

100 2nd

APPLICATIONS (ch 7)

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

MONATOMIC

ex GENERAL GAS: (CLASSICAL) AT FIXED T

$$E = \sum_{i=1}^N \frac{\vec{p}_i^2}{2m} + U(\vec{r}_1, \dots, \vec{r}_N)$$

MICRO INFO

Note: don't have awkward constraint on integrations as in QCD

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

SUM OVER cells in phase space (ho rarely important small case \rightarrow $2 \ln Z$)

IDEAL GAS:

$$U = 0$$

(ALSO r RESTRICTED TO BOX)

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

COMPLETELY FACTORS:
(wouldnt if $U \neq 0$)

SIMPLE

(GAUSSIAN)

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

\Rightarrow SO JUST ONE INTEGRAL TO DO

(will see later: didnt even need to do it, just deg vars)

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

20 \rightarrow

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

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

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

\Rightarrow EVERYTHING WE HAD BEFORE, + SOME MORE:

FULL $S = k(\ln Z + \beta \bar{E}) = Nk \left[\ln V + \frac{3}{2} \ln kT + \frac{3}{2} \ln \left(\frac{2\pi m}{h^2} \right) + \frac{3}{2} \right]$ e.2
(INCL CONST.)

ALSO $(\Delta^* E)^2 = \frac{\partial^2 \ln Z}{\partial \beta^2} = \frac{3}{2} N k^2 T^2 = k T^2 C_V$ } FLUCTUATIONS

$\Rightarrow \frac{\Delta^* E}{\bar{E}} = \left(\frac{2}{3N} \right)^{\frac{1}{2}} \sim \frac{1}{\sqrt{N}}$ } RECALL EST FOR MACRO SYS. $\sim \frac{1}{\sqrt{f}}$ (HERE $f=3N$)



EQUIPARTITION THM

- CLASSICAL \Rightarrow GEN'L, USEFUL

FOR f DOF:

$E = E(p_1, \dots, p_f, r_1, \dots, r_f)$
 \uparrow ANY KIND OF MOM \uparrow ANY KIND OF COORD

IF FOR ONE p_i (CHOOSE AS FIRST)

(0) E CONTINUOUS WRT p_i (SO CLASSICAL)

(1) $E = E_i(p_i) + E'(p_2 \dots p_f)$

\Rightarrow CAN SEPARATE CONTRIB FROM p_i

} - CAN TREAT AS SEP. SYS
 - WILL BE INDEP \Rightarrow FACTORS IN BOLTZM. PROB.

(2) $E_i(p_i) = b p_i^2$

\Rightarrow QUADRATIC (ANY b)

COMMON: $KE = \frac{p_i^2}{2m}$

EX IG: APPLIES TO ALL N PARTS, 3 DIR. EACH

CAN ALSO APPLY TO r

EX HARM OSC. POT. $E(r) = \frac{1}{2} K r^2$

CAN COMPUTE \bar{E}_i : (ave E from that term)

$\bar{E}_i = \frac{\int e^{-\beta E(p_1, \dots, p_f)} E_i dp_1 \dots dp_f}{\int e^{-\beta E(\dots)} dp_1 \dots dp_f}$

$$= \frac{\int_{-\infty}^{\infty} e^{-\beta \epsilon_1} \epsilon_1 dp_1 \int e^{-\beta \epsilon'} dp_2 \dots d r_f}{\int_{-\infty}^{\infty} e^{-\beta \epsilon_1} dp_1 \int \dots \dots}$$

CANCEL (as expected for p_i indep)

$$\bar{\epsilon}_1 = \frac{\int e^{-\beta \epsilon_1} \epsilon_1 dp_1}{\int e^{-\beta \epsilon_1} dp_1} = -\frac{\partial}{\partial \beta} \ln \left(\int e^{-\beta \epsilon_1} dp_1 \right)$$

