial S}{\partial T}\big|_V$, you might already know that the heat capacity at constant *volume* is given by

$$C_V = T\frac{\partial S}{\partial T}\bigg|_V = \frac{\partial E}{\partial T}\bigg|_V \tag{41}$$

Therefore,

$$\frac{\partial S}{\partial T}\bigg|_V = \frac{1}{T}\frac{\partial E}{\partial T}\bigg|_V \tag{42}$$

(If this isn't convincing, you can rigorously derive this using the same chain of reasoning that led to (29).)

To find $\frac{\partial S}{\partial V}\big|_T$, we need to use a Maxwell relation. The Maxwell relations come from the second derivatives of the energy functionals. In this case, we want to use the energy functional that is written in terms of T and V, which is the free energy F given by (4):

$$dF = -S\,dT - p\,dV \tag{43}$$

We can take the second derivative of F in one of two ways:

$$\frac{\partial^2 F}{\partial T\partial V} = \frac{\partial}{\partial T}\bigg|_V \left[\frac{\partial F}{\partial V}\bigg|_T\right] = -\frac{\partial p}{\partial T}\bigg|_V \tag{44}$$

$$\frac{\partial^2 F}{\partial V\partial T} = \frac{\partial}{\partial V}\bigg|_T \left[\frac{\partial F}{\partial T}\bigg|_V\right] = -\frac{\partial S}{\partial V}\bigg|_T \tag{45}$$

The second derivative of F doesn't depend on which order the derivatives are taken. Therefore, we can set (44) equal to (45):

$$\frac{\partial S}{\partial V}\bigg|_T = \frac{\partial p}{\partial T}\bigg|_V \tag{46}$$

To find $\frac{\partial V}{\partial T}\big|_p$, we can use a standard stat mech trick for finding the chain rule for partial derivatives (sometimes called a "cyclic relation"). Writing p in terms of T and V, we have

$$dp = \frac{\partial p}{\partial T}\bigg|_V dT + \frac{\partial p}{\partial V}\bigg|_T dV \tag{47}$$

If p is constant, $dp = 0$ and we can solve for $\frac{\partial V}{\partial T}$:

$$\begin{aligned} 0 &= \frac{\partial p}{\partial T}\bigg|_V dT + \frac{\partial p}{\partial V}\bigg|_T dV \quad \text{if } p \text{ is constant} \\ \frac{\partial p}{\partial V}\bigg|_T dV &= -\frac{\partial p}{\partial T}\bigg|_V dT \quad \text{if } p \text{ is constant} \\ \implies \qquad \frac{\partial V}{\partial T}\bigg|_p &= -\frac{\partial p/\partial T|_V}{\partial p/\partial V|_T} \qquad (48) \end{aligned}$$

Plugging (42), (46), and (48) into (40), we get

$$\frac{\partial S}{\partial T}\bigg|_p = \frac{1}{T}\frac{\partial E}{\partial T}\bigg|_V - \frac{\left(\partial p/\partial T|_V\right)^2}{\partial p/\partial V|_T} \tag{49}$$

Therefore,

$$C_p = T\frac{\partial S}{\partial T}\bigg|_p$$

$$C_p = \frac{\partial E}{\partial T}\bigg|_V - T\,\frac{\left(\partial p/\partial T\big|_V\right)^2}{\partial p/\partial V\big|_T} \tag{50}$$

We now have two equivalent general formulas for the heat capacity at constant pressure

$$C_p = \frac{\partial E}{\partial T}\bigg|_V - \left(\frac{\partial E}{\partial V}\bigg|_T + p\right)\frac{\partial p/\partial T\big|_V}{\partial p/\partial V\big|_T} \tag{51}$$

$$C_p = \frac{\partial E}{\partial T}\bigg|_V - T\,\frac{\left(\partial p/\partial T\big|_V\right)^2}{\partial p/\partial V\big|_T} \tag{52}$$

