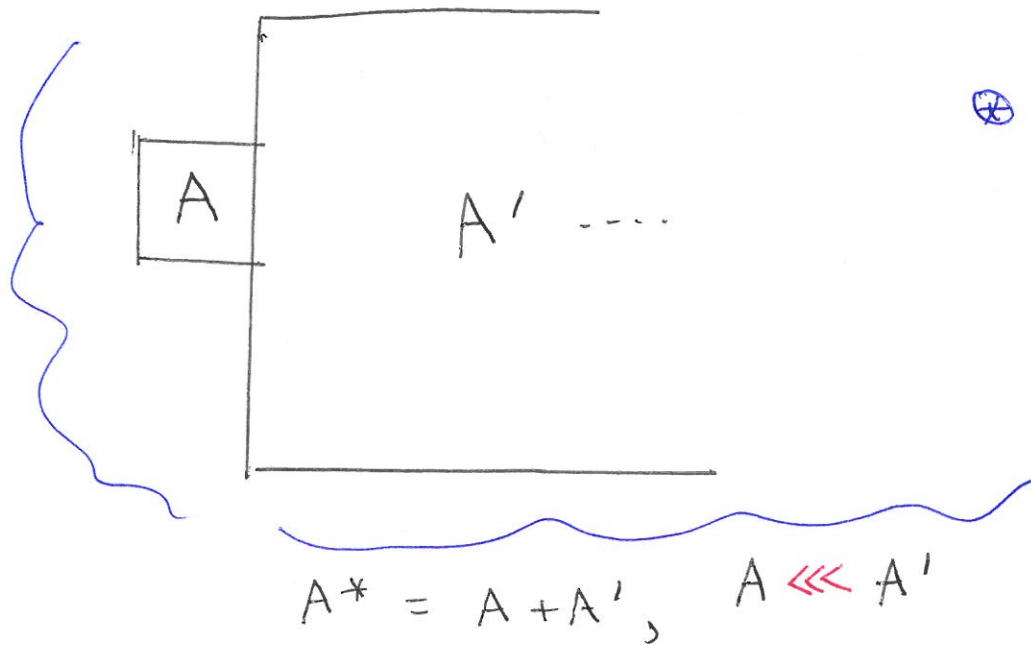


Fundamentals of Engineering Physics 2019

Week 13.

4.5. System in Contact with a Heat Reservoir



- ⊕ Consider a macroscopic system "A" in thermal contact with (free to exchange energy with) a much larger macroscopic system "A'".

- ⊗ What is the probability " P_r " of finding the system A in any one particular state "r" of energy E_r ?

From Eq. (5), $P(E) = \text{const} * \Omega(E) \Omega'(E^* - E)$ where

E is specified, but not " r ". (There can be many states with energy E).

∴ $P_r \propto \Omega'(E^* - E_r)$ (44) ($\because \Omega(E_r) = 1$ by definition).

⊛ Now, $\ln \Omega'(E^* - E_r) = \ln \Omega'(E^*) - \left[\frac{\partial}{\partial E'} \ln \Omega' \right] E_r + \dots$
 (expand Ω' around $E' = E^*$
 because $E_r \ll E^*$)

$$= \ln \Omega'(E^*) - \beta E_r \quad (46)$$

or

$$\Omega'(E^* - E_r) = \Omega'(E^*) e^{-\beta E_r} \quad (48)$$

and

$$P_r = C_1 e^{-\beta E_r} \quad (49)$$

where

$$\beta = \frac{1}{k_B T} \quad \text{Temperature of Reservoir}$$

⊛ Compare the probability of finding system A in any two of its states with different E_r .

Higher $E_r \rightarrow$ Lower $(E^* - E_r) \rightarrow$ Lower $\Omega'(E^* - E_r) \rightarrow$ Lower P_r !

Lower $E_r \rightarrow$ Higher $(E^* - E_r) \rightarrow$ Higher $\Omega'(E^* - E_r) \rightarrow$ Higher P_r !

$$P_r = C \underline{e^{-\beta E_r}} = e^{-\beta E_r} / \sum_r e^{-\beta E_r}$$

(51).

Boltzmann factor,

"Canonical Distribution"

An ensemble of systems all of which are in contact with a heat reservoir of temperature T ($\beta \equiv 1/k_B T$) is called the Canonical Ensemble.

⊛ Read Summary of Definitions on Page 176.

