Thermal Physics

Notes based on lectures for PH2202 (Thermal Physics)
at IISER Kolkata by Professor Koushik Dutta, Spring 2024

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1. Introduction

- The course will not be going over KTG in detail at the beginning - rather it will attempt to pick up from where the Chemical Thermodynamics course left off.
- This course will attempt to link thermodynamics to statistical mechanics.

2. Lecture 1

The goal here will be to find a **fundamental thermodynamic relation** for ideal gas, which is essentially the expression of the internal energy of the gas as a function of temperature, volume, and number density / number of molecules.

2.1. Setting up the requirements

Ideal Gas Equation — Definition 2.1.1

$$pV = nRT \qquad [1]$$

This equation has been derived **empirically** from Charle's Law, Boyle's law, etc.

Internal energy of Ideal Gas — Definition 2.1.2

$$U = \frac{3}{2}nRT \qquad [2]$$

This equation has been derived from the **kinetic theory of gases**

It is very important to note here that here we are commiting to using the *microscopic picture* of the ideal gas when we use this equation.

We are also going to be using the relation -

$$dU = TdS - pdV + \mu dN \qquad [3]$$

- This equation is essentially a combination of the 1st and the 2nd Laws of Thermodynamics.
- The last term is included to account for the chemical potential of the system.

Now, as stated earlier, our goal is to find

$$U = U(S, V, N)$$

$$\Rightarrow dU = \left(\frac{\partial U}{\partial S}\right)_{V,N} dS + \left(\frac{\partial U}{\partial V}\right)_{S,N} dV + \left(\frac{\partial U}{\partial N}\right)_{S,V} dN \qquad [4]$$

Comparing this with Equation 2, we get -

$$\begin{gathered} T = \left(\frac{\partial U}{\partial S}\right)_{V,N} \\ p = -\left(\frac{\partial U}{\partial V}\right)_{S,N} \\ \mu = \left(\frac{\partial U}{\partial N}\right)_{S,V} \end{gathered} \qquad [5]$$

Why are we considering μdN?

- μdN gives us the energy that is taken out or given by taking out ot putting in molecules
- μ is called the **chemical potential**.

Why are we expressing the internal energy as the function of these quantities only and not as a fucntion of other quantities like temperature, pressure, etc? It is because these are easily measurable quantitites.

2.2. The derivation

we will now derive fundamental thermodynamic relation using Equation 1 and Equation 2.

$$U = \frac{3}{2}nRT \Rightarrow T = \frac{2U}{3nR}$$

Now, we know from Equation 5 that

$$\left(\frac{\partial U}{\partial S}\right)_{V,N} = T = \frac{2U}{3nR}$$

$$\Rightarrow \frac{dU}{U} = \frac{2}{3}\frac{1}{nR}dS$$

Integrating,

$$\ln(U) = \frac{2}{3}\frac{S}{nR} + f(V, N) \qquad [6]$$

Where f is some function that is the constant of the integration.

Now,

$$pV = nRT \Rightarrow p = \frac{nRT}{V}$$

We know from Equation 5 that

$$\left(\frac{\partial U}{\partial V}\right)_{S,N} = -p = -\frac{nRT}{V}$$

Using Equation 2,

$$\left(\frac{\partial U}{\partial V}\right)_{S,N} = -\frac{2}{3}\frac{U}{V} \qquad [7]$$

Differentiating Equation 6 with respect to V, we get

$$\frac{\partial}{\partial V}(\ln U) = \frac{\partial}{\partial V}\left(\frac{2}{3}\frac{S}{nR} + f(V,N)\right)$$

$$\Rightarrow \frac{1}{U}\left(\frac{\partial U}{\partial V}\right)_{S,N} = \left(\frac{\partial f}{\partial V}\right)_{S,N}$$

Using Equation 7 here,

$$-\frac{2}{3}\frac{U}{V} = U\left(\frac{\partial f}{\partial V}\right)_{S,N}$$

$$\Rightarrow df = -\frac{2}{3}\frac{dV}{V}$$

Integrating,

$$f = -\frac{2}{3}\ln V + \ln(g(N))$$

Where g is the constant of integration (We may write it as a logarithm because it makes the manipulation easier later). Therefore we get,

$$\ln U = \frac{2}{3}\frac{S}{nR} - \frac{2}{3}\ln V + \ln(g(N)) \qquad [8]$$

We arrived at this using only the two equations Equation 1 and Equation 2. But now, we have a problem. The function of N, g, needs to be determined. We have exhausted our physical input - both the equations that we had have been used. What do we do now?

> We note the fact that the quantities V, S and N are all **extensive** in nature - so is the property U. This means that these properties are **directly proportional to the amount of mass in the system**.
>
> Say we decide to scale the entire system by some constant λ, i.e., $S \to \lambda S$, $V \to \lambda V$, $N \to \lambda N$.
>
> Then, from the extensive nature of U, we can definitively say that $U \to \lambda U$.
>
> We exploit this fact to finish our derivation.

First, we rewrite the equation.

$$U = g(N)V^{-\frac{2}{3}}e^{\frac{2}{3}\frac{S}{nR}} \qquad [9]$$

Now, we carry out the scaling operation as discussed.

$$U = g(\lambda N)(\lambda V)^{-\frac{2}{3}}e^{\frac{2}{3}\frac{\lambda S}{\lambda nR}}$$

$$\Rightarrow U = g(\lambda N)(\lambda V)^{-\frac{2}{3}}e^{\frac{2}{3}\frac{S}{nR}}$$

Here, the LHS needs to be λU. This can only be true if,

$$g(N) = kN^{\frac{5}{3}} \qquad [10]$$

Where k is some constant. Combining Equation 10 and Equation 9, we get

$$\boxed{U = kN\left(\frac{V}{N}\right)^{-\frac{2}{3}}e^{\frac{2}{3}\frac{S}{nR}}}$$

Which is the required relation.

To summarise, we have arrived at this equation using -

- 2 empirical equations
- The principle of extensivity

Question: Can this be derived from microscopic considerations , without empirical relations? What if $pV = nRT$ does not hold?

This is the goal of statistical mechanics, which we shall arrive at later in the course.

References