The Statistical Mechanical Derivation of the van der Waals Equation of State and its associated thermodynamic properties

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We will perform our derivation in the canonical ensemble, where we specify the number of molecules, N, the volume, V, and the temperature T. For a monatomic ideal gas, the well-known partition function is

$$Q_{IG} = \frac{1}{N!}\left(\frac{V}{\Lambda^3}\right)^N \tag{1}$$

where the thermal deBroglie wavelength is defined as

$$\Lambda = \sqrt{\frac{h^2}{2\pi m k_B T}} \tag{2}$$

where h is Planck's constant, k_B is Boltzmann's constant, and m is the mass of the molecule. The van der Waals fluid differs from an ideal gas in two ways. First, the molecules have a finite minimum molar volume, b. In other words, they can not be compressed to infinite density. This volume occupied by the molecules is not part of the accessible volume of the system. Therefore, the partition function becomes,

$$Q = \frac{1}{N!}\left(\frac{V - Nb}{\Lambda^3}\right)^N \tag{3}$$

where we have multiplied b by N to account for the total volume occupied by molecules. The second way in that a van der Waals fluid differs from an ideal gas is that the van der Waals molecule experiences a net attractive force to all other molecules. This attraction is based upon a mean field approximation. The energy associated with each molecule is linearly proportional to the molar density of the system,

$$E_{vdw} = -a\frac{N}{V} \tag{4}$$

This energetic term modifies the partition function to become

$$Q_{vdw} = \frac{1}{N!}\left(\frac{V-Nb}{\Lambda^3}\right)^N \exp\left(-\frac{NE_{vdw}}{k_B T}\right) = \frac{1}{N!}\left(\frac{V-Nb}{\Lambda^3}\right)^N \exp\left(\frac{N^2 a}{Vk_B T}\right) \tag{5}$$

As always, we require the natural log of the partition function

$$\ln(Q_{vdw}) = -\ln(N!) + N\ln\left(\frac{V-Nb}{\Lambda^3}\right) + \frac{N^2 a}{Vk_B T} \tag{6}$$

We use Stirling's approximation for the natural log of the factorial of a large number

$$\ln(Q_{vdw}) = -N\ln(N) + N + N\ln\left(\frac{V-Nb}{\Lambda^3}\right) + \frac{N^2 a}{Vk_B T} \tag{7}$$

The first thermodynamic property that we will calculate is the pressure because that is what everyone associates with the van der Waals equation of state.

$$p = k_B T\left(\frac{\partial \ln(Q)}{\partial V}\right)_{N,T} = \frac{k_B T}{\frac{V}{N} - b} - \frac{a}{\left(\frac{V}{N}\right)^2} = \frac{k_B T}{V_m - b} - \frac{a}{V_m^2} \tag{8}$$

where we have defined a molecular volume, $V_m \equiv \frac{V}{N}$. This is the van der Waals equation of state.

Now let's derive other thermodynamic functions. We will start with the molecular Helmholtz free energy,

$$A_m = \frac{A}{N} = -\frac{k_B T}{N}\ln(Q)_{N,T} = -k_B T\left[-\ln(N) + 1 + \ln\left(\frac{V-Nb}{\Lambda^3}\right) + \frac{Na}{Vk_B T}\right] \tag{9}$$

The molecular internal energy is

$$E_m = \frac{E}{N} = \frac{k_B T^2}{N}\left(\frac{\partial \ln(Q)}{\partial T}\right)_{N,V} = \frac{3}{2}k_B T - \frac{Na}{V} = \frac{3}{2}k_B T - \frac{a}{V_m} \tag{10}$$

Unlike the ideal gas, the internal energy of a vdW fluid is not only a function of temperature but also a function of molar volume. The chemical potential is

$$\mu = -k_B T\left(\frac{\partial \ln(Q)}{\partial N}\right)_{T,V} = -k_B T\left[\ln\left(\frac{V_m - b}{\Lambda^3}\right) - \frac{b}{V_m - b} + \frac{2a}{V_m k_B T}\right] \tag{11}$$

