Key points from recent lectures

microscopic theory of random walk explains $\frac{L^2}{D}$ time scale
where D is some dissipation coefficient

microscopic theory of ideal gas described by $PV = NkT$ gave

$$\left\langle \frac{1}{2} m v^2 \right\rangle = \frac{1}{2} m \langle v^2 \rangle = \frac{1}{2} m v_{rms}^2 = \frac{3}{2} kT$$

discovered connection between T of ideal gas and average kinetic energy

this discovery in turn suggests and leads to the <u>equipartition theorem</u>

$$U_{thermal} = \underset{\substack{\uparrow \\ \#\text{ molecules}}}{N} \cdot \underset{\substack{\uparrow \\ \#\text{ degrees of freedom} \\ \text{per molecule}}}{f} \cdot \frac{kT}{2} \leftarrow \text{temp of equil. system}$$

f = # of degrees of freedom
= # quadratic terms in energy of molecule

$$\begin{aligned} E &= \left.\frac{1}{2} m v_x^2 + \frac{1}{2} m v_y^2 + \frac{1}{2} m v_z^2 \right. \\ &\quad \left. + \frac{1}{2} I_x \omega_x^2 + \frac{1}{2} I_y \omega_y^2 + \frac{1}{2} I_z \omega_z^2 \right\} \text{center of mass terms} \\ &\quad + \sum_j \left\{ k_j (x_j - x_{j0})^2 + \frac{P_j^2}{2m} \right\} \Big\} \text{ internal vibrational terms} \end{aligned}$$

Broad Implications of kT

Equipartition thm suggests there is basic unit of thermal energy $\frac{kT}{2}$ or just kT

For <u>engineers</u>, you have to use energy to overcome noise, vibrations associated with kT

can grade quality of engineering by ratio $\frac{E}{kT}$ where E is energy to change something

For example, to store bit of memory in computer at room temp, $E/kT \gtrsim 10^5$ lots of room for improvement

going to small T means less energy to store, retrieve information

<u>Biology</u>: cells have to spend of order kT or more to overcome molecular chaos

example: neurons in brain operate by separating charge across lipid bilayer.

$$qV \simeq kT \Rightarrow V \simeq \frac{kT}{e} \simeq \frac{\left(1.4 \cdot 10^{-23} \frac{J}{K}\right)(300K)}{1.6 \cdot 10^{-19} \text{Coul}}$$

$$\simeq 30 mV$$

so neurons operate close to possible limits set by kT

Key point continued

Equipartition makes predictions of heat capacity at constant volume

$$C_V = \frac{dU_{thermal}}{dT} = N \cdot f \cdot \frac{k}{2}$$ indep of tem

for one mole of substance, $N = N_A$, $N_A k = R$ and

$$C_V = \frac{3}{2}R$$ atomic gas

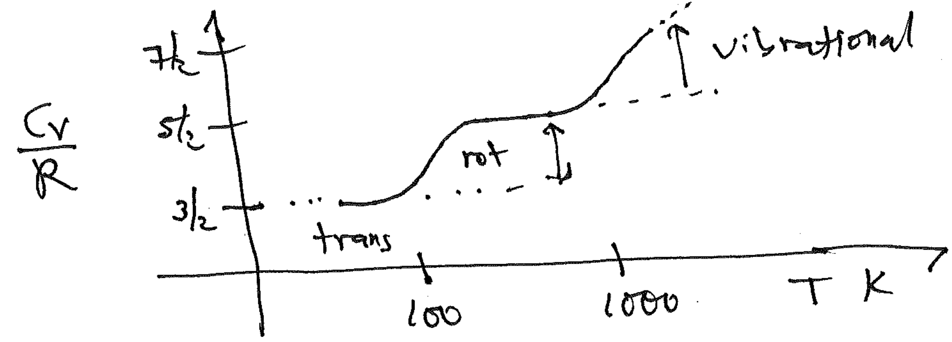
$$= \frac{7}{2}R$$ diatomic molecules

$$= 3R$$ crystalline solid — law of Dulong-Petit

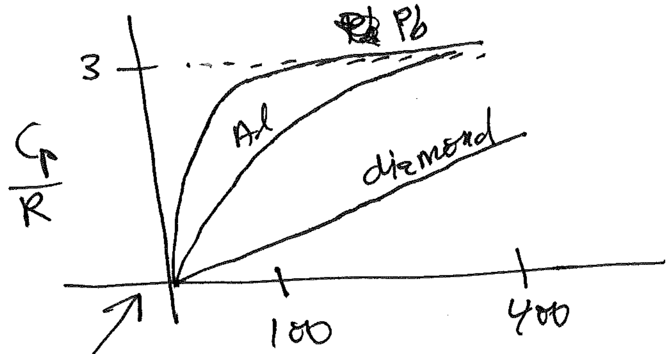
these are approximately correct at higher temperatures but fail badly as T decreases. Seems that $f = f(T)$ varies with temperature, decreasing ("freezing out") as T decreases.