Homework

Problem 4.8 on page 182.

" 4, 28 on page 189.

Ch. 6. Canonical Distribution in Classical Approx.

⊛ Classical Approximation is valid if quantum mechanical effects are not important (i.e., negligible).

* Discreteness of Energy Level
not important

if :

$$k_B T \gg \Delta E$$

(1)

* Uncertainty Principle
not important

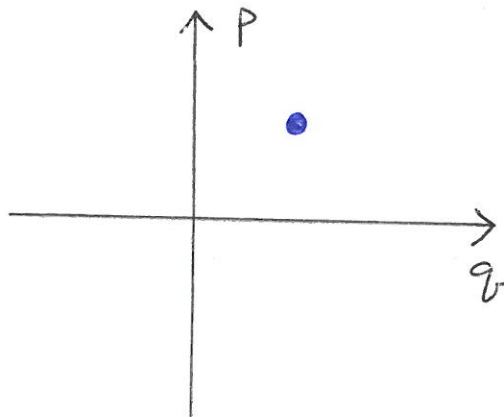
if

$$S_0 p_0 \gg \hbar$$

(3)

localization, momentum
of a particle.

Classical Description in Phase Space



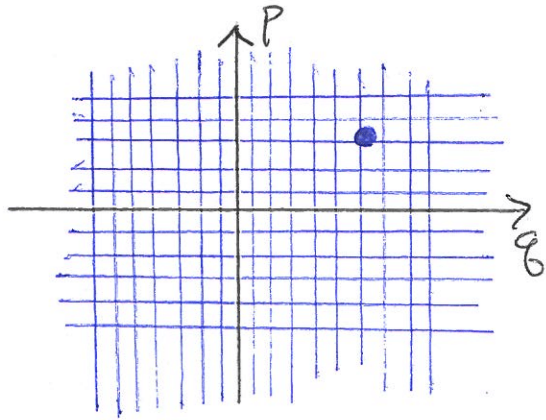
→ "phase space of "2f" dimensions"

$$\{q_1, q_2, \dots, q_f; p_1, p_2, \dots, p_f\}$$

"f" : number of degrees of freedom.

($f = 3N$ for N ptl's system in 3d).

The state of a system in classical mechanics can be described by specifying the particular cell r in phase space in which the coordinates and momenta of the system are found.



- The cell size $h_0 = \delta p \delta q$ can be made arbitrarily small in classical mechanics.
- But $h_0 < h$ would violate the uncertainty principle in quantum mechanics.

If an isolated system is in equilibrium, it is found with "equal probability" in each one of its accessible states, i.e., in each one of its accessible cells in phase space

— Recall: "Postulates of Equal A Priori Probabilities."

#

Example

In order to illustrate the classical notions in a very simple case, let us consider a single particle moving in one dimension under the influence of no forces, but confined within a box of length L . If we denote the position coordinate of this particle by x , the possible positions of the particle are then restricted by a condition of the form $0 < x < L$. The energy E of the particle of mass m is merely its kinetic energy so that

$$E = \frac{1}{2}mv^2 = \frac{1}{2}\frac{p^2}{m}$$

where v is the velocity and $p = mv$ is the momentum of the particle. Suppose that the particle is isolated and is thus known to have a constant energy in some small range between E and $E + dE$. Then its momentum must lie in some small range dp about the possible values $p = \pm\sqrt{2mE}$. The region of phase space accessible to this particle is then the one indicated by the dark areas

shown in Fig. 6.3. If phase space has been subdivided into small cells of equal size $\delta x \delta p = h_0$, this region contains a large number of such cells. These represent the accessible states in which the system can be found.

Suppose that the particle is known to be in equilibrium. Then the statistical postulate asserts that the particle is equally likely to be found with its coordinate x and momentum p in any one of the equal-size cells contained within the dark areas. This implies that the particle is as likely to have a momentum in the range dp near $+\sqrt{2mE}$ as in the range dp near $-\sqrt{2mE}$. It also implies that the position coordinate x of the particle is equally likely to lie anywhere within the length L of the box. For example, the probability that the particle is located in the left third of the box is $\frac{1}{3}$ since the number of accessible cells for which x lies in the range $0 < x < \frac{1}{3}L$ is one-third of the total number of accessible cells.

