

Reader
p.1

At low Temperature, predictions of classical stat mech typically break down.

Examples: Behavior of heat capacity
Ultraviolet Catastrophe in blackbody radiation
Behavior of entropy, 3rd law

Dilute Polyatomic Gases; Classical Stat Mech

Hamiltonian for each molecule of n atoms:

$$H_i = \sum_{i=1}^N \frac{p_i^2}{2m} + V(\vec{q}_1, \dots, \vec{q}_n)$$

↑ potential energy \rightarrow molecular bonds

Note: If the masses of the atoms in the molecule are inequivalent, rescale coords by $\sqrt{m_i/m}$ and momenta by $\sqrt{m/m_i}$.

Then the Hamiltonian has the above form, and the phase space measure is preserved.

Dilute \rightarrow ignore interactions between molecules

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

Strong chemical bonds \rightarrow treat molecule as heavy fixed shape + small deformations.

Contribution of deformations to Z_1 :

a) Minimize $V(\vec{q}_1, \dots, \vec{q}_n)$ to find equilibrium positions $(\vec{q}_1^*, \dots, \vec{q}_n^*)$.

b) Small deformations: keep leading terms in Taylor expansion about equilibrium positions:

$$\vec{q}_i = \vec{q}_i^* + \vec{u}_i$$

$$V = V^* + \frac{1}{2} \sum_{i,j=1}^n \sum_{\alpha,\beta=1}^3 \frac{\partial^2 V}{\partial q_{i\alpha} \partial q_{j\beta}} \bigg|_{\vec{q}_i^*} u_{i\alpha} u_{j\beta} + \mathcal{O}(u^3)$$

\uparrow
 $V(\vec{q}_1^*, \dots, \vec{q}_n^*)$

Note: no linear term in Taylor expansion because \vec{q}^* is a minimum $\rightarrow \frac{\partial V}{\partial q_i} = 0$.

c) Find normal modes by diagonalizing

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

(A $3n \times 3n$ matrix)

$3n$ eigenvalues $\{K_s\}$ — stiffness of modes

$3n$ eigenvectors $\{E_s\}$ $E_s^T E_s = 1$ normalized

Change variables from $\{u_{i\alpha}\}$ to $\{\tilde{u}_s\}$

$$\sum_{i=1}^n \sum_{\alpha=1}^3 u_{i\alpha} \vec{e}_{i\alpha}, \quad \begin{array}{l} \text{Basis vectors } \{\vec{e}_i\} \\ \downarrow \\ \vec{e}_i \cdot \vec{e}_i = 1 \end{array} \quad \begin{array}{l} \uparrow \\ \text{amplitude of eigennode} \end{array}$$

$$\Rightarrow \sum_{s=1}^{3n} \tilde{u}_s E_s$$

Conjugate momenta $p_s = m \dot{u}_s$

$$\mathcal{H}_1 = V^{\text{sp}} + \sum_{s=1}^{3n} \left[\frac{1}{2m} \tilde{p}_s^2 + \frac{k_s}{2} \tilde{u}_s^2 \right]$$

Think of $\frac{\partial^2 V}{\partial q_{i\alpha} \partial q_{j\beta}}$ as a $3n \times 3n$ matrix, $V^{(2)}$
(real, symmetric)

$u_{i\alpha}$ as a $3n$ -vector u

$$\frac{1}{2} \sum_{\substack{i\alpha \\ j\beta}} u_{i\alpha} \frac{\partial^2 V}{\partial q_{i\alpha} \partial q_{j\beta}} u_{j\beta} = \frac{1}{2} u^T V^{(2)} u$$

Diagonalize with an orthogonal transformation!

