

Dense Gases

The Configuration Integral and The Fundamental Relation

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Dense Gases

- Dense gases cannot be treated as though individual atoms/molecule do not interact.
- We will start by considering the most general form of the partition function.
- This will lead to an integral, called the Configuration Integral, that contains the interaction potential energy terms.

Canonical Partition Function

- The Canonical partition function is

$$Q = \sum_j e^{-\beta U_j}$$

- For a dense gas we can write

$$U_j = \sum_{i=1}^N (\varepsilon_i)_{\text{int}} + \sum_{i=1}^N \frac{|p_i|^2}{2m} + \phi(\vec{r}_1, \vec{r}_2, \dots)$$

Internal
Energy

Translational
Energy

Interparticle
Potential Energy

- Factoring out the internal energy

$$Q = \sum_j e^{-\beta U_j^{\text{int}}} \cdot \sum_j e^{-\beta (U_j^{\text{trans}} + \phi_j)}$$

- And noting since

$$U_j^{\text{int}} = \sum_{i=1}^N \epsilon_i^{\text{int}}$$

- We have

$$\sum_j e^{-\beta U_j^{\text{int}}} = \prod_i^N \underbrace{\sum_k e^{-\beta \epsilon_k^{\text{int}}}}_{q \text{ internal}}$$

- Thus

$$\sum_j e^{-\beta U_j^{\text{int}}} = q_{\text{int}}^N$$

- And

$$Q = q_{\text{int}}^N \cdot \sum_j e^{-\beta(U_j^{\text{trans}} + \phi_j)}$$

- Now, it pays to replace the sum with an integral (OK because translational energy states are closely spaced).

The Classical Form

- One can show

$$\sum_j e^{-\beta(U_j^{trans} + \phi_j)} = \frac{1}{N!h^{3N}} \int \cdots \int e^{-\beta H} d\vec{p}_1 d\vec{p}_2 \cdots d\vec{p}_N dr_1 dr_2 \cdots dr_N$$

- Where H is the classical Hamiltonian

$$H = \frac{1}{2m} \sum_{n=1}^N \left(p_{xn}^2 + p_{yn}^2 + p_{zn}^2 \right) + \phi(x_1, y_1, \dots, z_N)$$

Note: We can separate the integral into the product of two integrals, one over momentum, the other space.



Derivation

- McQuarie Chapter 10, Section 7
- Kirkwood, Phys. Rev. 44, 31 (1933); Phys. Rev. 45, 116 (1934).



Translational Energy

- The first term is just the translational energy

$$\left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}N}$$

- We define the second integral

$$Z_{\phi} = \int \cdots \int e^{-\phi/kT} dr_1 dr_2 \cdots dr_N$$

- As the “Configuration Integral” because it depends of the configuration, i.e. where all the atoms and molecules are located.



Canonical Partition Function

- The Canonical partition function thus becomes

$$Q = q_{\text{int}}^N \frac{1}{N!} \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}N} Z_{\phi}$$

This result is identical to that for an ideal gas, except for the presence of the configuration integral in place of the volume. If ϕ is zero, the integral is equal to the volume to the N power.

The Fundamental Relation

- The Canonical form of the Massieu function then becomes

$$\begin{aligned}\frac{S[1/T]}{k} &= -\frac{A}{kT} = \ln Q \\ &= N \left[\ln q_{\text{int}} - (\ln N - 1) + \frac{3}{2} \ln \left(\frac{2\pi mkT}{h^2} \right) \right] + \ln Z_{\phi}\end{aligned}$$

Evaluating Z_ϕ

- To analytically evaluate Z requires some simplifying assumptions. Typically:
 - The orientation of molecules is unimportant so that the force between any two molecules is a function of distance only. (Not true for highly non-symmetric molecules.)
 - The total potential energy is the sum of the pairwise potential energies between molecules. (This only strictly applies to not too dense gases.)

- Thus we can write

$$\phi(\vec{r}_1, \vec{r}_2, \dots) = \frac{1}{2} \sum_{i \neq j} \phi_{ij}(r_{ij}) = \sum_{1 \leq i < j \leq N} \phi_{ij}(r_{ij})$$

- Where

$$r_{ij} = \left| \vec{r}_i - \vec{r}_j \right|$$

- Introducing

$$f_{ij}(r_{ij}) = e^{-\phi_{ij}(r_{ij})} - 1$$

- We can write

$$e^{-\phi/kT} = \prod_{1 \leq i < j \leq N} e^{-\phi_{ij}(r_{ij})/kT} = \prod_{1 \leq i < j \leq N} (1 + f_{ij})$$

- If we assume the gas only weakly interacts, then $f_{ij} \ll 1$. If we drop all the higher order terms in the product, then

$$e^{-\phi/kT} \simeq 1 + \sum_{1 \leq i < j \leq N} f_{ij}$$

- Thus

$$Z_\phi \simeq \int \cdots \int \left(1 + \sum_{1 \leq i < j \leq N} f_{ij} \right) d\vec{r}_1 d\vec{r}_2 \cdots$$

- Integrating the first term

$$Z_\phi \simeq V^N + \int \cdots \int \sum_{1 \leq i < j \leq N} f_{ij} d\vec{r}_1 d\vec{r}_2 \cdots$$

- And since each f_{ij} depends only on r_{ij}

$$Z_\phi \simeq V^N + V^{N+1} 2\pi N^2 \int_0^\infty f(r) dr$$

Where we have assume all the f_{ij} are the same function.

Weakly Interacting Configuration Integral

- Thus, we can write Z in the form

$$Z_{\phi} \simeq V^N \left[1 - \frac{N^2 B(T)}{V} \right]$$

- $B(T)$ is called the 2nd Virial Coefficient

$$B(T) = -2\pi \int_0^{\infty} f(r) dr$$

Virial means force in Latin.

Generally

- More generally we can write

$$Z_{\phi} \simeq V^N \left[1 - \frac{N^2 B(T)}{V} + \cdots \right]$$

Higher order terms

