

§ 6.1 Dilute Polyatomic Gases

Hamiltonian for each molecule

$$\mathcal{H}_1 = \sum_{i=1}^n \frac{\vec{p}_i^2}{2m} + V(\vec{q}_1, \dots, \vec{q}_n)$$

↳ Information about the molecular bonds

→ (assumed all atoms have the same mass)

(claim: however if the masses are different, the Hamiltonian can be brought into the form above by rescaling \vec{q}_i by $\sqrt{\frac{m_i}{m}}$ (and the momenta by $\sqrt{\frac{m}{m_i}}$)

Ignoring the interactions b/w the molecules, the partition f^* of a dilute gas is

$$Z(N) = \frac{Z_1^N}{N!} = \frac{1}{N!} \left\{ \int \prod_{i=1}^n \frac{d^3 \vec{p}_i d^3 \vec{q}_i}{h^3} \exp \left[-\beta \sum_{i=1}^n \frac{\vec{p}_i^2}{2m} - \beta V(\vec{q}_1, \dots, \vec{q}_n) \right] \right\}$$

→ The chemical bonds are quite strong

→ At typically accessible temperatures, the molecules have a well defined shape & only undergo small deformation.

This can be calculated as follows:

(a) Find equilibrium position $(\vec{q}_1^*, \dots, \vec{q}_n^*)$ by minimizing V .

(b) Let $\vec{q}_i = \vec{q}_i^* + \vec{u}_i$ be some deformed position. The energy contribution is calculated by doing a Taylor expansion.

$$V = V^* + \frac{1}{2} \sum_{i,j=1}^n \sum_{\alpha, \beta=1}^3 \frac{\delta^2 V}{\delta q_{i,\alpha} \delta q_{j,\beta}} u_i \cdot \alpha u_j \cdot \beta + O(u^3)$$

(i, j label atoms, α, β coordinate component)

→ (since the expansion is about a stable configuration, the first derivatives are zero)

→ Now since V^* is the minimum value of V , and since u_i are arbitrary, thus the matrix of second derivatives must be positive (have all positive eigenvalues)

(b) The normal modes are obtained by diagonalizing the $3n \times 3n$ matrix

$$\frac{\delta^2 V}{\delta q_{i,\alpha} \delta q_{j,\beta}}$$

→ The resulting $3n$ eigenvalues, $\{K_s\}$ indicate the stiffness of each mode.

→ Say the matrix is given by A .

I find its eigenvalues & eigenvectors using these, I get a basis of the eigenvectors viz. $BX = Y$

where Y is the new basis

s.t.

BAB^{-1} is diagonal.

(Well if you have the old basis as $\begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}, \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}, \dots$ & you know the eigenvectors in this basis as

$$\begin{pmatrix} b_{11} \\ b_{12} \\ \vdots \end{pmatrix}, \begin{pmatrix} b_{21} \\ b_{22} \\ \vdots \end{pmatrix}, \dots$$

then

$$\begin{pmatrix} b_{11} & b_{12} & \dots \\ b_{21} & b_{22} & \dots \\ \vdots & \vdots & \ddots \end{pmatrix} \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} b_{11} \\ b_{12} \\ \vdots \end{pmatrix}$$

Let w on. $B' = \begin{pmatrix} b_{11} & b_{12} & \dots \\ b_{21} & b_{22} & \dots \\ \vdots & \vdots & \ddots \end{pmatrix}$ then $B'^{-1} = B$: clearly in the new basis what is $\begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}$ should be an eigenvector in the

But we're to show that this change of basis matrix is unitary. -2-

(This is done in (A)C.)

Anyway, now if I write my matrix as $A_{ij} = \frac{\partial^2 V}{\partial q_i \partial q_j}$

and $x_{ia} = u_{i,a}$, then

my sum is $x^T A x$

I can do a basis transformation to make A diagonal
viz $A' = B A B^{-1}$

& now my x transforms to $Bx = y$

so then

$$y^T (A') y$$

is what I get.

