

Two Ways to derive Ideal Gas Law

Method 1. splitting the system [1][2][3]

Method 1 circumvents the abstract concept of phase space, deriving the ideal gas law from a more direct approach.

Basic Settings:

system: ideal gas, isolated from its environment.

properties: constant N (number of particles).

constant V (volume)

constant E (internal energy)

(in equilibrium, a microcanonical ensemble)

Derivation Process:

Suppose that the total number of microscopic states of the entire system is Ω , which is a function of N , E and V .

$$\Omega(N, E, V) \quad d\Omega = \frac{\partial \Omega}{\partial N} dN + \frac{\partial \Omega}{\partial E} dE + \frac{\partial \Omega}{\partial V} dV$$

Randomly split the system into 2 subsystems, namely, subsystem 1 and subsystem 2. The number of particles, the internal energy and the volume of these two subsystems are: N_1, N_2 ; E_1, E_2 ; V_1, V_2 .

Correspondingly, the number of microscopic states of these two subsystems are: $\Omega_1(N_1, E_1, V_1)$, $\Omega_2(N_2, E_2, V_2)$

Because of the conservation of the entire system, we have:

$$N = N_1 + N_2$$

$$E = E_1 + E_2$$

$$V = V_1 + V_2$$

as for Ω , Ω_1 , Ω_2 , since in the system of ideal gas, the position of each particle is completely independent from the position and momentum of other particles, we have:

$$\Omega \propto V^N \quad \Omega_1 \propto V^{N_1} \quad \Omega_2 \propto V^{N_2}$$

(There is no solid boundary between the two subsystems.

Therefore, all particles can move in the space of the entire system)

Obviously:

$$\Omega(N, E, V) = \Omega_1(N_1, E_1, V_1) \cdot \Omega_2(N_2, E_2, V_2)$$

Suppose that the two subsystems have energy exchange, yet without any exchange of particles or any change in volume.

$$\frac{dE_1}{dt} \neq 0 \quad \frac{dE_2}{dt} \neq 0 \quad \frac{dV_1}{dt} = 0 \quad \frac{dV_2}{dt} = 0 \quad \frac{dN_1}{dt} = 0 \quad \frac{dN_2}{dt} = 0.$$

Apparently, $\frac{dE_1}{dt} = -\frac{dE_2}{dt}$, $\frac{dE_1}{dE_2} = -1$ (total energy is conserved)

Due to the principle of equal a priori probabilities, in equilibrium, Ω should reach its maximum value:

$$\Omega(E) = \Omega_1(E_1) \cdot \Omega_2(E_2) = \Omega_1(E_1) \cdot \Omega_2(E - E_1)$$

$$\frac{\partial \Omega}{\partial E_1} = \Omega_2 \frac{\partial \Omega_1}{\partial E_1} + \Omega_1 \frac{\partial \Omega_2}{\partial E_2} \cdot \frac{\partial E_2}{\partial E_1} = 0 \quad (\Omega \text{ reach its extrema})$$

Since $\frac{\partial E_2}{\partial E_1} = -1$,

$$\Omega_2 \frac{\partial \Omega_1}{\partial E_1} = \Omega_1 \frac{\partial \Omega_2}{\partial E_2} \quad \frac{1}{\Omega_1} \frac{\partial \Omega_1}{\partial E_1} = \frac{1}{\Omega_2} \frac{\partial \Omega_2}{\partial E_2}$$

$$\boxed{\frac{\partial(\ln \Omega_1)}{\partial E_1} = \frac{\partial(\ln \Omega_2)}{\partial E_2}}$$

Therefore, when the entire system is in equilibrium,

arbitrarily dividing it into two subsystems and looking into them
can have the above-mentioned result.

Let's switch into a macroscopic (thermodynamic) perspective.
When the system is in equilibrium, all parts of it share the same temperature, T .

Consider a basic thermodynamic equation:

$$dE = TdS - pdV \quad (\text{reversible process, no non-volume work})$$

$$\left(\frac{\partial S}{\partial E}\right)_V = \frac{1}{T} \quad (V \text{ is constant})$$

Therefore, when the entire ideal gas system is in equilibrium, the two subsystem must share the same temperature,

namely: $T_1 = T_2 \quad \frac{1}{T_1} = \frac{1}{T_2}$ (T_1, T_2 refer to the temperature of subsystem 1 and subsystem 2)

$$\left(\frac{\partial S_1}{\partial E_1}\right)_{V_1, N_1} = \left(\frac{\partial S_2}{\partial E_2}\right)_{V_2, N_2}$$

$$\frac{1}{T_i} = \left(\frac{\partial S_i}{\partial E_i}\right)_{V_i, N_i} \propto \frac{\partial(\ln \Omega_i)}{\partial E_i} \quad (i=1, 2)$$

$$\text{Let } \alpha = \frac{\partial(\ln \Omega_i)}{\partial E_i} \quad (i=1, 2)$$

For dimensionalization purpose, define k_B as a constant whose unit is energy \cdot (temperature) $^{-1}$, namely, $J \cdot K^{-1} (SI)$.