$C_V(T)$ Data

Show slide on projector



data for one mole of H_2



crystalline heat capacities

note how $C_P \to 0$ as $T \to 0$

this is general result, holds for all substances

aside: diamonds have highest known thermal diffusivity κ for insulator (feels cold to lips), valuable for coating electronics to remove heat

we will derive <u>all</u> features of these plots over the semester, great triumph of statistical physics + QM

please memorize these plots: vertical scale, horizontal scale crucial data to know

How To Sound Smart At A Cocktail Party of Scientists

Independently of these technical details and new concepts, have exposed you to subtle important idea: time scale or length scale or energy scale

To sound smart among scientists, ask a simple but devastating question: "<u>what sets the scale?</u>"

e.g., why are atoms as big as they are? $a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2}$

why are people (animals) of order meters?

what sets the size of planets? of their orbits?

why did evolution take ~2 billion years to produce multicellular life?

These scale questions often to profound difficult fascinating questions.

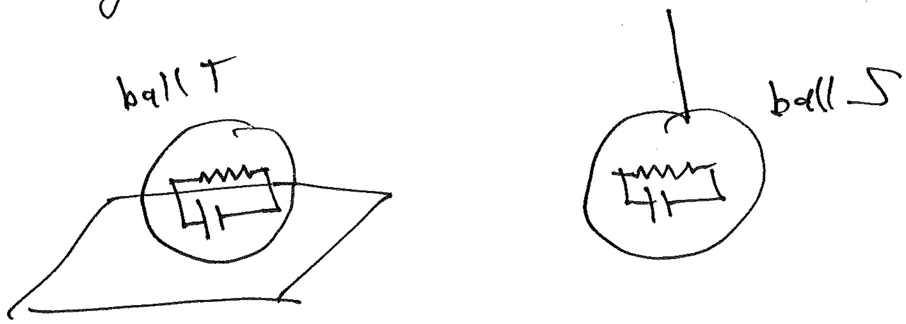
Section 1.5 of Schroeder

Heat, Work, Energy

will go quickly since Schroeder's discussion is clear and insightful and many of you have seen some of this before.

ideas are historically enormously important
  led to industrial revolution, humans no longer needed
    slaves or animals for labor
  gas expansion-compression heart of auto, airplane industries
  metaphor for many systems we will study later
  this semester

PRS Question to start you thinking about these concepts



two <u>identical</u> steel balls, say ~ 10 cm in diameter

one rests on table (label T)

one hangs from string (label S)

identical amounts of energy added to each ball by internal resistive heating. [Is this heat or work?]

Afterwards, which ball is hotter?

assume vacuum, table + string ideal insulators

Heat vs Work

Various actions can increase internal energy of an equilibrium system, $U_{thermal}$

change caused by temp difference: **heat** form of energy

conduction
convection
radiation

any other change defined to be **work** form of energy

~~chose~~
heat and work involve transfers of energy from one place to another, can not talk about "heat in object", or "energy in object from work".

conservation of energy implies

$$\underbrace{\Delta U_{thermal}}_{\text{change in internal energy}} = \underbrace{Q}_{\text{heat is positive if it increases }\Delta U} + \underbrace{W}_{\text{work is positive if it increases }\Delta U}$$

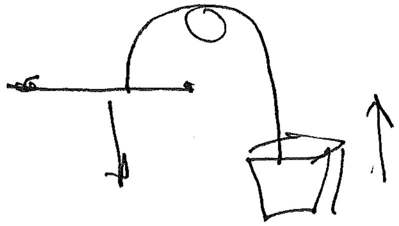
this is an arbitrary sign convention, watch out for other conventions