Now since A' is diagonal, I have

$$= \sum_i \lambda_i y_i^2 = \sum_s k_s \tilde{u}_s^2$$

where λ_i is the i^{th} eigenvalue.

Now (IDK how) I can also write my $\tilde{p}_s = m \tilde{u}_s$
giving $\{\tilde{u}_i\} \rightarrow \{\tilde{u}_s\}$

and since I've forced the transformation to be unitary,
 $\sum_i \tilde{p}_i^2 = \sum_s \tilde{p}_s^2$, thus the quadratic part of
the Hamiltonian is

$$H_1 = V^* + \sum_{s=1}^{3n} \left[\frac{1}{2m} \tilde{p}_s^2 + \frac{k_s}{2} \tilde{u}_s^2 \right]$$

Since each DOF contributes $\frac{k_B T}{2}$ to the energy,

$$\langle H_1 \rangle = V^* + \frac{3n}{2} k_B T + \frac{3m}{2} k_B T$$

m : # modes with non-0 stiffness.

Some symmetries of the potential form, result in zero eigenvalues

(a) Translation : since $V(\vec{r}_1 + \vec{c}, \dots, \vec{r}_n + \vec{c})$

$= V(\vec{r}_1, \dots, \vec{r}_n)$, as energy is stored in the COM coordinate $\vec{\delta} = \sum_{\alpha} \frac{\vec{r}_{\alpha}}{n}$
viz. $V(\vec{\delta}) = V(\vec{\delta} + \vec{c})$

(b) Rotation : Again, no energy stored for rotation.
Viz. $k_{\text{rot}} = 0$ for the corresponding stiffness.

$0 \leq \alpha \leq 3$ in general

but for rod shaped, $\alpha = 2$

& for single atom $\alpha = 0$

(for plane, $\alpha = 3$)

The remaining $m = 3n - 3 - \alpha$ eigenvectors of the matrix have non-zero stiffness & correspond to vibrational modes.

Thus energy per molecule is

$$\langle H \rangle = \frac{(6n - 3 - \alpha)}{2} k_B T$$

So Then

$$C_V = \frac{(6n - 3 - \alpha)}{2} k_B$$

$$\& C_P = C_V + k_B = \frac{(6n - 1 - \alpha)}{2} k_B$$



experiment agreement issues.

Quantize it

Vibrational modes:

A diatomic molecule has one vibrational mode with stiffness $k = m\omega^2$ (ω is the osc. freq.)

The classical partition Z^c is (for this mode i.e.)

$$Z_{\text{ib}}^c = \int \frac{dq dp}{h} \exp \left[-\beta \left(\frac{p^2}{2m} + \frac{m\omega^2 q^2}{2} \right) \right]$$

$$= \frac{1}{h} \sqrt{\left(\frac{2\pi m}{\beta}\right) \left(\frac{2\pi}{\beta m\omega^2}\right)} = \frac{2\pi}{h\beta\omega} = \frac{k_B T}{\hbar\omega}$$

$$\text{where } \tau = \frac{\hbar}{2\pi}$$

The corresponding energy stored in this mode

$$\langle H_{\text{ib}} \rangle = -\frac{\partial \ln Z}{\partial \beta} = \frac{\partial \ln (\beta \hbar\omega)}{\partial \beta} = \frac{1}{\beta} = k_B T$$

comes from $\frac{k_B T}{2}$ per kinetic & potential degrees of freedom.

In QM, we have (for a harmonic oscillator potential atleast)

$$H_{\text{ib}}^q = \hbar\omega \left(n + \frac{1}{2}\right)$$

with $n = 0, 1, 2, \dots$

Assumg that the prob of each discrete level is proportional to its Boltzmann weight

(Not justified yet), there's a normalization factor

$$Z_{\text{ib}}^q = \sum_{n=0}^{\infty} e^{-\beta \hbar\omega (n + \gamma_2)} = \frac{e^{-\beta \hbar\omega / 2}}{1 - e^{-\beta \hbar\omega}}$$