The molecular entropy is

$$S_m = \frac{S}{N} = \frac{E-A}{NT} = \frac{E_m - A_m}{T} = k_B\left[\frac{5}{2} + \ln\left(\frac{V_m - b}{\Lambda^3}\right)\right] \tag{12}$$

The molecular enthalpy is

$$H_m = \frac{H}{N} = \frac{E+PV}{N} = E_m + PV_m = \frac{3}{2}k_B T - 2\frac{a}{V_m} + \frac{k_B T V_m}{V_m - b} \tag{13}$$

The molecular Gibbs free energy is

$$G_m = \frac{G}{N} = \frac{H-TS}{N} = H_m - TS_m = -k_B T\left[1 - \frac{V_m}{V_m - b} + \ln\left(\frac{V_m - b}{\Lambda^3}\right)\right] - 2\frac{a}{V_m} \tag{14}$$

In addition to the basic thermodynamic properties, we can also calculate a variety of thermodynamic properties from the partial derivatives.

$$\left(\frac{\partial p}{\partial T}\right)_{V_m} = \frac{k_B}{V_m - b} \tag{15}$$

$$\left(\frac{\partial p}{\partial V_m}\right)_T = -\frac{k_B T}{(V_m - b)^2} + 2\frac{a}{V_m^3} \tag{16}$$

$$\left(\frac{\partial V_m}{\partial T}\right)_p = -\frac{\left(\frac{\partial p}{\partial T}\right)_{V_m}}{\left(\frac{\partial p}{\partial V_m}\right)_T} = \frac{1}{\frac{T}{V_m - b} - 2\frac{a(V_m - b)}{k_B V_m^3}} \tag{17}$$

The molecular constant volume-heat capacity is

$$C_v = \left(\frac{\partial E_m}{\partial T}\right)_{V_m} = \frac{3}{2}k_B \tag{18}$$

The molecular constant-pressure heat capacity is

$$C_p = \left(\frac{\partial H_m}{\partial T}\right)_p = \left(\frac{\partial E_m}{\partial T}\right)_p + p\left(\frac{\partial V_m}{\partial T}\right)_p \tag{19}$$

Now we need, the first term on the RHS. Going to the Tables of P.W. Bridgman, we have

$$\left(\frac{\partial E_m}{\partial T}\right)_p = C_V + T\left(\frac{\partial p}{\partial T}\right)_{V_m}\left(\frac{\partial V_m}{\partial T}\right)_p - p\left(\frac{\partial V_m}{\partial T}\right)_p \tag{20}$$

Substituting equation (20) into equation (19) yields

$$C_p = C_V + T\left(\frac{\partial p}{\partial T}\right)_{V_m}\left(\frac{\partial V_m}{\partial T}\right)_p = \frac{3}{2}k_B + k_B\frac{1}{1-2\frac{a(V_m-b)^2}{k_B T V_m^3}} \tag{21}$$

The constant-pressure heat capacity is a function of temperature and molar volume.

Now let's look at vapor-liquid equilibrium. The internal energy of vaporization is

$$\Delta E_m = E_m^V - E_m^L = a\left(\frac{1}{V_m^L} - \frac{1}{V_m^V}\right) \tag{22}$$

The enthalpy of vaporization is

$$\Delta H_m = H_m^V - H_m^L = \Delta E_m + p\Delta V_m = a\left(\frac{1}{V_m^L} - \frac{1}{V_m^V}\right) + p\Delta\left(V_m^V - V_m^L\right) \tag{23}$$

The entropy of vaporization is

$$\Delta S_m = S_m^V - S_m^L = k_B \ln\left(\frac{V_m^V - b}{V_m^L - b}\right) \tag{24}$$

The molecular Gibbs free energy of vaporization is

$$\Delta G_m = G_m^V - G_m^L = k_B T\left[\ln\left(\frac{V_m^L - b}{V_m^V - b}\right) + \frac{V_m^V}{V_m^V - b} - \frac{V_m^L}{V_m^L - b}\right] + 2a\left(\frac{1}{V_m^L} - \frac{1}{V_m^V}\right) \tag{25}$$

