Kramers Escape Rate Problem

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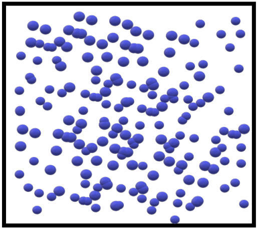
What you see in this talk?

- Quick Recap
- Basic Idea
- Quest for Solution
- Closing Remarks

AIM of this talk: To find the rate at which a Brownian particle escapes from a potential well over a potential barrier

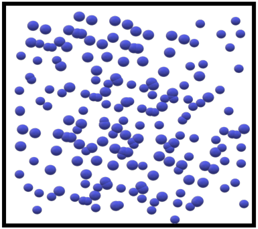
A Quick Recap



Using a box and some number of particles,

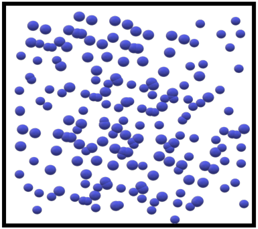
we want to make a system out of it.

A Quick Recap



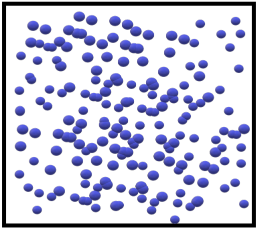
- Conditions: systems represents ideal gas & is in thermal equilibrium

A Quick Recap



- Conditions: systems represents ideal gas & is in thermal equilibrium
- Pick a particle at random
- Ask what is the equilibrium phase space density for this particle ?

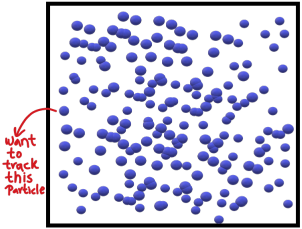
A Quick Recap



- Conditions: systems represents ideal gas & is in thermal equilibrium
- Pick a particle at random
- Maxwellian distribution for velocities applies,

$$f_{\text{eq}}(\vec{r}, \vec{v}) = \frac{1}{\text{Volume}} \left(\frac{m}{2\pi K_B T}\right)^{3/2} e^{-\frac{m|\vec{V}|^2}{2K_B T}}$$

A Quick Recap



- Conditions: systems represents ideal gas & is in thermal equilibrium
- Pick a particle at random
- Want to somehow track that particle

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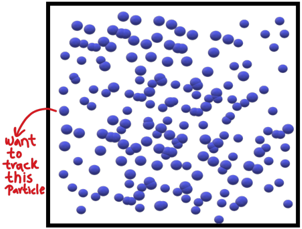
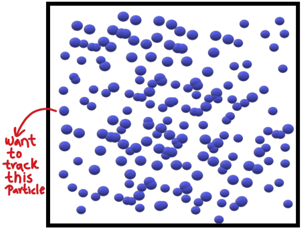


- Conditions: systems represents ideal gas & is in thermal equilibrium
- Pick a particle at random
- Want to somehow track that particle
- Given that at some instant of time it has (say) position r_0 and velocity v_0, ask what happens to it as a function of time?

A Quick Recap



- Conditions: systems represents ideal gas & is in thermal equilibrium
- Pick a particle at random
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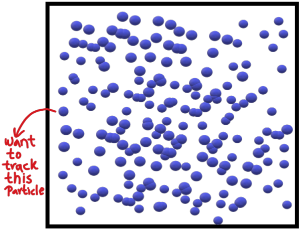
- We ask for the conditional PDF i.e. $f(\vec{r}, \vec{v}, t | \vec{r_0}, \vec{v_0}, t_0)$. Ask what's this equal to?