We have:

$$\left(\frac{\partial S_i}{\partial E_i}\right)_{V_i, N_i} = k_B \frac{\partial(\ln \Omega_i)}{\partial E_i} \quad (i=1, 2)$$

Integrate it with respect to E , we have:

$$\boxed{S = k_B \ln \Omega}, \text{ and } \alpha = \frac{1}{k_B T}$$

By supposing that the two subsystems only have energy exchange, we derive this:

$$\frac{\partial (\ln \Omega_i)}{\partial E_i} = \alpha = \frac{1}{k_B T} \quad (i=1, 2)$$

Similarly, we can define parameters β and γ as:

$$\frac{\partial (\ln \Omega_i)}{\partial N_i} = \beta, \quad \frac{\partial (\ln \Omega_i)}{\partial V_i} = \gamma \quad (i=1, 2)$$

$$\text{With } d\Omega = \frac{\partial \Omega}{\partial N} dN + \frac{\partial \Omega}{\partial E} dE + \frac{\partial \Omega}{\partial V} dV.$$

$$d(\ln \Omega) = \frac{\partial (\ln \Omega)}{\partial N} dN + \frac{\partial (\ln \Omega)}{\partial E} dE + \frac{\partial (\ln \Omega)}{\partial V} dV.$$

$$\text{So: } d(\ln \Omega) = \alpha dE + \beta dN + \gamma dV$$

Refer to thermodynamic equation in open systems:

$$dE = TdS - PdV + NdN \quad (\text{reversible process, no non-volume work})$$

(where $\mu = \left(\frac{\partial E}{\partial N}\right)_{S,V}$, chemical potential)

$$\boxed{dS = \frac{1}{T} dE + \frac{P}{T} dV - \frac{\mu}{T} dN}$$

Applying this to the ideal gas system where E and N remain constant,

$$dS = \frac{P}{T} dV \quad k_B d(\ln \Omega) = \frac{P}{T} dV$$

$$\frac{P}{k_B T} = \frac{d(\ln \Omega)}{dV} = \frac{d(\ln V^N)}{dV} = \frac{Nd \ln V}{dV} = \frac{N}{V}$$

($\Omega \propto V^N$, let the scale factor be 1)

Therefore, the conclusion is reached.

$$\boxed{PV = Nk_B T = \frac{N}{N_A} (N_A k_B) T = nRT}$$

(n : amount of substance, mol; N_A : Avogadro's Constant)

Method 2. phase space and ensemble theory [4][5][6]

Method 2 employs ensemble theory to derive ideal gas law. The very first step is to find partition function. Then, we can use partition function to derive a series of thermodynamic properties, which ultimately lead to ideal gas law.

Basic Settings: (classical mechanics)

system: ideal gas, connected to a heat bath.

properties: constant N (number of particles)

constant V (volume)

constant T (temperature)

(in equilibrium, a canonical ensemble)

Derivation Process:

First and foremost, the Hamiltonian of the system is:

$$\mathcal{H} = \sum_{i=1}^{3N} \frac{p_i^2}{2m} \quad (\text{ideal gas, the interaction between particles is negligible})$$

m : the mass of each particle

(Note: Ignoring the interaction between particles is completely for the sake of calculation convenience.

No multi-particle system can reach thermal equilibrium without the interaction between particles.)

Therefore, the partition function is:

$$Z = \frac{1}{N! h^{3N}} \int_{\Omega} e^{\left(\beta \sum_{i=1}^{3N} \frac{p_i^2}{2m}\right)} d^N p d^N q \quad \beta = \frac{1}{k_B T}$$

Ω is the part of phase space the microscopic states of this system occupy.

Since p and q are independent variables, the integral can be separated:

$$Z = \frac{1}{N! h^{3N}} \int_{\Omega} dq^{3N} \int_{\Omega} e^{\left(\beta \sum_{i=1}^{3N} \frac{p_i^2}{2m}\right)} dp^3 = \frac{1}{N!} \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3N}{2}} V^N$$

(explanation: $\int_{\Omega} dq^{3N} = V^N$, $\int_{\Omega} e^{\left(\beta \sum_{i=1}^{3N} \frac{p_i^2}{2m}\right)} dp^3 = (2\pi m k_B T)^{\frac{3N}{2}}$)

The partition function is the very key to solve this problem. After obtaining it, let's look into the process where we use Z to get a series of thermodynamic properties.

