

APPLICATIONS (ch 7)

{ large fraction of statistics problems \rightarrow find reasonable approx to Z }
 which only requires knowing $E(V)$ for

MONATOMIC

ex GENERAL GAS: (CLASSICAL) AT FIXED T

$$E = \sum_{i=1}^N \frac{p_i^2}{2m} + U(r_1, \dots, r_N)$$

$$Z = \int \frac{d^3r_1 \dots d^3r_N d^3p_1 \dots d^3p_N}{h_0^{3N}} e^{-\beta \left[\sum \frac{p^2}{2m} + U \right]}$$

(prob. in each cell)

IDEAL GAS:

$U = 0$

SUM OVER cells in phase space (no really important since $\ln Z$)

(ALSO N RESTRICTED TO BOX)

$$Z = \left[\int \frac{d^3r}{h_0^3} \right]^N \left[\int_{-\infty}^{\infty} dp e^{-\beta \frac{p^2}{2m}} \right]^{3N}$$

(V/h₀³)^N (2πm/β)^{1/2}

COMPLIETLY FACTORS: (wouldn't if U ≠ 0)

(GAUSSIAN)

N PARTICLES, PART WITH $p^2 = p_x^2 + p_y^2 + p_z^2$

\Rightarrow SO JUST ONE ^{SIMPLE} INTEGRAL TO DO

(will see later: didn't even need to do it, just chg vars)

$$\ln Z = N \left[\ln V - \frac{3}{2} \ln \beta + \frac{3}{2} \ln \left(\frac{2\pi m}{h_0^2} \right) \right]$$

$$\Rightarrow \bar{p} = \frac{1}{\beta} \frac{\partial \ln Z}{\partial V} = \frac{1}{\beta} \frac{N}{V} \Rightarrow \bar{p}V = NKT$$

$$\bar{E} = -\frac{\partial}{\partial \beta} \ln Z = \frac{3}{2} \frac{N}{\beta} = \frac{3}{2} NKT$$

$$C_V = \left(\frac{\partial \bar{E}}{\partial T} \right)_V = \frac{3}{2} Nk = \frac{3}{2} \nu R$$

AS BEFORE

$$\frac{3}{2} N k^2 T^2 =$$

e. 2

ALSO $(\Delta^* E)^2 = \frac{\partial^2 \ln Z}{\partial \beta^2} = k T^2 C_V$

$$\frac{\Delta^* E}{E} = \sqrt{\frac{2}{3N}} \sim \frac{1}{\sqrt{N}} \quad \left\{ \begin{array}{l} \text{agrees w/ rule of thumb} \\ \text{est; small for } N \text{ large} \end{array} \right.$$

LARGE CLASS OF SYSTEMS LIKE IG w/ $E \sim p^2 + \dots$

EQUIPARTITION THM: CLASSICAL

f DOF
DEPENDS ON f p's,
f r's

$$E(p_1, \dots, p_f, r_1, \dots, r_f)$$

- r_i could be any kind of position (linear, angle, etc)
 - E could dep. differently on diff p_i, r_i (some could be linear, some angles...)
- then $p =$ any mom

IF FOR ONE p_i (choose it to be first)
E: CONTINUOUS

- (1) $E = E_1(p_1) + E'(p_2, \dots, r_f) \Rightarrow$ SEPARATES
(~ can treat it as a separate system - even if just one contrib to E for 1 particle w/ many other contrib.)
- (2) $E_1(p_1) = b p_1^2 \Rightarrow$ QUADRATIC

COMMON: $K_E = \frac{p_1^2}{2m}$

IG: APPLIES TO ALL p_i

funny - can treat p_x as separate sys. from p_y for same particle)

(CAN ALSO WORK FOR r_i :

ex OSCILLATOR POT. E $E(r) = \frac{1}{2} k r^2$)

{ note for me: don't call p_i a dof; 'its' really 1 dof for (p_i, r_i) ; call it a quad. term in E }

THEN: CAN COMPUTE \bar{E}_1 (ave E for that qty):

$$\bar{E}_1 = \frac{\int e^{-\beta E(p_1, \dots, r_f)} E_1 dp_1 \dots dr_f}{\int e^{-\beta E(p_1, \dots, r_f)} dp_1 \dots dr_f}$$

$$= \frac{\int_{-\infty}^{\infty} e^{-\beta E_1} E_1 dp_1 \int e^{-\beta E'} dp_2 \dots dr_f}{\int_{-\infty}^{\infty} e^{-\beta E_1} dp_1 \int \dots}$$