Units of heat, work: joule and calorie

$1\ \text{cal} \simeq 4{,}2\ \text{J}$

$1\ \text{Cal} = 1\ \text{kcal} \simeq 4{,}200\ \text{J} \Rightarrow$ food calorie

exercise room



weight 100 lb, move ~1m

work done in Calories is about

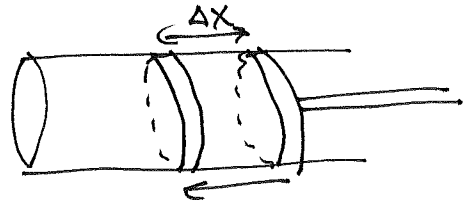
$$\underbrace{\underbrace{100\,\text{lb}\times\frac{0{,}45\,\text{kg}}{\text{lb}}}_{m}\times\underbrace{10\,\frac{\text{m}}{\text{s}^2}}_{a}}_{F}\times\underbrace{1\,\text{m}}_{\substack{\text{distance}\\ x}}\times\frac{1\,\text{cal}}{4{,}2\,\text{J}}\times\frac{1\,\text{Cal}}{10^3\,\text{cal}}$$

$$\simeq \frac{1}{10C}$$

~~10 reps~~ 3 sets of 10 reps burns only ~ 3 Cal ☹

hard to lose weight this way

Compression/Expansion Work



some substance exerts pressure on enviroment, either molecular collisions (liquids, gases) or chemical bonds (solids)

<u>compress</u> substance <u>adds</u> work to internal energy. How much?

move piston distance Δx

$$W = F\cdot\Delta x = (PA)\cdot\Delta x = P\,(A\cdot\Delta x)$$

$$\boxed{W = -P\,dV}$$

compressing ~~gas~~ substance mean $\Delta V < 0$, so need minus sign to get positive increase in energy

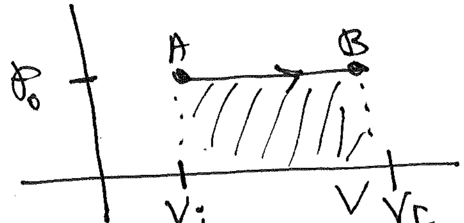
have to assume <u>quasistatic</u> process, slow compared to relaxation time for relative motion so always in equil. slower than speed of sound works in practice

general formula: $W = -\int_{V_1}^{V_2} P(V)\,dV$

provided quasistatic <u>and</u> P known $f^{\underline{n}}$ of V

Work Out Various Cases

(1) isobaric ("constant pressure") process



expansion

$$U = N \cdot f \cdot \frac{kT}{2} = \frac{f}{2}NkT = \frac{f}{2}PV$$

$$\boxed{\Delta U = \frac{f}{2}\Delta(PV)} = \frac{f}{2}(P_fV_f - P_iV_i)$$

$$= \frac{f}{2}(V_f - V_i)P_0 > 0$$

$$\boxed{\Delta U = Nf\frac{k}{2}\Delta T}$$

$$\Delta T = \frac{\Delta U}{Nf\left(\frac{k}{2}\right)} = \frac{V_f - V_i}{V_i} > 0$$

temperature increases even though gas is expanding!

easier to calculate ΔT from ideal gas law

$$P_0V_i = NkT_i \qquad P_0V_f = NkT_f$$

$$T_f = \left(\frac{V_f}{V_i}\right)T_i \Rightarrow \Delta T = T_f - T_i = = T_i\left(\frac{V_f - V_i}{V_i}\right) ✓$$

$$\boxed{W = -\int_{V_i}^{V_f} P(V)\,dV = -P_0\int_{V_i}^{V_f} dV = -P_0(V_f - V_i)} < 0$$

work is negative since gas expands

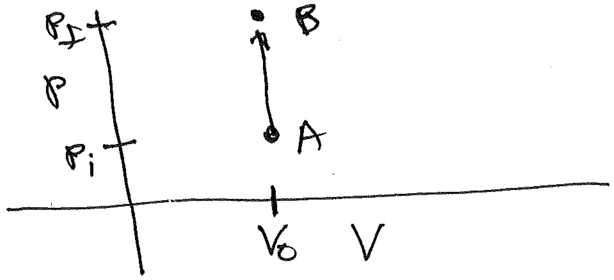
$$\boxed{Q = \Delta U - W = \frac{f}{2}(V_f - V_i)P_0 - \left[-P_0(V_f - V_i)\right] = \left(1 + \frac{f}{2}\right)P_0(V_f - V_i)}$$