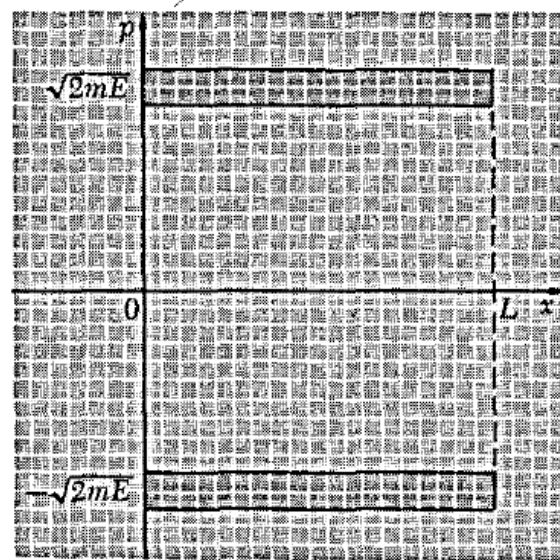


Fig. 6.3 Classical phase space for a single particle free to move in one dimension and confined within a box of length L . The particle, specified by a coordinate x and a momentum p , has an energy in the range between E and $E + \delta E$. The states accessible to the particle are indicated by the cells contained within the dark areas.

* Probability Density : $\mathcal{P}(q_1, \dots, q_f; p_1, \dots, p_f) dq_1 dq_2 \dots dq_f dp_1 \dots dp_f$

" The probability that the system A is found with q_i ~~within~~ between q_i and $q_i + dq_i$ ($i=1, \dots, f$) and with p_i between p_i and $p_i + dp_i$ ($i=1, \dots, f$), "

For canonical ensemble in contact with heat reservoir with temperature T ,

this is

$$\mathcal{P}(q_1, \dots, p_f) dq_1 \dots dp_f \propto e^{-\beta E_r} dq_1 \dots dp_f$$

(10),

(*) Note the difference between canonical ensemble and microcanonical ensemble in the previous slide.

6.2. Maxwell Velocity Distribution.

IV-37

(*) Consider an ideal gas in equilibrium at temperature " T_0 ".

Since $\epsilon = \frac{1}{2} m |\vec{v}|^2 = \frac{1}{2} \frac{|\vec{p}|^2}{m},$ (12)

$$\mathcal{P}(\vec{r}, \vec{p}) d^3\vec{r} d^3\vec{p} \propto e^{-\beta(p^2/2m)} d^3\vec{r} d^3\vec{p} \quad (14)$$

or

in (\vec{x}, \vec{v}) -space,

$$* \quad \mathcal{P}'(\vec{r}, \vec{v}) d^3\vec{r} d^3\vec{v} \propto e^{-\frac{1}{2} \beta m v^2} d^3\vec{r} d^3\vec{v} \quad (15)$$

(*) $f(\vec{v}) d^3\vec{v}$: mean number of particles which have a velocity between \vec{v} and $\vec{v} + d\vec{v}$.

(15) \rightarrow $f(\vec{v}) d^3\vec{v} = C e^{-\frac{1}{2} \beta m v^2} d^3\vec{v}$ "Maxwell Velocity Distribution" (17).

$$f(\vec{v}) d^3\vec{v} = n \left(\frac{\beta m}{2\pi} \right)^{3/2} e^{-\frac{1}{2} \beta m v^2} d^3\vec{v} \quad (21)$$

- The constant "C" has been determined by requiring $\int f(\vec{v}) d^3\vec{v} = n$ particle number density in configuration space.
- "C" $\int e^{-\frac{1}{2} \beta m v^2} d^3\vec{v} = n$, as explained on page 234.

- $\int_{-\infty}^{\infty} e^{-\alpha x^2} dx = \sqrt{\frac{\pi}{\alpha}}$ is a very useful identity.

- * Read derivations of useful integral formulas on pg 367-369 !
- * Read Sec. 6.3 on pg 235 - 238.

Make sure you understand the meaning of :

"distribution of speeds", "most probable speed", ~~the~~ "mean speed", and
 "the root-mean-square speed".