We also have a closed-form expression for E terms of T and V, given by the problem (note that we are using the corrected expression for E):

$$E = \frac{3}{2}N_mRT - \frac{aN_m^2}{V}$$

From the equation of state, we also have a closed-form expression for p in terms of T and V (1):

$$p = \frac{N_mRT}{V} - \frac{aN_m^2}{V^2}$$

From these two closed-form expressions, we can write all the partial derivatives we need:

$$\frac{\partial E}{\partial T}\bigg|_V = \frac{3}{2}N_mR \tag{53}$$

$$\frac{\partial E}{\partial V}\bigg|_T = \frac{aN_m^2}{V^2} \tag{54}$$

$$\frac{\partial p}{\partial T}\bigg|_V = \frac{N_mR}{V} \tag{55}$$

$$\frac{\partial p}{\partial V}\bigg|_T = -\frac{N_mRT}{V^2} + \frac{2aN_m^2}{V^3} \tag{56}$$

Using (51), we get

$$\begin{aligned}
C_p &= \frac{\partial E}{\partial T}\bigg|_V - \left(\frac{\partial E}{\partial V}\bigg|_T + p\right)\frac{\partial p/\partial T\big|_V}{\partial p/\partial V\big|_T} \\
&= \frac{3}{2}N_mR - \left(\frac{aN_m^2}{V^2} + \frac{N_mRT}{V} - \frac{aN_m^2}{V^2}\right)\frac{\frac{N_mR}{V}}{-\frac{N_mRT}{V^2} + \frac{2aN_m^2}{V^3}} \\
&= \frac{3}{2}N_mR - \frac{N_mRT}{V}\,\frac{\frac{N_mR}{V}}{-\frac{N_mRT}{V^2} + \frac{2aN_m^2}{V^3}} \\
&= \frac{3}{2}N_mR - \frac{N_mRT}{V}\,\frac{\frac{N_mR}{V}}{\frac{-N_mRTV + 2aN_m^2}{V^3}} \\
&= \frac{3}{2}N_mR - \frac{N_mR^2TV}{-RTV + 2aN_m} \\
&= N_mR\left[\frac{3}{2} + \frac{RTV}{RTV - 2aN_m}\right]
\end{aligned}$$

$$C_p = N_m R\left[\frac{3}{2} + \frac{1}{1 - \frac{2aN_m}{RTV}}\right] \tag{57}$$

Alternatively, using equivalent equation (52), we get

$$\begin{aligned} C_p &= \frac{\partial E}{\partial T}\bigg|_V - T\,\frac{\left(\partial p/\partial T\big|_V\right)^2}{\partial p/\partial V\big|_T} \\ &= \frac{3}{2}N_m R - T\frac{\left(\frac{N_m R}{V}\right)^2}{-\frac{N_m RT}{V^2} + \frac{2aN_m^2}{V^3}} \\ &= \frac{3}{2}N_m R - T\frac{\left(\frac{N_m R}{V}\right)^2}{\frac{-N_m RTV + 2aN_m^2}{V^3}} \\ &= \frac{3}{2}N_m R - \frac{N_m R^2 TV}{-RTV + 2aN_m} \\ &= N_m R\left[\frac{3}{2} + \frac{RTV}{RTV - 2aN_m}\right] \end{aligned}$$

$$C_p = N_m R\left[\frac{3}{2} + \frac{1}{1 - \frac{2aN_m}{RTV}}\right] \tag{58}$$

The problem asks for the specific heat c_p in terms of T and $\nu = V/N_m$. It won't be possible to write this answer in terms of these quantities alone, since there is a prefactor of N_m standing alone. For that reason, we should interpret the specific heat as the heat capacity *per mole*, which allows us to divide by the number of moles to get

$$c_p = \frac{C_p}{N_m} = R\left[\frac{3}{2} + \frac{1}{1 - \frac{2aN_m}{RTV}}\right] \tag{59}$$

Using the relation $\nu = \frac{V}{N_m}$, we get our final answer

$$\boxed{c_p = R\left[\frac{3}{2} + \frac{1}{1 - \frac{2a}{RT\nu}}\right]} \tag{60}$$

The model used in this problem is a simplified version of the Van der Waals gas, in which the volume occupied by a mole of gas particles b is set equal to zero.