> 0

Isobaric Case Continued

so have to add heat to gas during isobaric expansion, heat increases U and supplies work so physically have to bring object hotter than gas temp T_i to cause heat to transfer.

isochoric process (constant volume)



$$\Delta U = \frac{f}{2}(P_f V_f - P_i V_i) = \frac{f}{2} V_0 (P_f - P_i) > 0$$

$\Delta T > 0$ sine $\Delta U = N \frac{f}{2} k \Delta T$

$PV = NkT$ with V, N constant $\Rightarrow P \propto T$

so $T_f = \left(\frac{P_f}{P_i}\right) T_i \quad \Delta T = \left(\frac{P_f - P_i}{P_i}\right) T_i$

where $\boxed{T_i = \frac{P_i V_0}{Nk}}$

$$\boxed{W = -\int_{V_0}^{V_0} P(V)\,dV = 0}$$ no work done

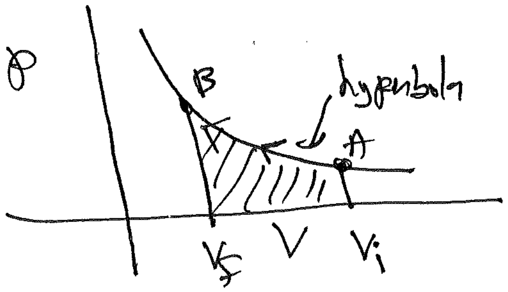
$$\boxed{Q = \Delta E - W = \Delta E = \frac{f}{2} V_0 (P_f - P_i) > 0}$$

so have to add heat to increase pressure

again have to bring hot object into contact with gas

object has to be hotter than max $T = T_f = \left(\frac{P_f}{P_i}\right) T_i$

Isothermal Process T con



$$PV = NkT$$

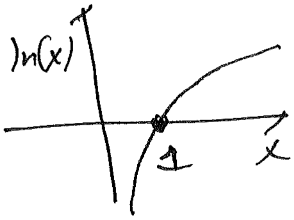
$$P = \frac{NkT}{V} = \frac{\text{const}}{V}$$

$$\Delta U = N\frac{f}{2}k\Delta T = 0$$ no energy change
no temp change

$$\Rightarrow \Delta T = 0$$

note: isothermal process has to be extremely slow, have to let T equil ~~heat~~ after each little step, utterly impractical to use in engineering, physics

$$W = -\int_{V_i}^{V_f} P(V)\,dV = -NkT\int_{V_i}^{V_f}\frac{dV}{V}$$



$$\boxed{W = NkT\ln\left[\frac{V_i}{V_f}\right]} > 0$$ since $V_i > V_f$
$\ln(x) > 0$ if $x > 1$

compression should increase energy but not here

$$\boxed{Q = \Delta U - W = -W = -NkT\ln\left[\frac{V_i}{V_f}\right] < 0}$$

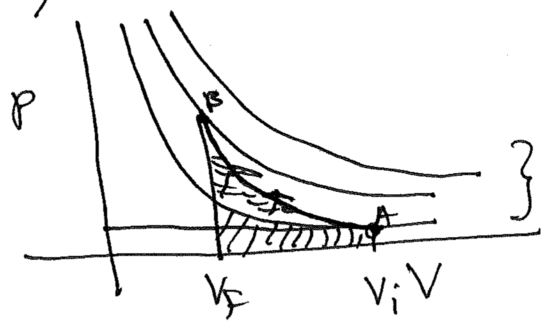
work done causes heat to transfer out of gas so need to apply cooler object to gas at just right way to maintain constant T

Adiabatic process, no heat transfer

has to occur rapidly, faster than relaxation times

$\Delta U = Q + W = W$ if $Q=0$

so if compression, $W > 0 \Rightarrow \Delta U > 0 \Rightarrow \Delta T > 0$



adiabatic curve has to lie <u>above</u> isothermal curve during compression since have to jump to higher temperature

adiabatic compression does more work than isothermal compression over same volume change $V_i \rightarrow V_f$

can derive form of curve

$$U = N \frac{f}{2} kT \Rightarrow dU = \frac{Nfk}{2} dT = -P\,dV$$

since $Q=0$, change in energy comes from work done.