CANCEL

$$\bar{E}_1 = \frac{\int e^{-\beta E_1} E_1 dp_1}{\int e^{-\beta E_1} dp_1} \quad (\text{what expect for separate subsp.})$$

$$\bar{E}_1 = -\frac{\partial}{\partial \beta} \ln \left(\int e^{-\beta E_1} dp_1 \right)$$

(→)

USED (1) SO FAR; INDEP. OF OTHER QTY'S

$$\text{USE (2): } \int_{-\infty}^{\infty} e^{-\beta \frac{1}{2} b p_1^2} dp_1 \rightarrow \beta^{-\frac{1}{2}} \int e^{-by^2} dy$$

$$\text{CHG VAR: } y \equiv \beta^{\frac{1}{2}} p_1$$

$$\ln(\quad) = -\frac{1}{2} \ln \beta + \ln \int e^{-by^2} dy$$

$$\bar{E}_1 = -\frac{\partial}{\partial \beta} \left(-\frac{1}{2} \ln \beta \right) = \frac{1}{2\beta} = \frac{1}{2} kT$$

β no
const -
 β indep

$$\bar{\epsilon}_1 = \frac{1}{2} kT$$

e. 4

NOTE: TRUE FOR ANY QUADR. TERM IN ϵ
 • DOESN'T MATTER WHAT k IS

quad
 any term in ϵ has $\bar{\epsilon} = \frac{1}{2} kT$

MONATOMIC IDEAL GAS

$$\epsilon_{\text{PARTICLE}} = \frac{1}{2m} (p_x^2 + p_y^2 + p_z^2)$$

$$\frac{p_x^2}{2m} = \frac{1}{2} kT \Rightarrow$$

$$\bar{\epsilon}_{\text{PART}} = \frac{3}{2} kT$$

$$\bar{\epsilon} = \frac{3}{2} NkT = \frac{3}{2} \nu RT \Rightarrow C_V = \frac{3}{2} R$$

ALSO: $C_p = C_V + R = \frac{5}{2} R \Rightarrow \gamma = \frac{C_p}{C_V} = \frac{5}{3} = 1.67$

DIATOMIC: 3 LINEAR + 2 ROTS

$$\epsilon_{\text{PART}} = \left(\text{tr.} \right) + \frac{1}{2I} (L_x^2 + L_y^2)$$

$$\bar{\epsilon} = \frac{5}{2} NkT$$

$$C_V = \frac{5}{2} R$$

$$\Rightarrow C_p = \frac{7}{2} R \quad \gamma = \frac{7}{5} = 1.40$$

of table

HARMONIC OSC: (GOOD MODEL FOR ATOMS IN SOLID)

skip

1D: $\epsilon = \frac{p^2}{2m} + \frac{1}{2} k_0 x^2$ { 2 QUADR. TERMS IN ϵ }

$$\bar{\epsilon} = \frac{1}{2} kT + \frac{1}{2} kT = kT$$

\Rightarrow on one,

⇒ C_v just counts dof:

ASIDE - REF. TO EXAM

SP. HEATS & QM: IG

SAW ON EXAM:

$H_2, O_2 \dots$



ONLY QUAP. CONTRIB. TO E

3 TRANSL + 2 ROT = 5

$C_v = \frac{5}{2} R$ $C_p = C_v + R$ (IG)

$\gamma = \frac{C_p}{C_v} = \frac{7}{5} = 1.40$

know: more likely to have E spread over

than from class mech - (alt)

① most likely config has E spread equally among all dof
② $E/k \approx \frac{1}{2} kT$

He



CP MONATOMIC:

3 TRANSL

$C_v = \frac{3}{2} R$ $C_p = \frac{5}{2} R$

$\gamma = \frac{5}{3} = 1.67$

IDEA: C_v IS SIMPLY \propto TO # PLACES TO PUT E

H_2 :