6.5, The Equipartition Theorem

⊗ Consider a system for which the energy can be expressed in a form

$$E = \epsilon_i(p_i) + E'(q_1, \dots, p_f, \text{except } p_i) \quad (43)$$

for specific "i"

If the system is in thermal equilibrium at temperature "T", the mean value of ϵ_i in Eq. (43) can be computed in a simple way.

$$\begin{aligned} \bar{\epsilon}_i &= \frac{\int \epsilon_i e^{-\beta E} dq_1 \dots dp_f}{\int e^{-\beta E} dq_1 \dots dp_f} = \frac{\int \epsilon_i e^{-\beta \epsilon_i} dp_i \cdot \int' e^{-\beta E'} dq_1 \dots dp_f \text{ (except } dp_i)}{\int e^{-\beta \epsilon_i} dp_i \cdot \int' e^{-\beta E'} dq_1 \dots dp_f \text{ ("")}} \\ &= - \frac{\partial}{\partial \beta} \left(\int e^{-\beta \epsilon_i} dp_i \right) / \int e^{-\beta \epsilon_i} dp_i = - \frac{\partial}{\partial \beta} \ln \left[\int_{-\infty}^{\infty} e^{-\beta \epsilon_i} dp_i \right] \quad (46) \end{aligned}$$

cancel !

• If ϵ_i is a quadratic function of p_i , i.e., $\epsilon_i = b p_i^2$,

the integral in Eq. (46) $\propto \frac{1}{\sqrt{\beta}} \Rightarrow \boxed{\bar{\epsilon}_i = \frac{1}{2} k_B T} ! \quad (48)$

* The Equipartition Theorem

If a system described by classical statistical mechanics is in equilibrium at the absolute temperature T , every independent quadratic term in its energy has a mean value equal to $\frac{1}{2}k_B T$.

Eg., Simple Harmonic Oscillator in thermal equilibrium at T ;

$$\rightarrow \text{" } \epsilon = \frac{1}{2m} p_x^2 + \frac{1}{2} \alpha x^2 \text{"}$$

\rightarrow The mean energy of SHO is $\text{" } \bar{\epsilon} = \frac{1}{2}k_B T + \frac{1}{2}k_B T = k_B T \text{"}$ (58)

because the equipartition theorem applies to the 2nd term as well.
(quadratic in x)

Homework

Problem 6.2 on pg 257,

6.14 and 6.15 on pg 261,

6.19 on pg 262,

Ch. 8. Elementary Kinetic Theory of Transport Processes ^{V-1.}

- ⊗ Molecules in a gas interact with each other through mutual collisions.
- * We assume that the gas is sufficiently dilute so that the following conditions are satisfied:
 - i) The time between collisions is much greater than the time involved in a collision
 - (i) The probability of three or more molecules involved in interaction simultaneously is negligibly small.
 - (ii) Mean separation between molecules is large compared to the de Broglie wavelength of a molecule \Rightarrow quantum mechanical effects can be ignored.

8.1. Mean Free Path

V-2,

⊗ The mean free time of the molecule: τ

The average time which the molecule travels before suffering its next collision after its preceding collision.

⊗ The mean free path of the molecule: l

The mean distance l which the molecule travels " "

Since on average, the molecules travel with their mean speed \bar{v} in random directions,