but $PV = NkT \Rightarrow$ $dU = \frac{Nfk}{2} dT = -NkT \frac{dV}{V}$

so $\frac{f}{2} \frac{dT}{T} = -\frac{dV}{V} \Rightarrow \frac{f}{2} \ln\left(\frac{T_f}{T_i}\right) = \ln\left(\frac{V_i}{V_f}\right) \Rightarrow V_f T_f^{f/2} = V_i T_i^{f/2}$

Adiabatic process continued

so $V T^{f/2} = \text{const}$ but $PV = NkT$

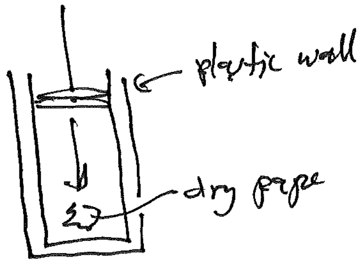
$$T = \frac{PV}{Nk}$$

$$\Longrightarrow \boxed{V^{\gamma} P = \text{const}}$$ adiabatic process

$\gamma = \frac{f+2}{f}$ = "adiabatic exponent"

$$\underset{\overset{\nearrow}{f=\infty}}{1} \le \gamma \le \underset{\nwarrow f=3 \text{ for atoms}}{\frac{5}{3}}$$

$\gamma = \frac{7}{5}$ for diatomic molecules



Example "fire syringe demo"

for air, $f = 5$, $\gamma = \frac{7}{5}$

$$T_f = T_i \left(\frac{V_i}{V_f}\right)^{2/f} \cong 300\,K\,(10)^{2/5} \simeq 750\,K \text{ hot!}$$

kindling temperature of paper $\simeq 520K$ so paper ignites

Diesel engine: compression ratio $\simeq 20 \Longrightarrow T_f \simeq 1000K$

Fuel droplets spontaneously combust

Adiabatic Processe and Speed of Sound

Isaac Newton in his Principia Mathematica tried to calculate speed of sound from first principle and got answer for air off by $\sim 10\%$

Reason is he didn't realize sound propagation was so fast so as to be adiabatic process

$$c_s = \sqrt{\frac{P}{\rho}}$$

Newton

$$c_s = \sqrt{\frac{\gamma P}{\rho}} = \sqrt{\frac{\gamma kT}{m}}$$

adiabatic process

since $\rho = \frac{(Nm)}{V}$

$$\frac{P}{\rho} = \frac{PV}{Nm} = \frac{kT}{m}$$

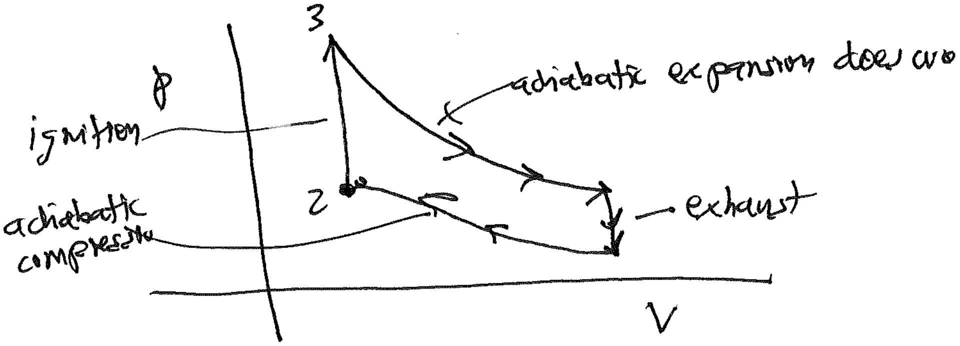
$\gamma \cong \frac{7}{5}$ for air, makes a difference

so degrees of freedom f also show up in speed of sound through adiabatic exponent γ

Heat Engines

Most important application of these ideas to cycles in P-V plane, use heat to do work (engine) or work to remove heat (refrigerator)

E.g., combustion engine in car can be approximated by so-called Otto cycle, see Fig. 4.5 on p. 131 of Schroed

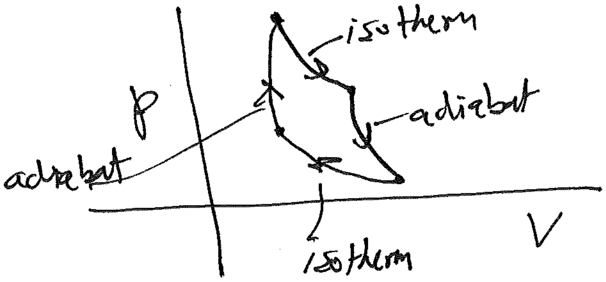


$$\text{efficiency} = \frac{\text{work done}}{\text{heat supplied}} \leq \underbrace{1 - \frac{T_c}{T_h}}_{\text{theoretical max. efficiency}}$$

