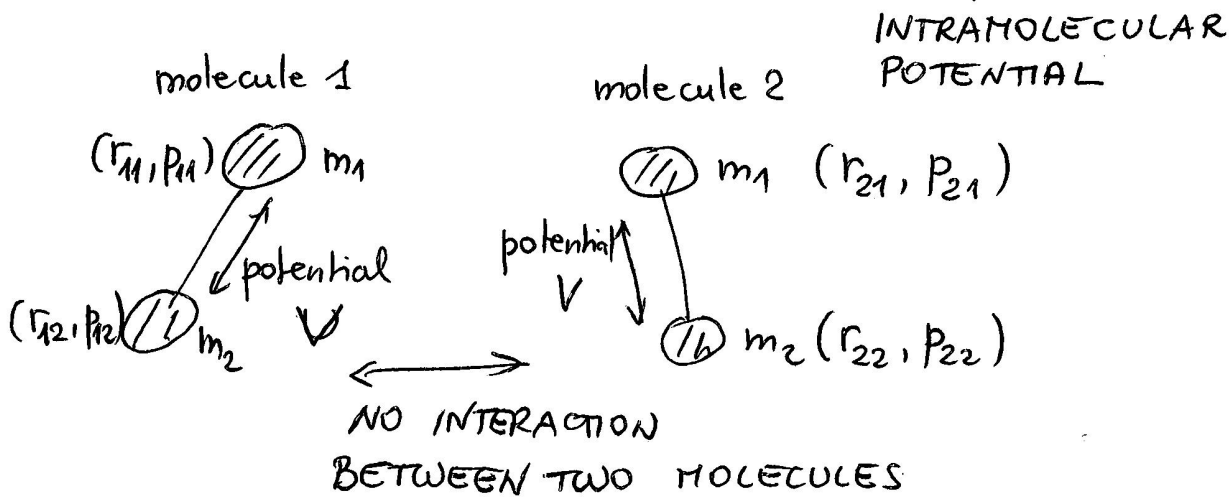


DIATOMIC GAS: COMPUTATION OF THE ENERGY ①

Ideal gas of diatomic molecules

$$H = \sum_{i=1}^N \left(\frac{p_{i1}^2}{2m_1} + \frac{p_{i2}^2}{2m_2} \right) + \sum_{i=1}^N V(\bar{r}_{i1} - \bar{r}_{i2})$$



NOTE: index i runs over N molecules
There are 2 atoms for molecule

$$Q = \int \frac{d^{3N} p_1 d^{3N} p_2 d^{3N} q_1 d^{3N} q_2}{h^{6N} N!} e^{-\beta H}$$

We work in the CANONICAL ensemble

$$= \frac{1}{h^{6N} N!} \int d^{3N} p_1 e^{-\beta \sum \frac{p_{i1}^2}{2m_1}} \cdot \int d^{3N} p_2 e^{-\beta \sum \frac{p_{i2}^2}{2m_2}} \times$$

$$\int dq_{11} dq_{12} e^{-\beta V(q_{11} - q_{12})} \cdot \int dq_{21} dq_{22} e^{-\beta V(q_{21} - q_{22})}$$

$$\times \dots \int dq_{N1} dq_{N2} e^{-\beta V(q_{N1} - q_{N2})}$$

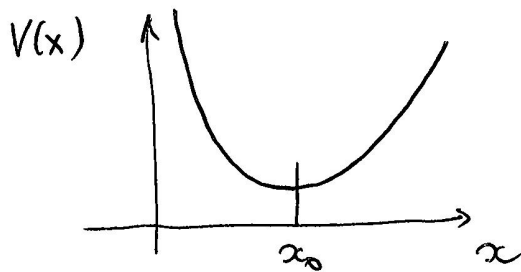
THE INTRAMOLECULAR POTENTIAL

②

The molecule is modelled as a pair of point particles (atoms). The potential $V(x)$ is the bonding potential: it keeps the two atoms together.