WHY NOT



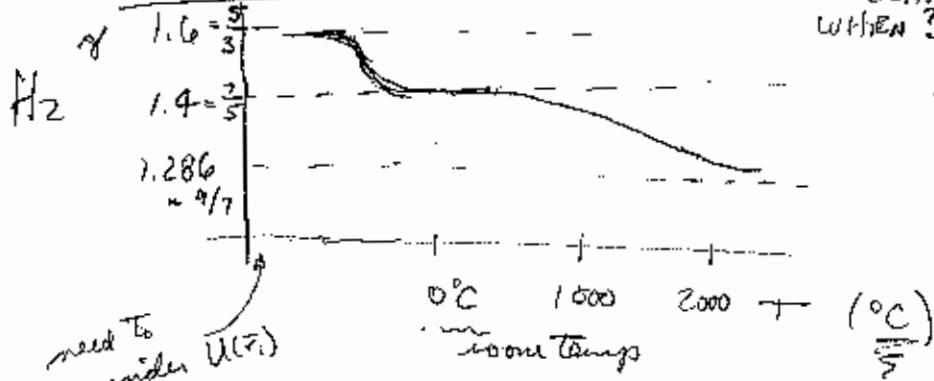
3 + 2 + 2 = 7



KE + PE

⇒ $\gamma = \frac{9}{7} = 1.286$?

IN FACT



OSCILLATOR FREEZES OUT ⇒ WHEN?

$\frac{E}{f} \sim kT$

TWO LOW TO EXCITE

OSC. ENERGIES

WHEN?

$kT \ll \Delta E_{osc}$

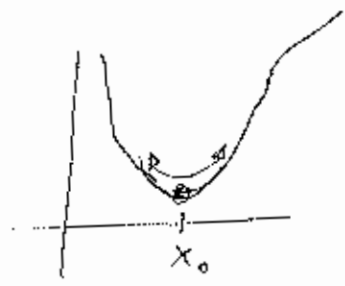
LOWER STILL → ROTATIONS FREEZE OUT

BUT TRANSLATIONS ~ CONTINUOUS

no they can move →, but they can't rotate

CV SOLIDS

AT MIN OF ANY POT U
(EQUIL. POSITION) \leftarrow const > 0



$$U(x) \sim U_0 + \frac{1}{2} U_0'' (x-x_0)^2 + \dots \text{ IF } x \text{ NEAR } x_0$$

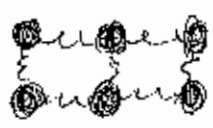
\approx HARM OSC

(cf 6.11) (TAY. SERIES:
1ST DERIV = 0
2ND $> 0 \Rightarrow K > 0$)

— WHY SO USEFUL IN PHYSICS:

ALL SMALL OSC. NEAR MIN \approx MASS ON SPRING

SOLID:



APPROXIMATE AS N ATOMS ^{EACH} IN 3d HARM OSC

$$E \approx \sum_{i=1}^{3N} \left(\frac{p_i^2}{2m} + \frac{1}{2} K_i r_i^2 \right) \quad \omega_i = \sqrt{K_i/m}$$

↓
just say

{ TRUE PICTURE A BIT INVOLVED:
↳ FOR ONE ATOM FORMED BY OTHERS WHICH ARE ALSO MOVING.

q_i = NORMAL MODE COORDS (ADV. MECHANICS)
= MOTION OF WHOLE GROUP,
RELATIVE MOTION BETWEEN, ETC

WILL HAVE DIFF K_i 'S

DEPENDS ON DETAILS, BUT ^{THIS ARG.} ONLY DEPENDS ON

{ NEAR EQUIL. $\Rightarrow E$ IS QUADRATIC }

FOR DISCUSSION

GOOD ENOUGH [^] TO THINK OF EACH ATOM IN ITS OWN H.O.

↓

CORRECT TREATMENT: QM

EACH DOF: $E_n = \frac{1}{2} \hbar \omega_i (n + \frac{1}{2})$

$\omega_i = \sqrt{K_i/m}$

—
—
— $\frac{1}{2} \hbar \omega$
— $E_0 = \frac{1}{2} \hbar \omega$

SPS $\bar{E} \sim kT \gg \Delta E = \hbar \omega$

$E \sim$ CONTINUOUS \Rightarrow CLASSICAL

CLASSICAL TREATMENT:

EQUIP. THM:

TWO QUADRATIC TERMS EACH DIRECTION

$\frac{p_i^2}{2m} + \frac{1}{2} K_i r_i^2$

$\bar{E}_{\text{per } i} = \frac{1}{2} kT \times 2 = kT$ } half KE, half p.