For the simplicity of expression, " \sum " is used instead of integrals.

$$Z = \sum_i e^{\beta \epsilon_i}, \quad E = \frac{1}{Z} \sum_i e^{\beta \epsilon_i} \cdot \epsilon_i, \quad i \text{ represents all microscopic states.}$$

$$\epsilon_i e^{\beta \epsilon_i} = \frac{\partial(e^{\beta \epsilon_i})}{\partial \beta}, \quad \text{after finding this,}$$

$$E = \frac{1}{Z} \sum_i \frac{\partial(e^{\beta \epsilon_i})}{\partial \beta} = \frac{1}{Z} \frac{\partial \sum_i e^{\beta \epsilon_i}}{\partial \beta} = \frac{1}{Z} \frac{\partial Z}{\partial \beta} = \frac{\partial(\ln Z)}{\partial \beta}$$

Recall: $dE = TdS - PdV$ (reversible process, no non-volume work, the number of particles is conserved)

$$\left(\frac{\partial E}{\partial V} \right)_{S, N} = -P \quad (\text{pressure})$$

$$P = -\frac{1}{Z} \sum_i \frac{\partial \epsilon_i}{\partial V} e^{\beta \epsilon_i}$$

$$\frac{\partial(e^{\beta \epsilon_i})}{\partial V} = \frac{\partial(e^{\beta \epsilon_i})}{\partial \beta} \cdot \underbrace{\frac{\partial \beta}{\partial V}}_0 + \frac{\partial(e^{\beta \epsilon_i})}{\partial \epsilon_i} \cdot \frac{\partial \epsilon_i}{\partial V} = \beta e^{\beta \epsilon_i} \frac{\partial \epsilon_i}{\partial V}$$

$$P = \frac{-1}{Z} \sum_i \frac{1}{\beta} \cdot \frac{\partial(e^{\beta \epsilon_i})}{\partial V} = \frac{-1}{Z\beta} \frac{\partial(\sum_i e^{\beta \epsilon_i})}{\partial V} = \frac{-1}{\beta} \cdot \frac{1}{Z} \frac{\partial Z}{\partial V}$$

$$P = \frac{-1}{\beta} \frac{\partial(\ln Z)}{\partial V}$$

$$\begin{aligned} \beta(dE + PdV) &= \beta \left(d\left(\frac{\partial(\ln Z)}{\partial \beta}\right) - \frac{1}{\beta} \frac{\partial(\ln Z)}{\partial V} dV \right) \\ &= \beta d\left(\frac{\partial(\ln Z)}{\partial \beta}\right) - \frac{\partial(\ln Z)}{\partial V} dV. \end{aligned}$$

When other variables remain constant,

$$d(\ln Z) = \frac{\partial(\ln Z)}{\partial \beta} d\beta + \frac{\partial(\ln Z)}{\partial V} dV$$

$$d\left(\beta \frac{\partial(\ln Z)}{\partial \beta}\right) = \frac{\partial(\ln Z)}{\partial \beta} d\beta + \beta \cdot d\left(\frac{\partial(\ln Z)}{\partial \beta}\right)$$

$$\beta(dE + PdV) = d\left(\beta \frac{\partial(\ln Z)}{\partial \beta} - \ln Z\right)$$

Recall: $dE = Tds - PdV$, $dS = \frac{dE + PdV}{T}$

$$\beta = \frac{-1}{k_B T} \quad \frac{-1}{k_B T} (dE + PdV) = \frac{-1}{k_B} dS = d\left(\beta \frac{\partial(\ln Z)}{\partial \beta} - \ln Z\right)$$

$$\text{so, } S = k_B \left(\ln Z - \beta \frac{\partial(\ln Z)}{\partial \beta} \right)$$

$$-TS = -k_B T \ln Z + \frac{\partial(\ln Z)}{\partial \beta} = -k_B T \ln Z + (-E)$$

$$E - TS = F = -k_B T \ln Z. \quad F \text{ is Helmholtz Free Energy.}$$

$$F = -k_B T \ln Z = \frac{\ln Z}{\beta}.$$

Recall:

$$Z = \frac{1}{N!} \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3}{2}N} \cdot V^N.$$

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

$$P = \frac{-1}{\beta} \frac{\partial(\ln Z)}{\partial V} = k_B T \frac{\partial(\ln Z)}{\partial V} = k_B T \cdot N \cdot \frac{1}{V}$$

(The first two terms of $\ln Z$ is independent to V)

$$PV = N k_B T. \text{ --- ideal gas law}$$

Or, we can take another approach:

$$dF = -SdT - PdV \quad P = -\left(\frac{\partial F}{\partial V}\right)_{T, N}$$

$$F = \frac{\ln Z}{\beta} = -\frac{1}{\beta} \ln N! + \frac{3N}{2\beta} \ln \left(\frac{2\pi m k_B T}{h^2} \right) + \frac{N}{\beta} \ln V$$

$$\frac{\partial F}{\partial V} = \frac{N}{\beta} \cdot \frac{1}{V} \quad P = -\frac{N}{\beta} \cdot \frac{1}{V} = N k_B T \frac{1}{V}$$

$$PV = N k_B T \text{ --- ideal gas law.}$$

Reference Materials:

[1][4] Thermodynamics and Statistical Physics (5th Edition).
Zhicheng Wang, Higher Education Press, page 257-265

[2] Statistical Physics (5th Edition). Lev. Davidovich. Landau.
Higher Education Press

[3][6]. Thermodynamics of Materials. - Lecture Notes.

Prof. Mingyi Zheng, Dr. Xiaoguang Qiao, Harbin Institute of Technology

[5]. Computer Simulation of Materials - Technical Notes.

Jaime Marian. University of California Los Angeles