

You've learned about partition functions and some uses, now we'll explore them in more depth using ideal monatomic, diatomic and polyatomic gases!

Before we start, remember:

$$Q(N, V, T) = \frac{q(V, T)^N}{N!}$$

What are N, V, and T?

We now apply this to the ideal gas where:

1. The molecules are independent.
2. The number of states greatly exceeds the number of molecules (assumption of low pressure).



Where can we put energy into a monatomic gas?

$$\mathcal{E}_{atomic} = \mathcal{E}_{trans} + \mathcal{E}_{elec}$$

Only into translational and electronic modes! 😊

The total partition function is the product of the partition functions from each degree of freedom:

$$q(V, T) = q_{trans}(V, T) q_{elec}(V, T)$$

↑ ↑ ↑
Total atomic Translational atomic Electronic atomic
partition function partition function partition function

We'll consider both separately...

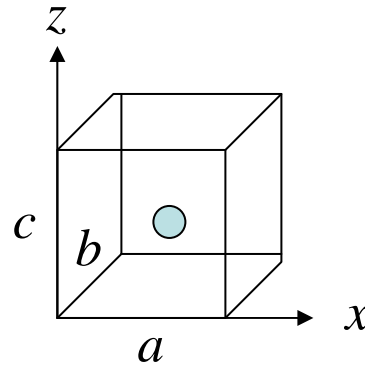


Translations of Ideal Gas: $q_{trans}(V, T)$

PFIG-3

General form of partition function: $q_{trans} = \sum_{states} e^{-\beta \epsilon_{trans}}$

Recall from QM slides...



$$\epsilon_{trans} = \frac{h^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2) \quad n_x, n_y, n_z = 1, 2, \dots, \infty$$

So what is q_{trans} ?



Let's simplify q_{trans} ...

$$q_{trans} = \sum_{n_x, n_y, n_z=1}^{\infty} e^{-\beta \varepsilon_{n_x, n_y, n_z}} = \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty} \exp \left[-\frac{\beta h^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2) \right]$$

Recall: $e^{a+b+c} = e^a e^b e^c$

$$q_{trans} = \sum_{n_x=1}^{\infty} \exp \left(-\frac{\beta h^2 n_x^2}{8ma^2} \right) \sum_{n_y=1}^{\infty} \exp \left(-\frac{\beta h^2 n_y^2}{8ma^2} \right) \sum_{n_z=1}^{\infty} \exp \left(-\frac{\beta h^2 n_z^2}{8ma^2} \right)$$

All three sums are the same because n_x, n_y, n_z have same form!

We can simplify expression to:



q_{trans} is nearly continuous

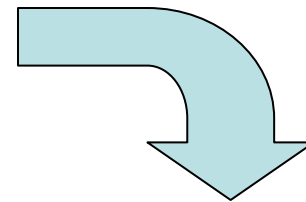
We'd like to solve this expression, but there is no analytical solution for the sum!

$$q_{trans}(V, T) = \left[\sum_{n=1}^{\infty} \exp\left(-\frac{\beta h^2 n^2}{8ma^2}\right) \right]^3$$

No fears... there is something we can do!

Since translational energy levels are spaced very close together, the sum is nearly continuous function and we can approximate the sum as an integral... which we can solve!

$$q_{trans}(V, T) = \left[\int_0^{\infty} dn \exp\left(-\frac{\beta h^2 n^2}{8ma^2}\right) \right]^3$$



Work the integral

Note limit change ...
only way to solve but adds very little error to result

$$q_{trans}(V, T) = \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} V$$

a^3



Translational energy, $\langle \mathcal{E}_{trans} \rangle$

PFIG-6

With q we can calculate **any** thermodynamic quantity!!

In Ch 17 (BZ notes) we showed this for the average energy ...

$$\langle \mathcal{E}_{trans} \rangle = k_B T^2 \left(\frac{\partial \ln q_{trans}}{\partial T} \right)_V \quad \text{here... } q_{trans}(V, T) = \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} V$$

$$\langle \mathcal{E}_{trans} \rangle = k_B T^2 \left(\frac{\partial}{\partial T} \ln \left[T^{3/2} \left(\frac{2\pi m k_B}{h^2} \right)^{3/2} V \right] \right)_V$$

As we found in BZ notes!
(Recall: this is *per atom*.)