4/28/05
→
extra
2/17/05

USED (1); NOW USE (2)

$$\int_{-\infty}^{\infty} e^{-\beta b p_1^2} dp_1 \xrightarrow{y \equiv \beta^{1/2} p_1} \beta^{-1/2} \int e^{-by^2} dy$$

$$\ln(\dots) = -\frac{1}{2} \ln \beta + \underbrace{\ln \int e^{-by^2} dy}_{\text{NO } \beta \rightarrow \text{IRREL.}}$$

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

⇒ $\bar{\epsilon}_1 = \frac{1}{2} kT$

⇒ ANY QUADR. TERM IN E CONTRIBUTES $\frac{1}{2} kT$ TO \bar{E}

⇒ b IRREL ⇒ TRUE FOR ANY MASS ($b = \frac{1}{2m}$)
" ANY SPR. CONST. ($b = \frac{1}{2} k$)

EX MON IG: $E = \frac{1}{2m} \sum_{i=1}^N (p_x^2 + p_y^2 + p_z^2)$

$$\bar{E}_{\text{PART.}} = \frac{3}{2} kT \quad \bar{E} = \frac{3}{2} NkT = \frac{3}{2} DRT$$

$$C_V = \frac{3}{2} R \quad \gamma = \frac{C_P}{C_V} = \frac{C_V + R}{C_V} = \frac{5}{3} = 1.666 \dots$$

QUAD TERMS

DIAT IG: $E = \sum^N \left(\frac{p^2}{2m} + \frac{1}{2} k (L_x^2 + L_y^2) \right)$

$$\bar{E} = \frac{5}{2} NkT \quad C_V = \frac{5}{2} R \quad \gamma = \frac{7}{5} = 1.40$$

cf TABLE

NOTE: C_V } QM

He (NOBLE) : MONATOMIC \Rightarrow 3 TRANSL DOF

(IF IG!) $C_V = \frac{3}{2}R$ $C_p = \frac{5}{2}R$ $\gamma = \frac{5}{3} = \underline{1.666}$

H₂, O₂ : DIAT. \Rightarrow 3 TRANSL + 2 ROT. = 5 QUAD DOF

$C_V = \frac{5}{2}R$ $C_p = \frac{7}{2}R$ $\gamma = \frac{7}{5} = \underline{1.40}$

\Rightarrow C_V COUNTS PLACES TO PUT E

\Rightarrow WORKS VERY WELL (CF TABLE)

MYSTERY: FOR H₂ WHY NOT

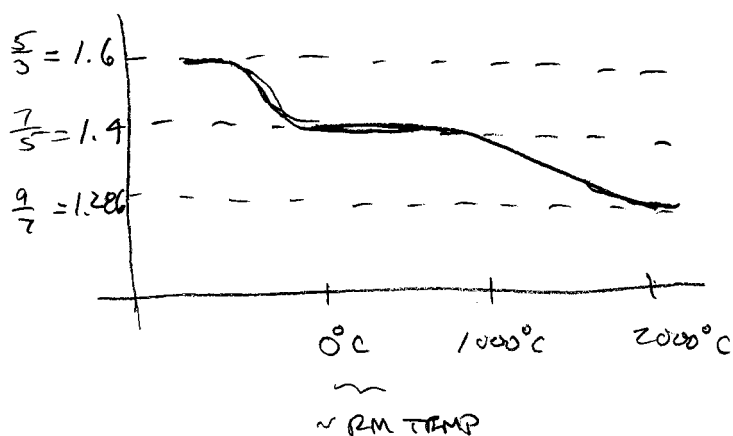


$\Rightarrow 3 + 2 + 2 = 7$?

\uparrow
KE + PE

$\Rightarrow \gamma = \frac{9}{7} = 1.286$

IN FACT:



FOR $T \sim 2000^\circ\text{C}$ CAN SEE OSC.