The high-temp limit

$$\lim_{\beta \rightarrow 0} Z_{vib}^g = \frac{1}{\beta \hbar \omega} = \frac{k_B T}{\hbar \omega}$$

which is the same as Z_{vib}^C (partly 'c' of h in the expression)

$$\begin{aligned} E_{vib}^g &= -\frac{\partial \ln Z}{\partial \beta} = \frac{\hbar \omega}{2} + \frac{\partial}{\partial \beta} \ln (1 - e^{-\beta \hbar \omega}) \\ &= \frac{\hbar \omega}{2} + \hbar \omega \frac{e^{-\beta \hbar \omega}}{1 - e^{-\beta \hbar \omega}} \end{aligned}$$

The resulting heat capacity is

$$C_{vib}^g = \frac{d E_{vib}^g}{dT} = k_B \left(\frac{\hbar \omega}{k_B T} \right)^2 \frac{e^{-\beta \hbar \omega}}{(1 - e^{-\beta \hbar \omega})^2}$$

see calculations

Rotational modes:

$$L = \frac{I}{2} (\dot{\theta}^2 + \sin^2\theta \dot{\phi}^2) \quad \leftarrow \text{Assumed for now.}$$

Specify the orientation of the molecule.

$$P_\theta = \frac{\partial L}{\partial \dot{\theta}} = I \dot{\theta}, \quad P_\phi = \frac{\partial L}{\partial \dot{\phi}} = I \sin^2\theta \dot{\phi}$$

The Hamiltonian for rotation is

$$\begin{aligned} H_{\text{rot}} &= \sum_\theta P_\theta \cdot \dot{\theta} - L = \frac{1}{2I} \left(P_\theta^2 + \frac{P_\phi^2}{\sin^2\theta} \right) = \frac{\vec{L}^2}{2I} \quad \text{angular momentum} \\ \boxed{L} &= I \dot{\theta}^2 + I \sin^2\theta \dot{\phi}^2 = \frac{-I \dot{\theta}^2}{2} - \frac{I \sin^2\theta \dot{\phi}^2}{2} \\ &= \frac{I \dot{\theta}^2}{2} + \frac{\sin^2\theta \dot{\phi}^2}{2} \\ &= \frac{I}{2} \left[\frac{P_\theta^2}{I^2} + \frac{P_\phi^2}{I^2 \sin^2\theta} \right] \\ \boxed{\square} \end{aligned}$$

From the classical partition function, we have

$$Z_{\text{rot}} = \frac{1}{h^2} \int_0^\pi d\theta \int_0^{2\pi} d\phi \int_{-\infty}^{\infty} dP_\theta dP_\phi e^{-\frac{\beta}{2I} \left(P_\theta^2 + \frac{P_\phi^2}{\sin^2\theta} \right)}$$

$$\text{verify } \rightarrow \quad = \left(\frac{2\pi I}{\beta} \right) \left(\frac{4\pi}{h^2} \right) = \frac{2I k_B T}{\hbar^2}$$

The energy stored is

$$\langle E_{\text{rot}} \rangle^c = -\frac{\partial \ln Z}{\partial \beta} = \frac{\partial}{\partial \beta} \ln \left(\frac{\beta \hbar^2}{2I} \right) = k_B T$$

$$= \frac{1 \cdot 2I \cdot \frac{\hbar^2}{2I}}{\beta \hbar^2} = \frac{1}{\beta}$$

as expected for 2 degrees of freedom.

In QM, allowed values of $\vec{L}^2 = \hbar^2 l(l+1)$

$l = 0, 1, \dots, k$ each state has a degeneracy $2l+1$ (along a selected dir, $L_z = -l, \dots, +l$)

Thus

$$Z_{\text{rot}}^g = \sum_{l=0}^{\infty} e^{-\frac{\beta \hbar^2 l(l+1)}{2I}} \cdot (2l+1)$$

$$= \sum_{l=0}^{\infty} e^{-\frac{\theta_{\text{rot}} l(l+1)}{T}} \cdot (2l+1)$$

where $\theta_{\text{rot}} = \frac{\hbar^2}{2IK_B}$ is the characteristic temp associated with quanta of rotational energy

While the sum can't be analytically evaluated, we look at its high & low temp limits.