Next consider the electronic contribution to q : q_{elec}

Again, start from the general form of q , but this time sum over levels rather than states:

$$q_{elec} = \sum_{\text{levels}} g_{ei} e^{-\beta \epsilon_{ei}}$$

↑
↑
 Degeneracy of level i Energy of level i

We choose to set the lowest electronic energy state at zero, such that all higher energy states are *relative* to the ground state.

$$\epsilon_1 = 0$$

For monatomic gases!



Can we simplify q_{elec} ?

$$q_{elec}(T) = g_{e1} + g_{e2}e^{-\beta\epsilon_{e2}} + g_{e3}e^{-\beta\epsilon_{e3}} + \dots$$

terms are getting small rapidly...

The electronic energy levels are spaced far apart, and therefore we *typically only need to consider the first term or two in the series...*

General rule of thumb:
At 300 K, you only need to keep terms where $\epsilon_{ej} < 10^3 \text{ cm}^{-1}$ ($e^{-\beta\epsilon} > 0.008$)

TABLE 4.1 (18.1)
Some atomic energy levels.^a

Atom	Electron configuration	Degeneracy $g_e = 2J + 1$	Energy/cm ⁻¹
H	1s	2	0.
	2p	2	82 258.907
	2s	2	82 258.942
	2p	4	82 259.272
He	1s ²	1	0.
	1s2p	3	159 850.318
		1	166 271.70
Li	1s ² 2s	2	0.
	1s ² 2p	2	14 903.66
		4	14 904.00
	1s ² 3s	2	27 206.12
F	1s ² 2s ² 2p ⁵	4	0.
		2	404.0
	1s ² 2s ² 2p ⁴ 3s	6	102 406.50
		4	102 681.24
		2	102 841.20
		4	104 731.86
		2	105 057.10

^aFrom C.E. Moore, "Atomic Energy Levels" *Natl. Bur. Std. Circ. 1 467*, U.S. Government Printing Office, Washington D.C., 1949



$$q_{elec}(T) = g_{e1} + g_{e2}e^{-\beta\epsilon_{e2}} + g_{e3}e^{-\beta\epsilon_{e3}} + \dots$$

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General trends,

1. Noble gas atoms:

$$\epsilon_{e2} = 10^5 \text{ cm}^{-1} \text{ (at 300K, keep ___ term(s))}$$

2. Alkali metal gas atoms:

$$\epsilon_{e2} = 10^4 \text{ cm}^{-1} \text{ (at 300K, keep ___ term(s))}$$

3. Halogen gas atoms:

$$\epsilon_{e2} = 10^2 \text{ cm}^{-1} \text{ (at 300K, keep ___ term(s))}$$



In general it is sufficient to keep only the first two terms for q_{elec}

$$q_{elec}(T) \approx g_{e1} + g_{e2} e^{-\beta \varepsilon_{e2}}$$

However, you should always keep in mind that for very high temperatures (like on the sun) or smaller values of ε_{ej} (like in F) that additional terms may contribute.

If you find that the second term is of reasonable magnitude (>1% of first term), then you must check to see that the third term can be neglected.



For a *monatomic ideal gas* we have:

$$Q(N, V, T) = \frac{(q_{trans}(V, T)q_{elec}(V, T))^N}{N!}$$

with

$$q_{trans}(V, T) = \left(\frac{2\pi mk_B T}{h^2} \right)^{3/2} V$$

$$q_{elec}(T) \approx g_{e1} + g_{e2} e^{-\beta \epsilon_{e2}}$$



Finding thermodynamic parameters... U PFIG-12

We can now calculate the average energy, $U = \langle E \rangle$

$$U = \langle E \rangle = k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_V = N k_B T^2 \left(\frac{\partial \ln q}{\partial T} \right)_V = N k_B T^2 \left(\frac{\partial \ln q_{trans} q_{elec}}{\partial T} \right)_V$$

Plug in q_{trans} and q_{elec} ...

$$U = N k_B T^2 \left(\frac{\partial}{\partial T} \ln \left(\left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} V (g_{e1} + g_{e2} e^{-\beta \epsilon_{e2}}) \right) \right)_V$$

$$U = \frac{3}{2} N k_B T + \frac{N g_{e2} \epsilon_{e2} e^{-\beta \epsilon_{e2}}}{q_{elec}}$$

Electronic contribution typically small (i.e., negligible)

So ...