$\gamma = 9/7$

FOR $T \sim \text{RM TEMP}$. OSC FREEZES OUT $\Rightarrow \gamma = 7/5$

$kT \ll \Delta E_{\text{osc}}$

(one excitation costs too much \rightarrow doesn't happen)

FOR $T \ll \text{RM TEMP}$

$\gamma \rightarrow \frac{5}{3}$

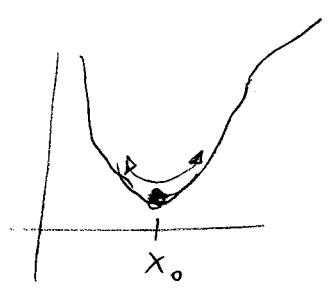
\Rightarrow ROTATIONS FREEZE OUT

$kT \ll \Delta E_{\text{rot}}$

\Rightarrow CAN EST. ΔE FROM QM BY WATCHING DOF'S FREEZE OUT OF C_V (THEN $kT \lesssim \Delta E$)

C_V SOLIDS

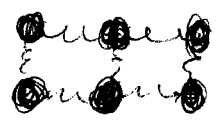
NEAR MIN OF ANY POT U
(EQUIL. POSITION) $\text{const} > 0$



$U(x) \sim U_0 + \frac{1}{2} U_0'' (x-x_0)^2 + \dots$ IF X 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 MOLECULES, EACH IN 3d HARM OSC

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

↓
 just say

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

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

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

—
—
— $\frac{3}{2} \hbar \omega$
— $E_0 = \frac{1}{2} \hbar \omega$

skip

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 U

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)

[Table
pg 254]

$T \approx$ ROOM TEMP WORKS GREAT

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

(slightly larger) but note diamond

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.