$$- \boxed{l \simeq \bar{v} \tau} \quad (1)$$

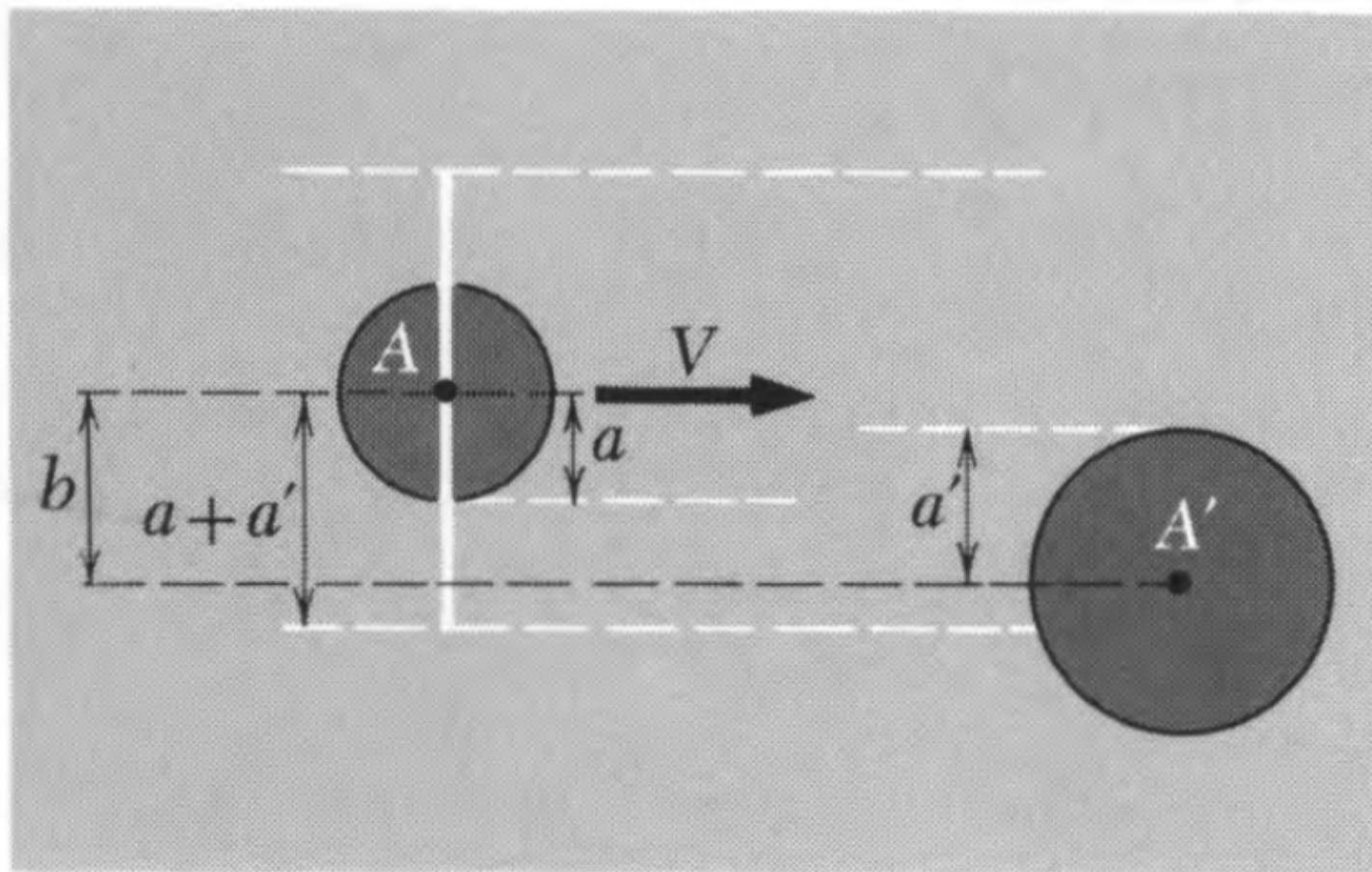


Fig. 8.1 Diagram illustrating a collision between two hard spheres having radii a and a' . The solid white line indicates an imaginary circular disk which is carried by the sphere of radius a and has a radius $(a + a')$.

(*) Scattering Cross Section

- Hard Sphere Model: A collision will occur only if the center of molecule A' lies within the volume swept ~~is~~ out by the area σ of the imaginary circular disk carried by A .

$$\rightarrow \sigma = \pi (a + a')^2 = \pi d^2$$

"total scattering cross section". (for identical molecules)
 $d = a + a' = 2a$

- (*) In reality, two real molecules can interact even at some distance apart.

\Rightarrow Concept of "effective cross section" needs to be introduced.