$$u \rightarrow \tilde{u} = O u, \quad O^T O = \mathbb{1}$$

$$V_{\text{diag}}^{(2)} \equiv O V^{(2)} O^T = \begin{pmatrix} k_1 & & 0 \\ & k_2 & \dots \\ 0 & \dots & k_{3n} \end{pmatrix}$$

$$\begin{aligned} \frac{1}{2} \tilde{u}^T V_{\text{diag}}^{(2)} \tilde{u} &= \frac{1}{2} (u^T O^T) (O V^{(2)} O^T) (O u) \\ &= \frac{1}{2} u^T V^{(2)} u \end{aligned}$$

$$= \frac{1}{2} \sum_{s=1}^{3n} k_s \tilde{u}_s^2$$

Phase space measure: $\prod_{i\alpha} dy_{i\alpha} dp_{i\alpha} = \prod_s d\tilde{u}_s d\tilde{p}_s$
(preserved)

Average energy:

$$Z(N) \approx \frac{1}{N!} \left[\int_{S=1}^{3n} \prod_{s=1}^{3n} \frac{d\tilde{q}_s d\tilde{p}_s}{h^2} \exp \left[-\beta \sum_{s=1}^{3n} \frac{\tilde{p}_s^2}{2m} - \beta \sum_{s=1}^{3n} \frac{\kappa_s}{2} \tilde{q}_s^2 \right] \right]^N$$

$$= \frac{1}{N! (h^2)^{3nN}} \left(\frac{2\pi m}{\beta} \right)^{3nN/2} \prod_S \left(\frac{2\pi}{\kappa_S \beta} \right)^{N/2} \cdot V_0$$

product over nodes
with non-spring κ_s

Volume of
STTd's over
modes with $\kappa_s \neq 0$

Suppose there are n_k nodes with $\kappa_s \neq 0$

$$\text{Then } \ln Z(N) = \dots - N(3n + n_k) \cdot \frac{1}{2} \ln \beta$$

independent of β

The only dependence on β

$$E = - \frac{\partial \ln Z}{\partial \beta} = N(3n + n_k) \cdot \frac{1}{2} k_B T$$

quadratic
degrees of freedom

★ \rightarrow Each quadratic degree of freedom
(p's and q's that appear quadratically in H)
gives a contribution of $\frac{1}{2} k_B T$ to the
internal energy.

Symmetries can force some k_s to zero:

a) Translation symmetry: $V(\vec{r}_i + \vec{c}) = V(\vec{r}_i)$

→ no energy stored in center of mass coordinates

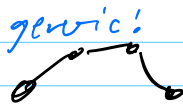
$$\vec{Q} = \sum_{i=1}^n \frac{\vec{r}_i}{n}$$

→ 3 values $K_{\text{translation}} = 0$

b) Rotation symmetry: Rotating the molecule does not change the potential energy

→ $K_{\text{rot}} = 0$.

$r = \#$ independent rotations, depends on shape of molecule:



$r=3$

single atom:



$r=0$

rod shaped:



$r=2$

nonvanishing stiffness parameters k_s (vibrational modes)

$$3n - 3 - r$$

Energy per molecule: $\langle \mathcal{H}_1 \rangle = \underbrace{3n}_{\text{from } P_s} + \underbrace{(3n - 3 - r)}_{\text{from } \tilde{U}_s} k_B T$

$$\langle \mathcal{H}_1 \rangle = \frac{6n - 3 - r}{2} k_B T$$

Heat capacity/molecule:

$$C_V = \frac{d\langle E \rangle}{dT} = \frac{6n-3-r}{2} k_B$$

$$C_P = C_V + k_B = \frac{6n-1-r}{2} k_B$$

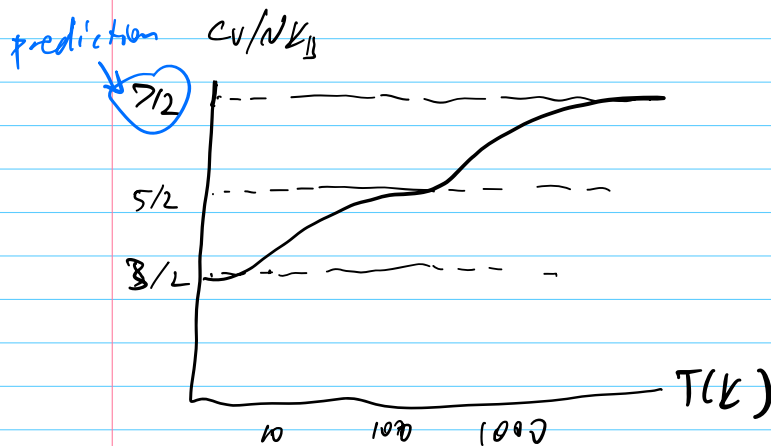
Recall adiabatic processes have PV^γ fixed