A Quick Recap



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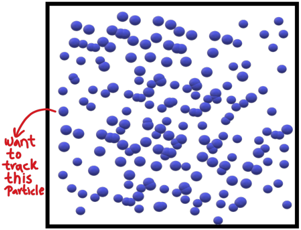
- Intuitively, we can guess:
  - At $(t - t_0) \to \infty$, it's equal to $f_{\text{eq}}(\vec{r}, \vec{v})$ and particle will relax to equilibrium and looses its memory of what was its initial values

A Quick Recap



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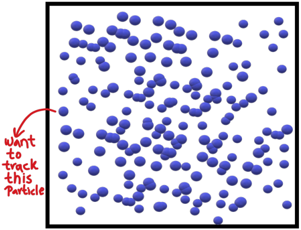
- Intuitively, we can guess:
  - At $(t - t_0) \to \infty$, it's equal to $f_{eq}(\vec{r}, \vec{v})$
  - At $(t - t_0) \to 0$, it's equal to $\delta^{(3)}(\vec{r} - \vec{r_0})\delta^{(3)}(\vec{v} - \vec{v_0})$

A Quick Recap



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- - At $(t - t_0) \to \infty$, it's equal to $f_{\text{eq}}(\vec{r}, \vec{v})$
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- Ask what's in-between t and t_0?

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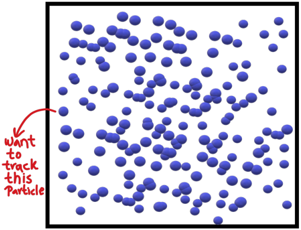

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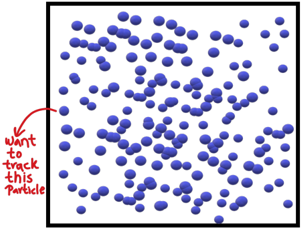
- Ask what's in-between t and t_0?
- A very HARD question because it turns out to be a many body problem due to particle-particle correlation

A Quick Recap



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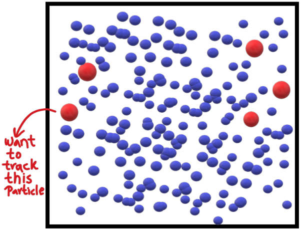
- Ask what's in-between t and t_0?
- Lets add one more condition to make our problem easier!

A Quick Recap

- Conditions: systems represents the ideal gas and in thermal equilibrium, and has very few bigger particles i.e. Brownian particles
- Guess the equation of motion for this particle?



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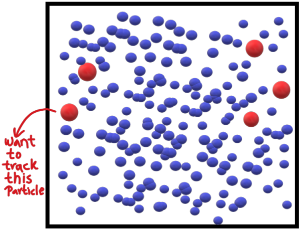


- Conditions: systems represents the ideal gas and in thermal equilibrium, and has Brownian particles
- Gives Langevin equation

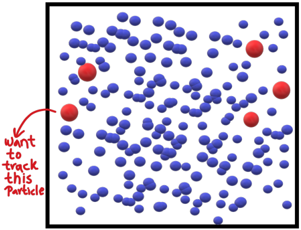
$$\frac{da_j(t)}{dt} = h_j(\mathbf{a}) + \delta F_j(t)$$

where, $\{a_1, \ldots, a_N\}$ are N dynamical variables, h_j is some non-linear deterministic function but without memory, and $\delta F(t)$ is a random force (noise) which is generated by Gaussian white noise with delta correlated second moment i.e.

$$\langle \delta F_j(t) \rangle = 0,$$

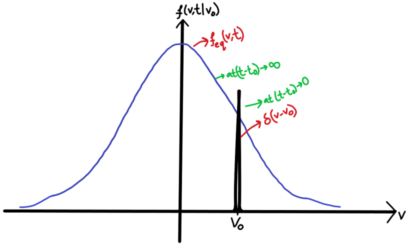
$$\langle \delta F_j(t) \delta F_k(t') \rangle = 2B_{jk}\delta(t - t')$$

A Quick Recap



- Langevin equation
  $$\frac{da_j(t)}{dt} = h_j(\boldsymbol{a}) + \delta F_j(t)$$
- Fokker-Planck suggested, instead of fluctuating, stochastic trajectories $a_j(t)$, why not we're interested in the probability phase-space distribution $f(\boldsymbol{a}, t)$ averaged over the noise $\delta F(t)$?
- Using Gaussian white noise property i.e. $\langle \delta F_j(t) \rangle = 0$,
  $$\langle \delta F_j(t) \delta F_k(t') \rangle = 2B_{jk}\delta(t - t')$$
- Then which results

