Helmholtz Free Energy and the Ideal Gas

Class Notes

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1 Review: The Monoatomic Ideal Gas

Last time, we computed the partition function of an ideal gas with N indistinguishable particles at temperature T in a volume V. The partition function is:

$$Z = \frac{1}{N!}\left(\frac{V}{\lambda_Q^3}\right)^N \tag{1}$$

where λ_Q is the thermal de Broglie wavelength:

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

From the partition function, we computed the average energy:

$$\langle E\rangle = -\frac{\partial}{\partial\beta}\ln Z = \frac{3}{2}Nk_BT \tag{3}$$

And the heat capacity at constant volume for a monoatomic ideal gas:

$$C_V = \left(\frac{\partial\langle E\rangle}{\partial T}\right)_V = \frac{3}{2}Nk_B \tag{4}$$

1.1 Entropy and the Sackur-Tetrode Equation

What about the entropy? We can compute the entropy using the canonical probability distribution $p(n) = \frac{e^{-\beta E_n}}{Z}$. Using the Gibbs entropy formula:

$$\begin{aligned} S &= -k_B\sum_n p(n)\ln(p(n)) \\ &= \frac{\langle E\rangle}{T} + k_B\ln Z \end{aligned}$$

Substituting our expressions for $\langle E\rangle$ and Z, and applying Stirling's approximation, we arrive at the **Sackur-Tetrode equation**:

$$S = Nk_B\left[\ln\left(\frac{V}{N\lambda_Q^3}\right) + \frac{5}{2}\right] \tag{5}$$

2 The Equation of State (Pressure)

We can derive the pressure of the gas from the thermodynamic definition $P = T\left(\frac{\partial S}{\partial V}\right)_{E,N}$. Applying this to the Sackur-Tetrode equation, we isolate the volume dependence:

$$\begin{aligned} P &= TNk_B \frac{\partial}{\partial V}[\ln V + \text{terms independent of } V] \\ &= TNk_B \left(\frac{1}{V}\right) = \frac{Nk_BT}{V} \end{aligned}$$

Rearranging this gives the familiar **Ideal Gas Law**:

$$\boxed{PV = Nk_BT} \tag{6}$$

If we plot the compressibility factor $Z_c = \frac{PV}{Nk_BT}$ against pressure, an ideal gas forms a perfectly horizontal line at $Z_c = 1$. Real gases like Helium (He), Hydrogen (H_2), and Ammonia (NH_3) deviate slightly from this value depending on the pressure, but for many conditions, the ideal gas law is a very good approximation.

3 Helmholtz Free Energy

Now, let us go back to the expression for entropy in terms of the partition function:

$$S = \frac{\langle E\rangle}{T} + k_B \ln Z \tag{7}$$

Multiplying the entire equation by T:

$$TS = \langle E\rangle + k_BT \ln Z \tag{8}$$

We can rearrange this to isolate the partition function term:

$$-k_BT \ln Z = \langle E\rangle - TS \tag{9}$$

We define this new quantity as the **Helmholtz Free Energy**, denoted by F:

$$\boxed{F \equiv \langle E\rangle - TS = -k_BT \ln Z} \tag{10}$$

Here, the word "free" does not mean "without cost" (nothing is free!). Rather, it should be interpreted as the **"available" energy** of the system to do useful work. The free energy captures the fundamental thermodynamic competition between minimizing energy ($\langle E\rangle$) and maximizing entropy (S).

4 Thermodynamic Relations

Let us take the total differential of the Helmholtz free energy, $F = \langle E\rangle - TS$:

$$dF = d\langle E\rangle - SdT - TdS \tag{11}$$

Recall the fundamental thermodynamic identity for the internal energy:

$$dE = TdS - PdV \tag{12}$$

Substituting this into our expression for dF:

$$dF = (TdS - PdV) - SdT - TdS$$
$$\Rightarrow dF = -PdV - SdT$$

This result shows that F is naturally a function of Volume and Temperature: $F(V, T)$. Mathematically, F is the **Legendre transform** of the internal energy $\langle E \rangle$, moving from a function of (S, V) to a function of (T, V).

From the total differential $dF = -PdV - SdT$, we can easily read off the following partial derivatives:

$$P = -\left(\frac{\partial F}{\partial V}\right)_T \tag{13}$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V \tag{14}$$

5 The Boltzmann Distribution in Terms of F

Going back to our definition of the Helmholtz free energy:

$$F = -k_B T \ln Z \quad \Longrightarrow \quad \ln Z = -\frac{F}{k_B T} = -\beta F \tag{15}$$

Exponentiating both sides gives the partition function in terms of F:

$$Z = e^{-\beta F} \tag{16}$$

We can substitute this directly into the canonical Boltzmann distribution:

$$p(n) = \frac{e^{-\beta E_n}}{Z} = \frac{e^{-\beta E_n}}{e^{-\beta F}} \tag{17}$$

$$\boxed{p(n) = e^{\beta(F - E_n)}} \tag{18}$$

This provides a very clean, alternative way to write the probability of a system occupying a specific microstate n.