ONE MOLE:
 }
 $v=1$
 $N=N_A$
 $C_V = C_V$

$\bar{E} = 3 N_A kT = 3RT$

$C_V = \left(\frac{\partial \bar{E}}{\partial T} \right)_V = 3R$

$C_V = 3R = 25 \text{ J/mole} \cdot \text{°K}$

ALL SOLIDS (CLASSICAL)
(only depends on harm. osc approx)

T \approx ROOM TEMP

WORKS GREAT

[Table
pg 254]

($C_p \approx C_V$ for solids but easier to measure)

(slightly larger) but note diamond

2 QUESTIONS

(1) CAN WE UNDERSTAND DIAMOND?

(2) WHY DOESN'T $C_V \rightarrow 0$ FOR $T \rightarrow 0$?

$$\left\{ \text{recall } \Delta S = \int_{T_i}^{T_f} \frac{dQ}{T} = \int_{T_i}^{T_f} \frac{C_V(T) dT}{T} \right\}$$

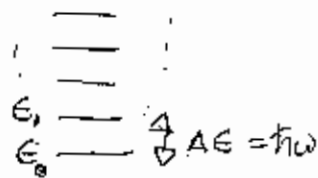
BOTH PROBLEMS AT LOW T

QM: 1 OSCILLATOR (put together later)

use ϵ for
1 osc,
 $\bar{\epsilon}$ for whole
system

$$E_n = \hbar\omega \left(n + \frac{1}{2}\right) \quad n=0, 1, 2, \dots$$

$$\omega = \left(\frac{K}{m}\right)^{\frac{1}{2}} \quad \left\{ \begin{array}{l} \text{large } K, \text{ small } m: \\ \omega \text{ large, } \Delta E \text{ large} \end{array} \right.$$



IF $kT \not\gg \Delta E$, CLASSICAL APPROX NOT VALID

DO IT RIGHT:

$$Z = \sum_{n=0}^{\infty} e^{-\beta E_n} = \sum_{n=0}^{\infty} e^{-\beta \hbar\omega \left(n + \frac{1}{2}\right)}$$

$$= e^{-\frac{1}{2}\beta \hbar\omega} \sum_{n=0}^{\infty} \left(e^{-\beta \hbar\omega}\right)^n$$

RECALL

$$\sum_{n=0}^{\infty} x^n = 1 + x + x^2 + \dots = \frac{1}{1-x}$$

$$\Rightarrow Z = e^{-\frac{1}{2}\beta \hbar\omega} \frac{1}{1 - e^{-\beta \hbar\omega}}$$

$$\ln Z = -\frac{1}{2}\beta \hbar\omega - \ln(1 - e^{-\beta \hbar\omega})$$

$$\bar{\epsilon} = -\frac{\partial}{\partial \beta} \ln Z = \hbar\omega \left(\frac{1}{2} + \frac{1}{e^{\beta \hbar\omega} - 1}\right)$$

\Rightarrow GOOD FOR LOW $\frac{1}{2}$ HIGH T (UNTIL HARM OSC APPROX BREAKS)

LARGE T:IF $kT \gg \hbar\omega$, EXPECT CLASSICAL:

$$\text{ie } \beta\hbar\omega \equiv \frac{\hbar\omega}{kT} \ll 1 \quad \left. \begin{array}{l} \text{\{ note the value of} \\ \text{\textit{the exp. depends on}} \\ \text{\textit{this directly}} \end{array} \right\}$$

TAYLOR SERIES:

$$e^{\beta\hbar\omega} \approx 1 + \beta\hbar\omega + \dots$$

(SMALL ARG)

$$\Rightarrow \bar{E} \approx \hbar\omega \left(\frac{1}{2} + \frac{1}{1 + \beta\hbar\omega + \dots - 1} \right)$$

$$\frac{1}{2} + \frac{1}{\beta\hbar\omega}$$

↑
DOMINATES

$$\approx \frac{1}{\beta} = kT$$

$$\text{SO } \boxed{\bar{E} = kT = 2 \cdot \left(\frac{1}{2} kT \right)} \quad \checkmark$$