Since the molecular Gibbs free energy of vaporization is zero at equilibrium, this gives a condition for vapor-liquid equilibrium, namely,

$$k_B T\left[\ln\left(\frac{V_m^L - b}{V_m^V - b}\right) + \frac{V_m^V}{V_m^V - b} - \frac{V_m^L}{V_m^L - b}\right] + 2a\left(\frac{1}{V_m^L} - \frac{1}{V_m^V}\right) = 0 \tag{26}$$

The chemical potentials should also be equal at equilibrium

$$\Delta\mu = \mu_V - \mu_L = k_B T\left[\ln\left(\frac{V_m^L - b}{V_m^V - b}\right) + \frac{b}{V_m^V - b} - \frac{b}{V_m^L - b}\right] - 2a\left(\frac{1}{V_m^V} - \frac{1}{V_m^L}\right) \tag{27}$$

This expression doesn't look the same as equation (26), but if you get a common denominator in equations (26) and (27) then it turns out that they are identical equations.

So at VLE, given the temperature, we have three unknowns: the vapor molar volume, the liquid molar volume, and the vapor pressure. The two molar volumes are found by simultaneously solving equation (27) and the condition of mechanical equilibrium, namely

$$\Delta p = p_V - p_L = \frac{k_B T}{V_m^V - b} - \frac{a}{V_m^{V\,2}} - \frac{k_B T}{V_m^L - b} + \frac{a}{V_m^{L\,2}} = 0 \tag{28}$$

Once the molar volumes are known, the vapor pressure can be obtained by evaluating equation (8) at either molar volume.

For a certain application, we may want to know the change in the molar volume as a function of temperature along the two-phase boundary of the phase diagram, also known as the saturation line. In order to obtain an analytical expression for this derivative, we must differentiate both equation (27) and (28) with respect to temperature. We will then obtain two derivatives, one for the liquid and one for the vapor. We will combine the two equations to solve for the two derivatives individually. We begin by differentiating equation (27) with respect to temperature along the saturation line.

$$\begin{aligned} &k_B T\left[\frac{1}{V_m^L - b}\left.\frac{\partial V_m^L}{\partial T}\right|_{sat} - \frac{1}{V_m^V - b}\left.\frac{\partial V_m^V}{\partial T}\right|_{sat} - \frac{b}{\left(V_m^V - b\right)^2}\left.\frac{\partial V_m^V}{\partial T}\right|_{sat} + \frac{b}{\left(V_m^L - b\right)^2}\left.\frac{\partial V_m^L}{\partial T}\right|_{sat}\right] \\ &+ k_B\left[\ln\left(\frac{V_m^L - b}{V_m^V - b}\right) + \frac{b}{V_m^V - b} - \frac{b}{V_m^L - b}\right] + 2a\left(\frac{1}{V_m^{V\,2}}\left.\frac{\partial V_m^V}{\partial T}\right|_{sat} - \frac{1}{V_m^{L\,2}}\left.\frac{\partial V_m^L}{\partial T}\right|_{sat}\right) = 0 \end{aligned} \tag{29}$$

Next we differentiate equation (28)

$$-\frac{k_B T}{\left(V_m^V - b\right)^2}\left.\frac{\partial V_m^V}{\partial T}\right|_{sat} + \frac{k_B}{V_m^V - b} + 2\frac{a}{V_m^{V\,3}}\left.\frac{\partial V_m^V}{\partial T}\right|_{sat} + \frac{k_B T}{\left(V_m^L - b\right)^2}\left.\frac{\partial V_m^L}{\partial T}\right|_{sat} - \frac{k_B}{V_m^L - b} - 2\frac{a}{V_m^{L\,3}}\left.\frac{\partial V_m^L}{\partial T}\right|_{sat} = 0 \tag{30}$$

Now we solve these two equations for the two partial derivatives. Take equation (30) and combine like terms.