(a) For $T \gg \theta_{\text{rot}}$, the sum may be replaced by an integral

$$\begin{aligned} \lim_{T \rightarrow \infty} Z_{\text{rot}}^g &= \int_0^{\infty} dx (2x+1) e^{-\frac{\theta_{\text{rot}} x(x+1)}{T}} \\ &= \int_0^{\infty} dy e^{-\theta_{\text{rot}} y/T} = \frac{T}{\theta_{\text{rot}}} = Z_{\text{rot}}^c \end{aligned}$$

(b) For $T \ll \theta_{\text{rot}}$, the first few terms dominate the sum.

$$\lim_{T \rightarrow 0} Z_{\text{rot}}^g = 1 + 3e^{-2\theta_{\text{rot}}/T} + O(e^{-6\theta_{\text{rot}}/T})$$

leading to

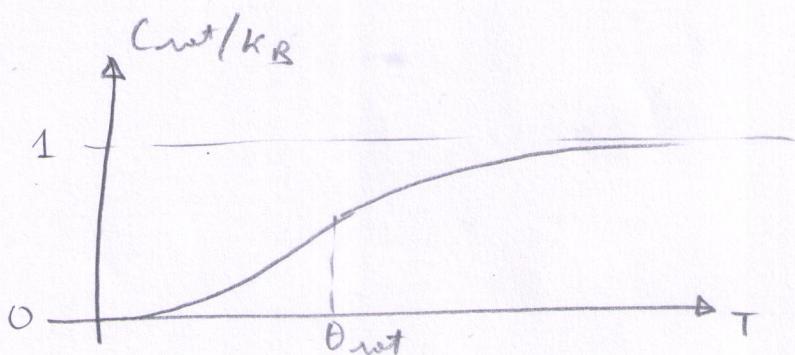
$$E_{\text{rot}} = -\frac{\partial \ln Z}{\partial \beta} \approx -\frac{\partial}{\partial \beta} \ln [1 + 3e^{-2\theta_{\text{rot}}/T}]$$

$$\approx 6k_B \theta_{\text{rot}} \cdot e^{-2\theta_{\text{rot}}/T}$$

The resulting heat capacity is

$$\frac{\partial E}{\partial T} = C_{\text{rot}} = 3k_B \left(\frac{2\theta_{\text{rot}}}{T} \right)^2 e^{-\frac{2\theta_{\text{rot}}}{T}} + \dots$$

This vanishes at low temperature.



$$\theta_{\text{rot}} \sim 1 - 10K$$

<TODO: 6.5>

CALCULATIONS ETC.

D1

$$Y = A X$$

$$X' \Rightarrow BX$$

$$B^{-1} X' = X$$

$$A B^{-1} X' = AX = Y$$

$$\Gamma Y' = BY$$

$$\underline{B^{-1} Y' = Y}$$

$$\Rightarrow B A B^{-1} X' = Y'$$

D2. Show that all basis charge matrices are unitary.

$$B |x\rangle = |y\rangle$$

$$\Rightarrow \langle y| = \langle x| B^+$$

$$\begin{aligned} \langle y| \langle y| &= B |x\rangle \langle x| B^+ \\ \sum_y \langle y| \langle y| &= I = B \left(\sum_x |x\rangle \langle x| \right) B^+ \\ &= B B^+ \end{aligned}$$

That does it

$$B B^+ = I$$

D3. If I'm given how g_i transforms, can I find how p_i transforms?

$$\mathcal{H}(p_i, g_i)$$

Assume \mathcal{H} remains invariant (value)

the

$$\dot{p}_i = - \frac{\partial \mathcal{H}}{\partial g_i} \qquad \dot{g}_i = \frac{\partial \mathcal{H}}{\partial p_i} \qquad \frac{\partial^2 \mathcal{H}}{\partial q \partial p} = \frac{\partial^2 \mathcal{H}}{\partial p \partial q}$$

$$\text{Now say } \dot{g}_i \rightarrow \sum_j p_{ij} \dot{g}_j$$

$$\dot{p}_i \rightarrow \sum_j \frac{1}{a_{ij}} \dot{p}_j$$

$$\frac{\partial^2 \mathcal{H}}{\partial q \partial p} = \frac{\partial^2 \mathcal{H}}{\partial p \partial q}$$

$$\frac{\partial}{\partial q} g_j = - \frac{\partial}{\partial p} p_j$$

D4 Equipartition Theorem.