⇒ NOTE \hbar GOES AWAY (always does in classical limit)

⇒ 2 BECAUSE 1 OSC: (ie IN 1D) $\frac{p^2}{2m} + \frac{1}{2}Kx^2$

SMALL T:

$$T \sim 0 \quad \beta\hbar\omega \gg 1 \quad e^{\beta\hbar\omega} \text{ LARGE}$$

$$\bar{E} \sim \hbar\omega \left(\frac{1}{2} + \underbrace{e^{-\beta\hbar\omega}}_{\sim 0} + \dots \right)$$

$$\boxed{\bar{E} = \frac{1}{2} \hbar\omega = \epsilon_0} \quad \checkmark$$

indep of T
(equip. then fails)

RECALL

$$S = k(\ln Z + \beta \bar{E})$$

$$\ln Z \approx \ln \left\{ e^{-\frac{1}{2}\beta \hbar \omega} \frac{1}{1 - e^{-\beta \hbar \omega}} \right\}^0 \approx -\beta(\frac{1}{2}\hbar\omega)$$

$$\Rightarrow \boxed{S \rightarrow k(-\beta(\frac{1}{2}\hbar\omega) + \beta(\frac{1}{2}\hbar\omega)) = 0} \quad \checkmark$$

(1 osc)

MACRO SYS: SOLID

\Rightarrow MANY K_i 's (AND ω_i 's)

SIMPLEST MODEL: (EINSTEIN)

\Rightarrow ALL SAME

1 MOLE

$$\bar{E} = 3 N_A \bar{E} = 3 N_A \hbar \omega \left(\frac{1}{2} + \frac{1}{e^{\beta \hbar \omega} - 1} \right)$$

$\underbrace{\hspace{2em}}$
EACH MOLECULE \Rightarrow 3 OSC

(just add energies).

some algebra

$$C_V = C_V = \left(\frac{\partial \bar{E}}{\partial T} \right)_V = \frac{3 N_A \hbar \omega}{k T^2} \left[\frac{e^{\beta \hbar \omega} \hbar \omega}{(e^{\beta \hbar \omega} - 1)^2} \right]$$

(1 MOLE)

DEF

$$\Theta_E \equiv \frac{\hbar \omega}{k}$$

"EINSTEIN TEMP"

(const, dep. on ω)
 $\hbar \omega = \frac{\hbar \omega}{kT} = \Theta_E / T$

$$\boxed{C_V(T) = 3R \left(\frac{\Theta_E}{T} \right)^2 \frac{e^{\Theta_E/T}}{(e^{\Theta_E/T} - 1)^2}}$$

T VS Θ_E DETERMINES WHEN CLASSICAL APPROX OK
 ($T \sim \Theta_E$ when $kT \approx \hbar \omega = \Delta E$) (i.e. WHEN T IS LARGE; NOTE $k\Theta_E = \hbar \omega = \Delta E$; Θ_E IS DIVID. LINE.)

CLASSICAL LIMIT:

$$T \gg \Theta_E$$

$$C_V \rightarrow 3R \quad (\text{TAYLOR SERIES}) \quad \checkmark$$

$T \rightarrow 0$:

$$\Theta_E/T \gg 1$$

$$C_V \rightarrow 3R \left(\frac{\Theta_E}{T}\right)^2 e^{-\Theta_E/T} \rightarrow 0 \quad \checkmark$$

AS IT MUST

CF PLOT (pg 256)

\Rightarrow MUCH BETTER THAN IT SHOULD BE
(IN PRACTICE, DON'T KNOW ω ; DETERMINE Θ_E
FROM SINGLE MEAS., PREDICT REST OF CURVE.)

DIAMOND?

MOST SOLIDS: $\Theta_E \sim \text{RM TEMP}$
($\omega/T \sim 1$)

DIAMOND: HARD, K ; ω ; LARGE
 ΔE BIG

$$\Theta_E \sim 1300^\circ \text{K}$$

\Rightarrow HARD SOLIDS \rightarrow LOW C_V

\Rightarrow NEED HIGH T BEFORE $C_V \rightarrow 3R$

ROOM TEMP: CAN'T UNDERSTAND DIAMOND

w/OUT QM

(could talk about diatomic gases f-trans)

\Rightarrow THEORETICALLY INTERESTING
(very similar to b-body
spectrum)

(1) can see need for QM (2) can est. Δ
from $\Theta_E = \hbar\omega/k$

Table 7·7·1 Values* of c_p (joules mole⁻¹ deg⁻¹) for some solids at $T = 298^\circ\text{K}$

Solid	c_p	Solid	c_p
Copper	24.5	Aluminum	24.4
Silver	25.5	Tin (white)	26.4
Lead	26.4	Sulfur (rhombic)	22.4
Zinc	25.4	Carbon (diamond)	6.1

* "American Institute of Physics Handbook," 2d ed., McGraw-Hill Book Company, New York, 1963, p. 4-48.