→ can measure γ

prediction:

Monatomic	He	$n=1$	$r=0$	$\gamma=5/3$
Diatomic	O_2, CO	$n=2$	$r=2$	$\gamma=7/5$
Linear triatomic	CO_2	$n=3$	$r=2$	$\gamma=15/13$
Planar triatomic	H_2O	$n=3$	$r=3$	$\gamma=14/12$
Tetra-atomic	NH_4	$n=4$	$r=3$	$\gamma=20/18$

Experiment: Diatomic molecules



Explanation: Different sets of modes are active in different temperature regimes.

- Energies are quantized.

Vibrational Modes

Consider a mode with stiffness $K = m\omega^2$,
 ω = frequency of oscillation

$$\begin{aligned} Z_{\text{vib}}^{\text{classical}} &= \int \frac{dp dq}{h} \exp \left[-\beta \left(\frac{p^2}{2m} + \frac{m\omega^2 q^2}{2} \right) \right] \\ &= \frac{1}{h} \left(\frac{2\pi m}{\beta} \right) \left(\frac{2\pi}{\beta m \omega^2} \right) \\ &= \frac{k_B T}{h\omega}, \quad h = h/2\pi \end{aligned}$$

$$\langle H_{\text{vib}} \rangle^{\text{classical}} = -\frac{\partial \ln Z}{\partial \beta} = k_B T$$

Compare with Quantum Mechanics:

Simple harmonic oscillator: $\langle H_{\text{vib}} \rangle^{\text{quantum}} = (n + 1/2) h\omega$

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

Suppose $p(n) \propto e^{-\beta(n+1/2)h\omega}$

$$\Rightarrow Z_{\text{vib}}^{\text{quantum}} = \sum_{n=0}^{\infty} e^{-\beta h\omega(n+1/2)} = \frac{e^{-\beta h\omega/2}}{1 - e^{-\beta h\omega}}$$

High-T (small- β) limit:

$$Z_{\text{vib}}^{\text{quantum}} \rightarrow \frac{1}{1 - (1 - \beta \hbar \omega)} = \frac{k_B T}{\hbar \omega}$$
$$= Z_{\text{vib}}^{\text{classical}}$$

(Note that the factors of \hbar in the classical phase space measure helped get the normalization of Z_{vib} to agree w/ the quantum theory.)

Small T (large β) limit:

$$Z_{\text{vib}}^{\text{quantum}} \rightarrow e^{-\beta \hbar \omega / 2} \neq Z_{\text{vib}}^{\text{classical}}$$

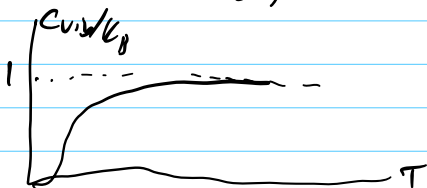
Low-T physics is sensitive to quantum effects.

vibrational energy:

$$E_{\text{vib}}^{\text{quantum}} = -\frac{\partial \ln Z}{\partial \beta} = \frac{\hbar \omega}{2} + \frac{\hbar \omega e^{-\beta \hbar \omega}}{1 - e^{-\beta \hbar \omega}}$$

Contribution to heat capacity:

$$C_{\text{vib}}^{\text{quantum}} = \frac{dE_{\text{vib}}^{\text{quantum}}}{dT} = k_B \left(\frac{\hbar \omega}{k_B T} \right)^2 \frac{e^{-\beta \hbar \omega}}{(1 - e^{-\beta \hbar \omega})^2}$$



Crossover to classical-like behavior happens

$$\text{at } T \gtrsim \theta_{\text{vib}} \equiv \frac{h\nu}{k_B}.$$

$$\text{Typically, } \theta_{\text{vib}} \sim 10^{3-4} \text{ K.}$$