$$U \approx$$

or

$$\bar{U} =$$

molar energy



Molar heat capacity for a *monatomic ideal gas*:

$$\bar{C}_V = \left(\frac{d\bar{U}}{dT} \right)_{N,V}$$

$$\bar{C}_V = \left(\frac{d\left(\frac{3}{2}RT\right)}{dT} \right)_{N,V} = \frac{3}{2}R$$

Could also find heat capacity: $C_V = \frac{3}{2}Nk_B$



$$P = k_B T \left(\frac{\partial \ln Q}{\partial V} \right)_{N,T} = N k_B T \left(\frac{\partial \ln q}{\partial V} \right)_T = N k_B T \left(\frac{\partial \ln(q_{trans} q_{elec})}{\partial V} \right)_T$$

Plug in q_{trans} and q_{elec} ...

$$P = N k_B T \left(\frac{\partial}{\partial V} \ln \left(\left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} V (g_{e1} + g_{e2} e^{-\beta \epsilon_{e2}}) \right) \right)_T$$

Only function of V

So... $P =$ or $\bar{P} =$

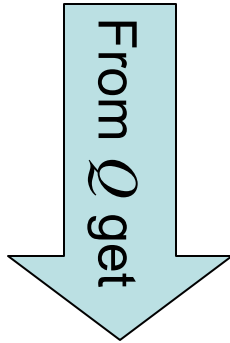
Look familiar??

molar pressure



Partition Function:

$$Q(N, V, T) = \frac{q(V, T)^N}{N!}$$



$$q_{trans}(V, T) = \left(\frac{2\pi mk_B T}{h^2} \right)^{3/2} V \quad q_{elec}(T) \approx g_{e1} + g_{e2} e^{-\beta \epsilon_{e2}}$$

Energy

$$U \approx \frac{3}{2} N k_B T \quad \bar{U} = \frac{3}{2} RT \quad (\text{molar})$$