A Quick Recap



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- Using Gaussian white noise property i.e. $\langle \delta F_j(t) \rangle = 0,$
  $$\langle \delta F_j(t) \delta F_k(t') \rangle = 2B_{jk}\delta(t - t')$$
- Then which results
  $$\frac{\partial}{\partial t}\langle f(\boldsymbol{a}, t)\rangle = -\frac{\partial}{\partial a_j} h_j(\boldsymbol{a})\langle f(\boldsymbol{a}, t)\rangle$$
  $$+\frac{\partial}{\partial a_j} B_{jk} \frac{\partial}{\partial a_k}\langle f(\boldsymbol{a}, t)\rangle$$

A Quick Recap but lets be little forward in our quest

- Consider the same Brownian particle but is in an external potential $U(x)$ so, the corresponding Langevin equations of motion is $\dot{x}(t) = \frac{p(t)}{m}, \dot{p}(t) = -U'(x) - \zeta \frac{p}{m} + \delta F(t)$ where ζ is the frictional coefficient due to particles viscosity

A Quick Recap but lets be little forward in our quest

- Langevin equations of motion is

  $\boxed{\dot{x}(t) = \frac{p(t)}{m}, \dot{p}(t) = -U'(x) - \zeta \frac{p}{m} + \delta F(t)}$

- Assume the magnitude of the frictional force $\zeta \frac{p}{m}$ is much larger than the magnitude of the Brownian particle inertial force $\dot{p}(t)$. In-other words, $\dot{p}(t)$ is negligible. i.e. $\boxed{\dot{p}(t) \approx 0}$

A Quick Recap but lets be little forward in our quest

- Langevin equations of motion is
  $\dot{x}(t) = \frac{p(t)}{m}, \dot{p}(t) = -U'(x) - \zeta \frac{p}{m} + \delta F(t)$
- Assume $\dot{p}(t) \approx 0$
- Becomes $\dot{x}(t) = -\frac{1}{\zeta} U'(x) + \frac{1}{\zeta} \delta F(t)$
- Comparing with general Langevin equation $\frac{da_j(t)}{dt} = h_j(\mathbf{a}) + \delta F_j(t)$ and substitute required quantities in Fokker-Planck (FP) equation $\frac{\partial}{\partial t}\langle f(\mathbf{a}, t)\rangle = -\frac{\partial}{\partial a_j} h_j(\mathbf{a}) \langle f(\mathbf{a}, t)\rangle + \frac{\partial}{\partial a_j} B_{jk} \frac{\partial}{\partial a_k} \langle f(\mathbf{a}, t)\rangle$ then, FP equation reduces to Smoluchowski equation i.e.

$$\frac{\partial}{\partial t}\langle f(x,t)\rangle = \frac{\partial}{\partial x}\frac{U'(x)}{\zeta}\langle f(x,t)\rangle + \frac{\partial^2}{\partial x^2}\frac{K_B T}{\zeta}\langle f(x,t)\rangle$$

A Quick Recap but lets be little forward in our quest

- Smoluchowski equation i.e.

$$\frac{\partial}{\partial t}\langle f(x,t)\rangle = \frac{\partial}{\partial x}\frac{U'(x)}{\zeta}\langle f(x,t)\rangle + \frac{\partial^2}{\partial x^2}\frac{K_B T}{\zeta}\langle f(x,t)\rangle$$
$$= \left(\frac{K_B T}{\zeta}\right)\frac{\partial}{\partial x}\left[e^{-U/K_B T}\left(\frac{\partial}{\partial x}e^{U/K_B T}\langle f(x,t)\rangle\right)\right]$$
$$= D\frac{\partial}{\partial x}e^{-U/K_B T}\frac{\partial}{\partial x}e^{U/K_B T}\langle f(x,t)\rangle$$

where D is the diffusion coefficient $D = K_B T/\zeta$ and equal to the strength of the fluctuating force B by fluctuation-dissipation theorem