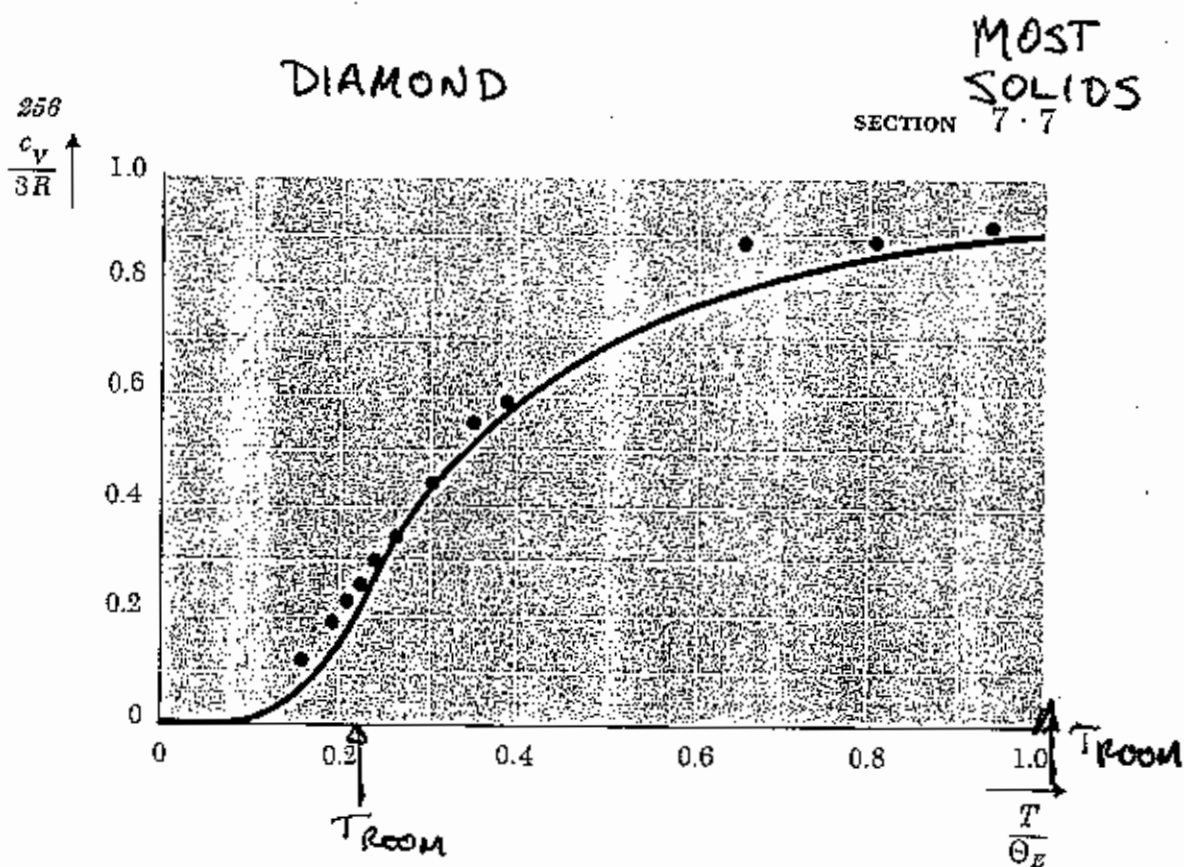


Fig. 7·7·1 Temperature dependence of c_v according to the Einstein model. The points are experimental values of c_v for diamond, the fit to the curve being achieved by choosing $\Theta_E = 1320^\circ\text{K}$ (after A. Einstein, *Ann. Physik*, vol. 22, p. 186 (1907)).