$$\left(-\frac{k_B T}{\left(V_m^V - b\right)^2} + 2\frac{a}{V_m^{V\,3}}\right)\left.\frac{\partial V_m^V}{\partial T}\right|_{sat} + \left(\frac{k_B T}{\left(V_m^L - b\right)^2} - 2\frac{a}{V_m^{L\,3}}\right)\left.\frac{\partial V_m^L}{\partial T}\right|_{sat} = \frac{k_B}{V_m^L - b} - \frac{k_B}{V_m^V - b} \tag{31}$$

$$\left.\frac{\partial V_m^L}{\partial T}\right|_{sat} = \frac{\dfrac{k_B}{V_m^L - b} - \dfrac{k_B}{V_m^V - b} + \left(\dfrac{k_B T}{\left(V_m^V - b\right)^2} - 2\dfrac{a}{{V_m^V}^3}\right)\left.\dfrac{\partial V_m^V}{\partial T}\right|_{sat}}{\left(\dfrac{k_B T}{\left(V_m^L - b\right)^2} - 2\dfrac{a}{{V_m^L}^3}\right)} \tag{32}$$

Next we combine terms in equation (29)

$$\begin{aligned} &\left(\frac{k_B T}{V_m^L - b} + \frac{k_B T b}{\left(V_m^L - b\right)^2} - \frac{2a}{{V_m^L}^2}\right)\left.\frac{\partial V_m^L}{\partial T}\right|_{sat} - \left(\frac{k_B T}{V_m^V - b} + \frac{k_B T b}{\left(V_m^V - b\right)^2} - \frac{2a}{{V_m^V}^2}\right)\left.\frac{\partial V_m^V}{\partial T}\right|_{sat} \\ &= -k_B\left[\ln\left(\frac{V_m^L - b}{V_m^V - b}\right) + \frac{b}{V_m^V - b} - \frac{b}{V_m^L - b}\right] \end{aligned} \tag{33}$$

$$\left.\frac{\partial V_m^L}{\partial T}\right|_{sat} = \frac{-k_B\left[\ln\left(\dfrac{V_m^L - b}{V_m^V - b}\right) + \dfrac{b}{V_m^V - b} - \dfrac{b}{V_m^L - b}\right] + \left(\dfrac{k_B T}{V_m^V - b} + \dfrac{k_B T b}{\left(V_m^V - b\right)^2} - \dfrac{2a}{{V_m^V}^2}\right)\left.\dfrac{\partial V_m^V}{\partial T}\right|_{sat}}{\left(\dfrac{k_B T}{V_m^L - b} + \dfrac{k_B T b}{\left(V_m^L - b\right)^2} - \dfrac{2a}{{V_m^L}^2}\right)} \tag{34}$$

Now we equate (32) and (34), and solve to obtain

$$\left.\frac{\partial V_m^V}{\partial T}\right|_{sat} = \frac{\dfrac{\dfrac{k_B}{V_m^L - b} - \dfrac{k_B}{V_m^V - b}}{\left(\dfrac{k_B T}{\left(V_m^L - b\right)^2} - 2\dfrac{a}{{V_m^L}^3}\right)} + \dfrac{k_B\left[\ln\left(\dfrac{V_m^L - b}{V_m^V - b}\right) + \dfrac{b}{V_m^V - b} - \dfrac{b}{V_m^L - b}\right]}{\left(\dfrac{k_B T}{V_m^L - b} + \dfrac{k_B T b}{\left(V_m^L - b\right)^2} - \dfrac{2a}{{V_m^L}^2}\right)}}{\dfrac{\left(\dfrac{k_B T}{V_m^V - b} + \dfrac{k_B T b}{\left(V_m^V - b\right)^2} - \dfrac{2a}{{V_m^V}^2}\right)}{\left(\dfrac{k_B T}{V_m^L - b} + \dfrac{k_B T b}{\left(V_m^L - b\right)^2} - \dfrac{2a}{{V_m^L}^2}\right)} - \dfrac{\left(\dfrac{k_B T}{\left(V_m^V - b\right)^2} - 2\dfrac{a}{{V_m^V}^3}\right)}{\left(\dfrac{k_B T}{\left(V_m^L - b\right)^2} - 2\dfrac{a}{{V_m^L}^3}\right)}} \tag{35}$$

We can obtain the corresponding partial derivative for the liquid phase by substituting equation (35) into equation (32).