A Quick Recap but lets be little forward in our quest

- Smoluchowski equation i.e.

$$\begin{aligned}\frac{\partial}{\partial t}\langle f(x,t)\rangle &= \frac{\partial}{\partial x}\frac{U'(x)}{\zeta}\langle f(x,t)\rangle + \frac{\partial^2}{\partial x^2}\frac{K_B T}{\zeta}\langle f(x,t)\rangle \\ &= \left(\frac{K_B T}{\zeta}\right)\frac{\partial}{\partial x}\left[e^{-U/K_B T}\left(\frac{\partial}{\partial x}e^{U/K_B T}\langle f(x,t)\rangle\right)\right] \\ &= D\frac{\partial}{\partial x}e^{-U/K_B T}\frac{\partial}{\partial x}e^{U/K_B T}\langle f(x,t)\rangle\end{aligned}$$

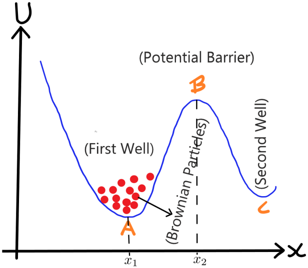
- Also, follows the equation of continuity i.e.

$$\frac{\partial}{\partial t}\langle f(x,t)\rangle = -\frac{\partial}{\partial x}\left(-De^{-U/K_B T}\frac{\partial}{\partial x}e^{U/K_B T}\langle f(x,t)\rangle\right) = -\frac{\partial}{\partial x}J(x,t)$$

where $J(x,t)$ is flux density such that

$$J(x,t) = -De^{-U/K_B T}\frac{\partial}{\partial x}e^{U/K_B T}\langle f(x,t)\rangle$$

Basic Idea of Kramers Problem



Hendrik Anthony (Hans) Kramers, while studying the chemical kinetics:

> *". . . . A particle moves in an external field of force, but - in addition to this - is subject to the irregular forces of a surrounding medium in temperature equilibrium (Brownian motion). The* **conditions are such, that the particle is originally caught in a potential hole but may escape in the course of time by passing over a potential barrier***. We want* **to calculate the probability of escape** *in its dependency on temperature and viscosity of the medium . . . "*
>
> *– Excerpt taken from [Kramers, 1940]*

Photo credit: Hans Kramers (top-left corner), photo taken from Prabook.

Solving Kramers Problem

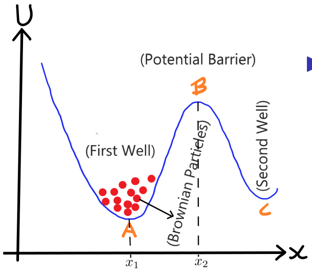
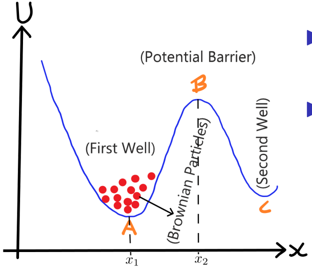


Figure: First well (A) with position x_1, potential barrier (B) with position x_2 and second well (C).

- When we start at A, with which rate does a particle come to point C?
- Two limiting cases: extremely strong force of friction and extremely weak force of friction. Later one is difficult so, we choose first case and use Smoluchowski equation i.e.

$$\frac{\partial}{\partial t}\langle f(x,t)\rangle = \frac{\partial}{\partial x}\left(De^{-U/K_BT}\frac{\partial}{\partial x}e^{U/K_BT}\langle f(x,t)\rangle\right)$$

Solving Kramers Problem



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- Smoluchowski equation i.e.

$$\frac{\partial}{\partial t}\langle f(x,t)\rangle = \frac{\partial}{\partial x}\left(De^{-U/K_BT}\frac{\partial}{\partial x}e^{U/K_BT}\langle f(x,t)\rangle\right)$$

