Statistical Molecular Thermodynamics

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Video 3.4

Ideal Gas Equation of State Redux

Monatomic Ideal Gas Heat Capacity

The molar heat capacity of a substance expresses the energy required to raise the temperature of 1 mole of that substance by 1 K.

Thus, multiplication of the molar heat capacity by a measured temperature rise will provide the amount of energy that *was supplied* to the system to induce that temperature increase.

Monatomic Ideal Gas Heat Capacity

The change in energy associated with a change in temperature (the molar heat capacity) can be expressed as a derivative; in particular, at constant volume,

$$\overline{C}_V = \left(\frac{\partial \overline{U}}{\partial T}\right)_V$$

From our prior work, however, we have

$$\left(\frac{\partial \overline{U}}{\partial T}\right)_V = \left(\frac{\partial \left\langle \overline{E} \right\rangle}{\partial T}\right)_V = \left(\frac{\partial \left(\frac{3}{2} RT\right)}{\partial T}\right)_V = \frac{3}{2} R$$

Statistical thermodynamics can be used to understand "where the energy goes" when a system is heated (and why the capacity to store energy is different for different substances).

Further Manipulation of Q

$$Q(N,V,\beta) = \sum_j e^{-\beta E_j(N,V)}$$

More differential calculus:

$$\frac{\partial \ln Q}{\partial Q} = \frac{1}{Q} \qquad \left(\frac{\partial Q}{\partial V}\right)_{N,\beta} = -\beta \sum_j \left(\frac{\partial E_j(N,V)}{\partial V}\right) e^{-\beta E_j(N,V)}$$

So,

$$\left(\frac{\partial \ln Q}{\partial V}\right)_{N,\beta} = -\frac{\beta}{Q} \sum_j \left(\frac{\partial E_j(N,V)}{\partial V}\right) e^{-\beta E_j(N,V)} = \beta \sum_j \left(-\frac{\partial E_j(N,V)}{\partial V}\right) p_j(N,V,\beta)$$

or:

$$\sum_j \left(-\frac{\partial E_j(N,V)}{\partial V}\right) p_j(N,V,\beta) = k_B T \left(\frac{\partial \ln Q}{\partial V}\right)_{N,\beta}$$

Pressure As an Ensemble Average

$$\sum_j \left(-\frac{\partial E_j}{\partial V}\right) p_j(N,V,\beta) = k_B T\left(\frac{\partial \ln Q}{\partial V}\right)_{N,\beta}$$

Later, we will prove: $$P = -\left(\frac{\partial E}{\partial V}\right)_N$$

If pressure is like energy, i.e., an average over weighted ensembles, then,

$$\boxed{\langle P \rangle} = \sum_j P_j(N,V)\, p_j(N,V,\beta)$$

$$= \sum_j \left(-\frac{\partial E_j}{\partial V}\right)_N p_j(N,V,\beta) = \boxed{k_B T\left(\frac{\partial \ln Q}{\partial V}\right)_{N,\beta}}$$

Pressure of a Monatomic Ideal Gas

$$\langle P \rangle = k_{\mathrm{B}} T \left(\frac{\partial \ln Q}{\partial V} \right)_{N,\beta} \qquad Q(N,V,\beta) = \frac{\left[q(V,\beta) \right]^N}{N!} \qquad q(V,\beta) = \left(\frac{2\pi m}{h^2 \beta} \right)^{3/2} V$$

Again, $\ln Q = N \ln q - \ln N!$

$$= \frac{3}{2} N \left(\ln 2\pi m - \ln h^2 - \ln \beta \right) + N \ln V - \ln N!$$

And, $$k_{\mathrm{B}} T \left(\frac{\partial \ln Q}{\partial V} \right)_{N,\beta} = k_{\mathrm{B}} T \frac{N}{V} = \langle P \rangle$$

observed

When $N = N_{\mathrm{A}}$, $$\frac{RT}{\overline{V}} = P$$

The Ideal Gas Equation of State!

The Big Picture, So far

- The partition function encompasses all possible states of an ensemble
- Thermodynamic functions can be computed from the partition function (the central one is internal energy)
- For "simple" partition functions, the relevant calculations are straightforward and give results that agree with, and rationalize, both classical thermodynamics and experiment
- We have yet to *derive* the ideal monatomic gas partition function, but the one presented is consistent with the ideal gas equation of state