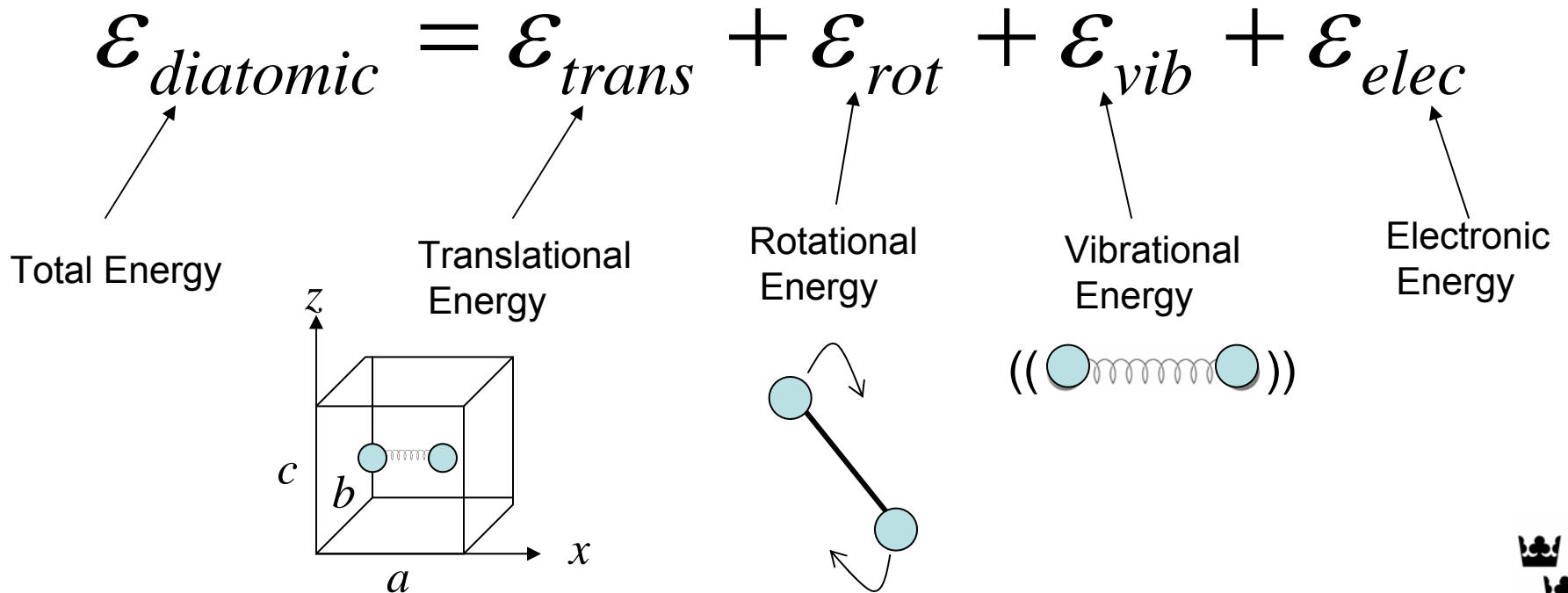
Heat Capacity

Pressure



In addition to trans. and elec. degrees of freedom, we need to consider:

1. Rotations
2. Vibrations



Q. What will the form of the molecular diatomic partition function be given:

$$\mathcal{E}_{diatomic} = \mathcal{E}_{trans} + \mathcal{E}_{rot} + \mathcal{E}_{vib} + \mathcal{E}_{elec} ?$$

Ans.

Q. How will this give us the diatomic partition function?

Ans.

Now all we need to know is the form of q_{trans} , q_{rot} , q_{elec} , and q_{vib} .

Start with q_{trans} : This is the same as in the monatomic case but with $m = m_1 + m_2$!



We define the zero of the electronic energy to be separated atoms at rest in their ground electronic energy states.

With this definition,

$$\varepsilon_{e_1} = -D_e$$

And...

Note the slight difference in q_{elec} between monatomic and diatomic gases!

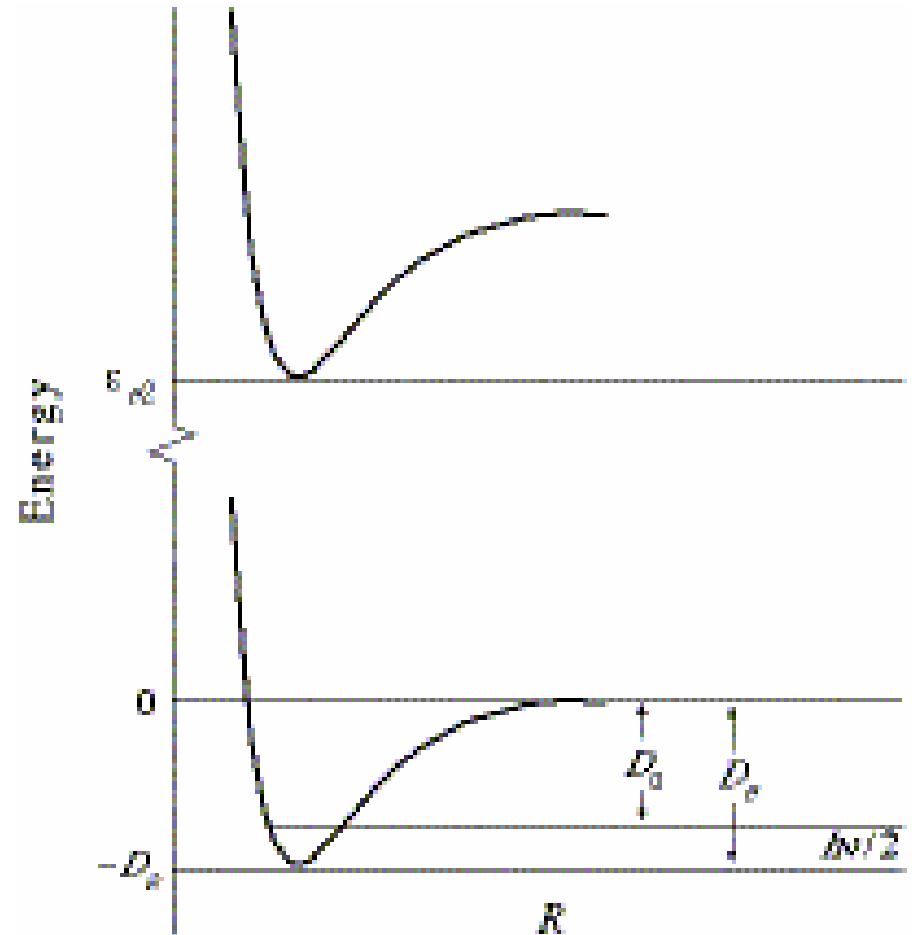


Figure 18.2