It is obviously an EFFECTIVE potential.

The typical shape is



The potential diverges for $x \rightarrow 0$, due to the hard-core repulsion between the two atoms.

For large x it is usually assumed that $V(x) = \infty$ (the molecule never breaks)

$x = x_0$ corresponds to the typical bond length.

In our statistical mechanics approach, we MUST assume $V(x) = \infty$ for $x \rightarrow \infty$, i.e. the stability of the molecules. This is fine for temperatures T

$$x_0 \text{ that } kT \ll E_I$$

↑
thermal energy

↖ energy needed to break the molecular bond

Integrals over momenta: as in the monoatomic case ^③
 Integrals over coordinates: all equal.

$$Q = \frac{1}{N!} \frac{1}{(\lambda_1 \lambda_2)^{3N}} \left[\int d^3q_1 d^3q_2 e^{-\beta V(q_1 - q_2)} \right]^N$$

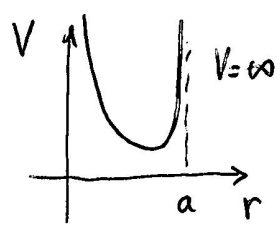
$$\lambda_1 = \frac{h}{(2m_1 \pi kT)^{1/2}} \quad \lambda_2 = \frac{h}{(2m_2 \pi kT)^{1/2}} \quad \text{DeBroglie lengthscales of the two atoms}$$

Now we discuss the integral in q .

To simplify the discussion, we make the assumptions

(a) the system is ONE-dimensional so that
 $0 \leq q_1 \leq L$, $0 \leq q_2 \leq L$ (L plays the role of)
 volume

(b) $V(q_1 - q_2)$, which is only a function of



$|q_1 - q_2|$ is such that

$$V(|q_1 - q_2|) = \infty \text{ if } |q_1 - q_2| > a$$

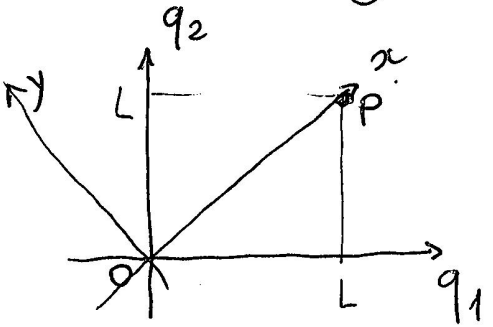
It is important to realize that a is microscopic ($a \sim$ a few nanometers) and L is macroscopic ($L \sim$ cm)

To perform the calculation, we change variables

$$X = \frac{1}{2} (q_1 + q_2)$$

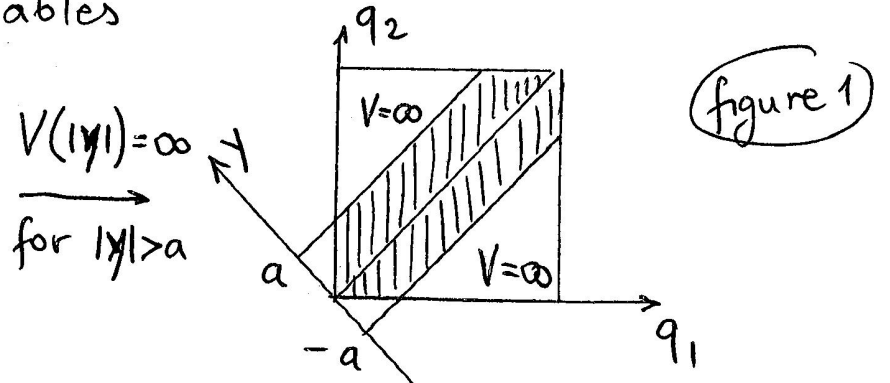
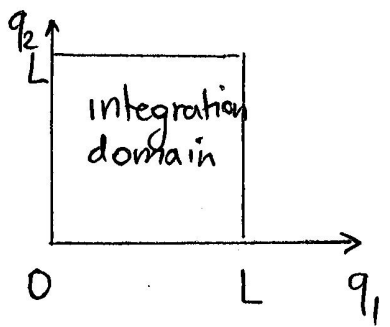
$$y = q_2 - q_1 \quad |\text{jacobian}| = 1$$