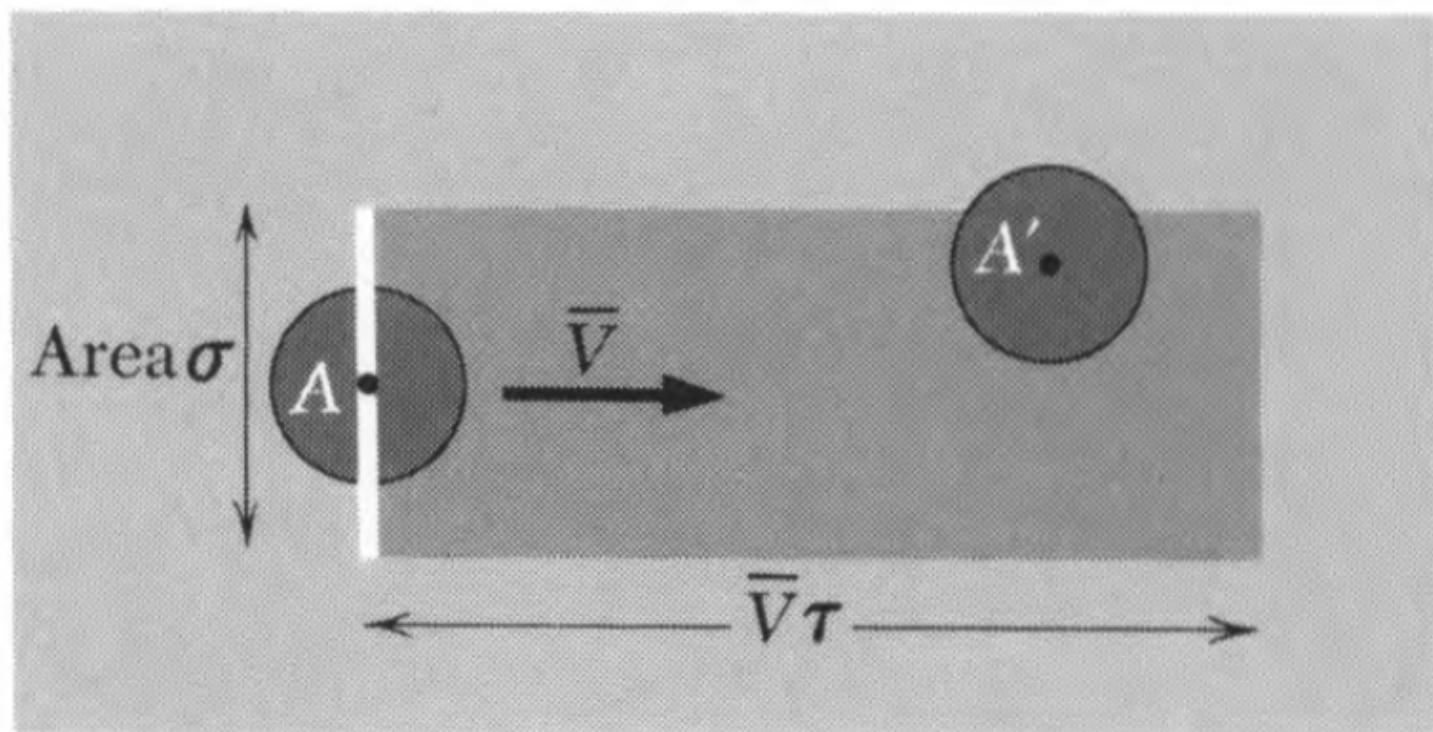


Fig. 8.2 Diagram illustrating the collisions suffered by a particular molecule A when it encounters another molecule whose center is located within the volume swept out by the area σ of the imaginary disk carried by A .

(*) Considering the imaginary disk of area σ , carried by the molecule A traveling toward another molecule A' sweeping out in a time "t", a volume $\sigma(\bar{V}t)$, we obtain

"mean relative speed" $\left(\sigma \bar{V} \tau \right) n = 1$ another molecule in the volume.

mean free time

Volume of a disk (cylinder),

$$\tau = \frac{1}{n \sigma \bar{V}} \quad (4)$$

Obviously, $\tau \downarrow$ as $n \uparrow$, $\sigma \uparrow$ and $\bar{V} \uparrow$
all contribute to more frequent encounters.

$$l \cong \bar{v} \tau \cong \frac{\bar{v}}{V} \frac{1}{n\sigma} \cong \frac{1}{\sqrt{2} n \sigma}$$

(5), (9)

For ideal gas, $\bar{P} = nk_B T \Rightarrow \frac{1}{n} = \frac{k_B T}{\bar{P}}$, i.e.,

At a given temperature, the mean free path \propto $1/\text{pressure of gas}$

Typical example: $T \approx 300^\circ \text{K}$, $\bar{P} \approx 10^6 \text{ dynes/cm}^2$,

$$a \approx 10^{-8} \text{ cm}$$

\Rightarrow

$$\sigma \sim 12 \times 10^{-16} \text{ cm}^2$$

$$l \sim 2 \times 10^{-5} \text{ cm}, \quad \bar{v} \approx 4 \times 10^4 \text{ cm/sec}$$

$$\tau \sim \frac{l}{\bar{v}} \sim 5 \times 10^{-10} \text{ sec.}$$

Indeed, $l \gg d = 2a$ is satisfied.