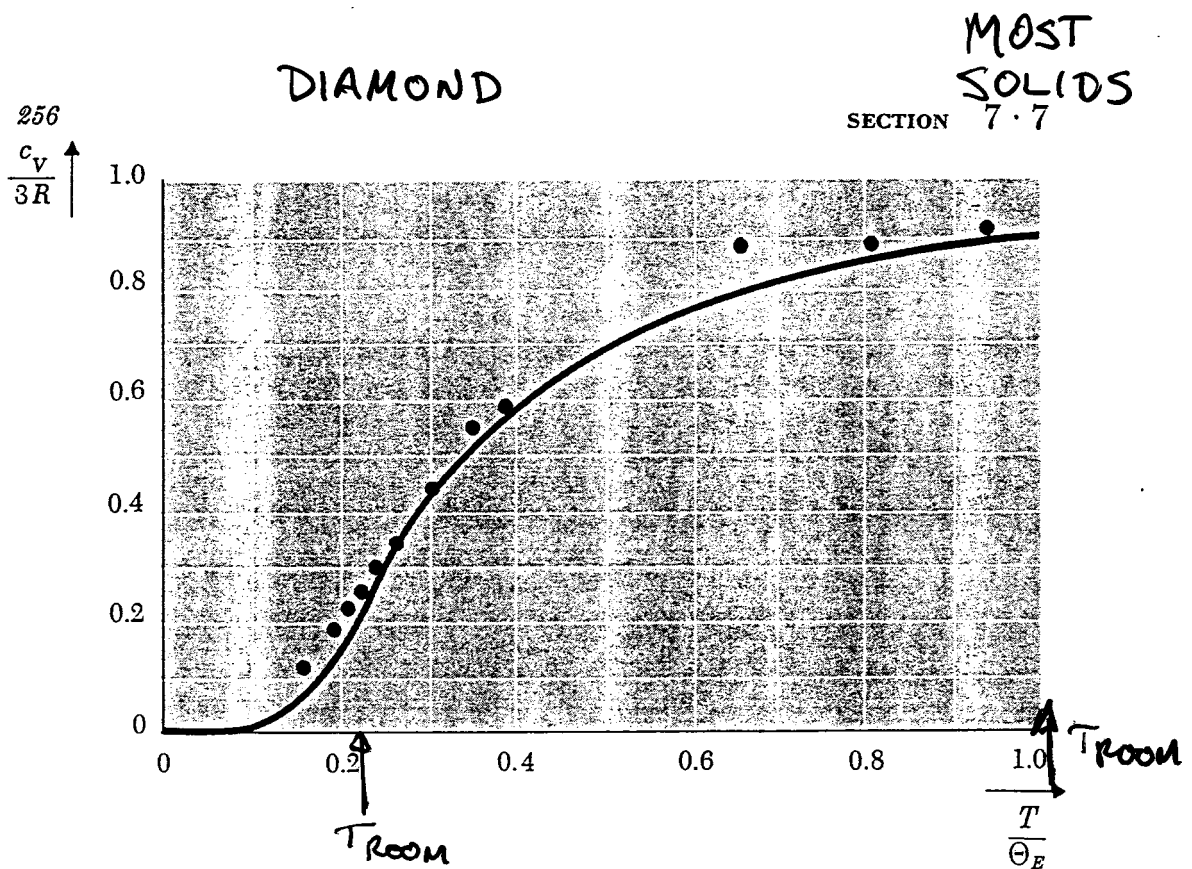


Fig. 7·7·1 Temperature dependence of c_v according to the Einstein model. The points are experimental values of c_v for diamond, the fit to the curve being achieved by choosing $\Theta_E = 1320^\circ\text{K}$ (after A. Einstein, *Ann. Physik*, vol. 22, p. 186 (1907)).

2 QUESTIONS

- (1) CAN WE UNDERSTAND DIAMOND?
- (2) WHY DOESN'T $C_V \rightarrow 0$ FOR $T \rightarrow 0$?

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

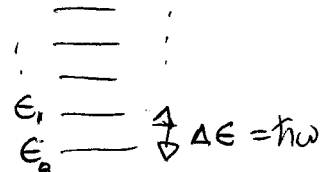
BOTH PROBLEMS AT LOW T

QM: 1 OSCILLATOR in eqn of sp at T (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 BOTH LOW $\} \}$ HIGH T (UNTIL HARM OSC APPROX BREAKS)

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

$$\text{ie } \beta\hbar\omega \equiv \frac{\hbar\omega}{kT} \ll 1$$

} note the value of
the exp. depends on
this directly

TAYLOR SERIES:

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

(SMALL ARG)

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

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

↑

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. theorem
fails)

RECALL

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

$$\ln Z \approx \ln \left\{ e^{-\frac{1}{2}\beta \hbar \omega} \frac{1}{1 - e^{-\beta \hbar \omega}} \right\}^3 \approx -\beta(\frac{1}{2}\hbar\omega)$$

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

(1 osc)
T → 0

MACRO SYS: SOLID

⇒ MANY K_i 's (AND ω_i 's)

SIMPLEST MODEL: (EINSTEIN)

⇒ ALL SAME

1 MOLE

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

EACH MOLECULE ⇒ 3 OSC

(just add energies).

V would come in via ω (compress → diff K etc)

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"

≡ property of specific solid
(const, dep. on ω)
↳ $\beta \hbar \omega = \frac{\hbar \omega}{k T} = \Theta_E / T$

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

- Θ_E = PROPERTY OF SUBSTANCE

- VALUE GIVES T WHEN CLASSICAL APPROX OK

($T \sim \Theta_E$ when $kT \sim \hbar \omega = \Delta E$) (ie 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) $\left\{ \begin{array}{l} \text{PLOTTED VS } T/\Theta_E \Rightarrow \text{APPLIES} \\ \text{TO ALL SOLIDS} \end{array} \right\}$

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

DIAMOND ?

MOST SOLIDS: $\Theta_E \sim RM$ TEMP
 ($uT/\Theta_E \sim 1$ AT " u ")

CF PLOT:
 already at 90%
 of classical limit
 $C_V/3R = 1$

DIAMOND: HARD, K ; $\ddagger W$; LARGE

ΔE BIG

$$W = \sqrt{K/m}$$

$$\Theta_E \sim 1300^\circ K$$

\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

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

(could talk about distance gas of time)

(... .. T. is)

(1) can see need for QM (2) can est. ΔE