D5 Then for a dilute polyatomic gas

$$C_p = C_v + k_B$$

D6 we use the integral of

$$\int_{-\infty}^{\infty} dx \exp[-ax^2]$$

$$\ln \frac{A}{B} = \ln A - \ln B$$

$$\frac{f}{g} = \frac{fg' - fg'}{g^2}$$

D7 For $E_{wh}^q = \frac{\hbar\omega}{2} + \hbar\omega \frac{e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}}$

$$\text{Then show } C_{wh}^q = \frac{dE_{wh}^q}{dT} = \frac{fg'}{g^{-1}} = \frac{f'}{g^{-1}} - \frac{(fg')'}{(g^{-1})^2}$$

$$= k_B \left(\frac{\hbar\omega}{k_B T} \right)^2 \frac{e^{-\beta\hbar\omega}}{(1 - e^{-\beta\hbar\omega})^2}$$

so we must have

$$\hbar\omega \frac{d}{dT} \left(\hbar\omega \frac{e^{-\frac{\hbar\omega}{k_B T}}}{1 - e^{-\frac{\hbar\omega}{k_B T}}} \right) = \hbar\omega \left(\frac{\hbar\omega}{k_B} \right) \cdot \left(\frac{-1}{T^2} \right) \cdot e^{-\frac{\hbar\omega}{k_B T}}$$

$$+ \hbar\omega e^{-\frac{\hbar\omega}{k_B T}} \left[\frac{-1}{(1 - e^{-\frac{\hbar\omega}{k_B T}})^2} \cdot (-1) \left(\frac{\hbar\omega}{k_B} \right) \cdot \left(\frac{-1}{T^2} \right) \right]$$

$$= \frac{(\hbar\omega)^2}{k_B T^2} e^{-\frac{\hbar\omega}{k_B T}} \left[\frac{1}{(1 - e^{-\frac{\hbar\omega}{k_B T}})^2} + \frac{(1 - e^{-\frac{\hbar\omega}{k_B T}})}{(1 - e^{-\frac{\hbar\omega}{k_B T}})^2} \right] \frac{2 + e^{-\beta\hbar\omega}}{2 + e^{-\beta\hbar\omega}}$$

WRONG

try

$$\begin{aligned} \hbar\omega \frac{d}{dT} & \left(\frac{e^{-\beta \hbar\omega/kT}}{1 - e^{-\beta \hbar\omega/kT}} \right) \\ = \hbar\omega & \frac{\frac{d}{dT} (e^{-\beta \hbar\omega/2}) (1 - e^{-\frac{\beta \hbar\omega}{2}}) - e^{-\frac{\beta \hbar\omega}{2}} \frac{d}{dT} (e^{-\frac{\beta \hbar\omega}{2}})}{(1 - e^{-\frac{\beta \hbar\omega}{2}})^2} \\ = \hbar\omega & \left(\frac{\hbar\omega}{k_B T} \right) \cdot e^{-\frac{\beta \hbar\omega}{2}} \cdot \left(\frac{-1}{T^2} \right) (1 - e^{-\frac{\beta \hbar\omega}{2}}) - \\ & e^{-\frac{\beta \hbar\omega}{2}} \cdot \left(\frac{\hbar\omega}{k_B T} \right) \cdot e^{-\frac{\beta \hbar\omega}{2}} \left(\frac{-1}{T^2} \right) \\ & \hline \\ = \frac{k_B}{Z} & \left(\frac{\hbar\omega}{k_B T} \right)^2 \left[(1 - e^{-\frac{\beta \hbar\omega}{2}}) - 1 \right] \\ & \hline \\ & (1 - e^{-\frac{\beta \hbar\omega}{2}})^2 \end{aligned}$$

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