T_c = temp cold reservoir

T_h = temp. hot reservoir

can achieve theoretical efficiency with utterly impractical but insightful Carnot cycle



Section 1.6 Heat Capacities

Now we know 1st law of thermo $\Delta U = Q + W$

can go back + discuss heat capacities

$$C = \frac{Q}{\Delta T} = \frac{\Delta U - W}{\Delta T}$$

C is ambiguous because of W, need to specify circumstances

If constant volume, $W = PdV = 0$ so

$$C_V = \frac{\Delta U}{\Delta T} \sim \left(\frac{dU}{dT}\right)_V \leftarrow \text{means hold } V \text{ constant}$$

"energy capacity" better name

Another common case is constant pressure

$$C_P = \frac{Q}{\Delta T} = \frac{\Delta U - W}{\Delta T} = \frac{\Delta U + PdV}{\Delta T}$$

$$\boxed{C_P = \frac{dU}{dT} + P\frac{dV}{dT}} = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P$$

for ideal gas, $V = \frac{NkT}{P} \Rightarrow P\left(\frac{\partial V}{\partial T}\right)_P = Nk$

$$\boxed{C_P = C_V + Nk}$$ ideal gas

Heat Capacity Continued

But for ideal gas $C_V = Nf\frac{kT}{2}$

$$C_p = Nf\frac{kT}{2} + Nk = \left(\frac{f}{2}+1\right)Nk = \gamma\frac{Nkf}{2}$$

conclude $\boxed{\frac{C_p}{C_V} = \gamma}$

so γ more useful than we thought, gives ratio heat capacities

Ruchardt experiment: to measure $C_p/C_V = \gamma$ for gas

Note: C_V, C_p proportional to amount of material present, "extensive" variable or quantity

often useful to work with specific heat lower case c

$$c_V = \frac{C_V}{m} \quad m = \text{mass of system}$$

don't confuse the two quantities

Latent Heat At Phase Transitions

Need one more concepto to ~~relate to~~ combine with heat capacity to solve many practical problems involving heat and work: latent heat, 3 kinds

solid → gas	sublimation	inverse called deposition
solid → liquid	melting	freezing
liquid → gas	vaporization	condensation

at these phase transitions, $\Delta T = 0$ so $C = \frac{Q}{\Delta T} = \infty$!

latent heat $= \frac{Q}{m}$ heat to convert unit mass from one phase to another

usually constant pressure assumed

$$L_{ice \to water} \simeq 3.3 \cdot 10^5 \, \frac{J}{kg}$$

$$L_{water \to steam} \simeq 2.3 \cdot 10^6 \, \frac{J}{kg} \simeq 7 \times L_{ice \to water} \Big\} \text{why bigger?}$$

these are much larger than specific heat of H_2O

1 kg from T=0°C to 100°C $Q \simeq 4.2 \cdot 10^5 \, J/kg$

Worked example: heat capacity and latent heat

Iron meteor found in Antarctica

Microscopic examination shows meteor was completely liquified upon entering atmosphere

Question: what was minimum speed of meteor if initial temperature $T_i = -125°C$ upon entering atmosphere.

energy needed to warm meteor to melting temperature and to melt meteor

energy comes from kinetic energy $\frac{1}{2}mv^2$

data: Fe melts at $1808°C$ $\qquad T_{boiling} \simeq 3023°C$

$L_{solid \to liq} \simeq 2.9 \cdot 10^5 \frac{J}{kg}$

$T_{liq \to gas} \simeq 6.3 \cdot 10^6 \frac{J}{kg}$ $\qquad C_p \cong 450 \frac{J}{kg\text{-}°C}$

energy to warm: $m \cdot (T_{melt} - T_i) C_p$

energy to melt: $m \cdot L_{solid \to liq}$

$\Delta T = T_{melt} - T_i$
$= 3023 - (-125)$
$\simeq 3148 \simeq 3200 K$

$$m\left[L_{s \to l} + \Delta T C_p\right] \simeq \frac{1}{2}mv^2$$

mass divides out

$$v \gtrsim \sqrt{2(C_p \Delta T + L_{s \to l})} \simeq 2\,\frac{km}{s}$$