The change of variables



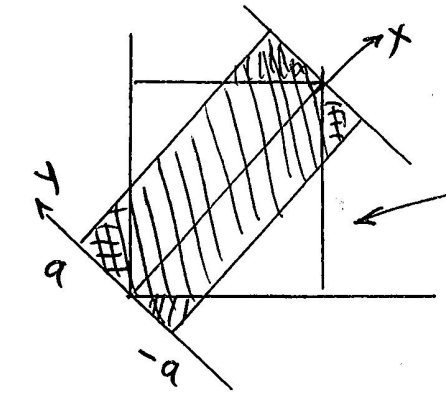
Note: point P has $x = \frac{L+L}{2} = L$
 the "length" of the diagonal
 in the x variable is L.

Now, we should discuss the integration domain in the new variables



If $V = \infty \rightarrow e^{-\beta V} = 0$.
 We should integrate only over the shaded area

Now, we make an approximation



We integrate over the shaded area

Four small triangles added (the four corners)

Now we verify that the total integral is of order $L a$ while the integrals over the small triangles are of order a^2 . Therefore, they are negligible

figure 2

Indeed using the variable (x, y)

total shaded area

$$\int dq_1 dq_2 e^{-\beta V(q_1, -q_2)} = \int_0^L dx \int_{-a}^a dy e^{-\beta V(y)}$$

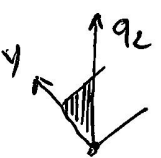
$$= L \int_{-a}^a dy e^{-\beta V(y)} \sim La$$

↑
extensive

Small triangle

$$\int dq_1 dq_2 e^{-\beta V(q_1, -q_2)} = \int_0^a dy \int_0^y dx e^{-\beta V(y)} \sim a^2$$

↑
negligible



Therefore, we obtain

$$\int_0^L dq_1 \int_0^L dq_2 e^{-\beta V(q_1, -q_2)} = L \int_{-a}^a dy e^{-\beta V(y)} + O(1)$$

$$= L \int_{-\infty}^{+\infty} dy e^{-\beta V(y)} + O(1)$$

again we use $V(y) = \infty$ for $|y| \geq a$.

The general result [3 dim, no restriction on $V(x)$]

$$\int d^3 q_1 d^3 q_2 e^{-\beta V(q_1, -q_2)} = V \int_{\mathbb{R}^3} d^3 y e^{-\beta V(y)}$$

↑
volume

Putting everything together

$$Q = \frac{1}{N!} \left(\frac{I}{\lambda_1^3 \lambda_2^3} \right)^N V^N \quad I = \int_{\mathbb{R}^3} d\vec{r} e^{-\beta V(r)}$$

We can define $\frac{1}{\lambda_{\text{eff}}^3} = \frac{I}{\lambda_1^3 \lambda_2^3}$ so that

$$Q = \frac{1}{N!} \frac{V^N}{\lambda_{\text{eff}}^{3N}} \quad \left| \begin{array}{l} \text{This is the same result} \\ \text{we obtained for the monatomic} \\ \text{case. It is enough to} \\ \text{replace } \lambda \text{ with } \lambda_{\text{eff}}. \end{array} \right.$$

Implications: same equation of state
 same chemical potential ($\lambda \rightarrow \lambda_{\text{eff}}$)
 same free energy ($\lambda \rightarrow \lambda_{\text{eff}}$)

$$F(N, V, T) = NkT \left(\ln(\rho \lambda_{\text{eff}}^3) - NkT \right)$$

↑
of molecules (not atoms)

$$\rho = \frac{N}{V} \quad (\text{density of molecules})$$