At stationary, $\frac{\partial}{\partial t}\langle f(x,t)\rangle = 0$ then, the flux density $J(x,t)$ becomes constant. i.e.

$$J(x,t) = -De^{-U/K_BT}\frac{\partial}{\partial x}e^{U/K_BT}\langle f(x,t)\rangle \neq 0$$

Solving Kramers Problem

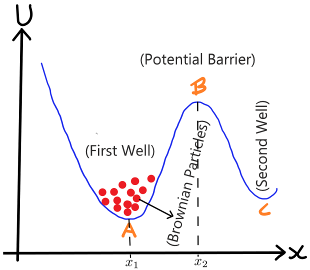


Figure: First well (A) with position x_1, potential barrier (B) with position x_2 and second well (C).

- For simplicity, replace the notation $J(x,t)$ by J, $\langle f(x,t)\rangle$ by F and U/K_BT by $\tilde{U}$ then flux density looks

$$J = -De^{-\tilde{U}}\frac{\partial}{\partial x}e^{\tilde{U}}f$$

$$\text{or,}\ \frac{Je^{\tilde{U}}}{D} = -\frac{\partial}{\partial x}e^{\tilde{U}}f$$

$$\implies \int_{x_1}^{x_2}\frac{Je^{\tilde{U}}}{D}dx = -\int_{x_1}^{x_2} d\left(e^{\tilde{U}}f\right)$$

$$\implies -\left[e^{\tilde{U}}f\right]_{x_1}^{x_2}$$

$$\therefore \frac{J}{D} = \frac{-e^{\tilde{U}(x_2)}f(x_2) + e^{\tilde{U}(x_1)}f(x_1)}{\int_{x_1}^{x_2} e^{\tilde{U}}dx}$$

Solving Kramers Problem

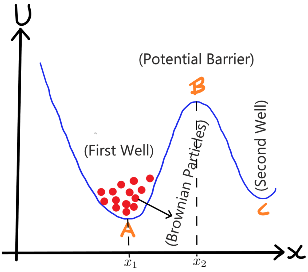


Figure: First well (A) with position x_1, potential barrier (B) with position x_2 and second well (C).

- Since no particle can get to x_2 from the right so this $f(x_2) = 0$ that gives

$$\frac{J}{D} = \frac{-e^{\tilde{U}(x_2)} f(x_2) + e^{\tilde{U}(x_1)} f(x_1)}{\int_{x_1}^{x_2} e^{\tilde{U}} dx}$$

becomes

$$\frac{J}{D} = \frac{e^{\tilde{U}(x_1)} f(x_1)}{\int_{x_1}^{x_2} e^{\tilde{U}} dx}$$

Solving Kramers Problem

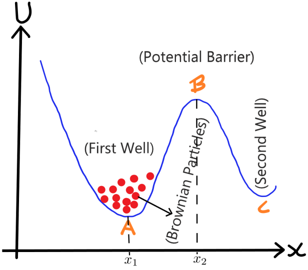


Figure: First well (A) with position x_1, potential barrier (B) with position x_2 and second well (C).

- For a high barrier, we can expand $\tilde{U}$ near the maximum (i.e. $\tilde{U}'(x_2) = 0$ and $\tilde{U}''(x_2) < 0$) at x_2 using Taylor's expansion and replace $\tilde{U}(x_2)$ by $\tilde{U}_2$ gives

$$\tilde{U} \approx \tilde{U}_2 - \frac{|\tilde{U}_2''|}{2}(x - x_2)^2$$

$-|\tilde{U}_2''|$ ensure the potential barrier is always concave downward. So,

$$\int_{x_1}^{x_2} e^{\tilde{U}} dx \approx e^{\tilde{U}_2} \int_{x_1}^{x_2} e^{-\frac{|\tilde{U}_2''|}{2}(x-x_2)^2} dx$$

$$\approx \frac{1}{2} e^{\tilde{U}_2} \int_{-\infty}^{\infty} e^{-\frac{|\tilde{U}_2''|}{2}(x-x_2)^2} dx = e^{\tilde{U}_2} \sqrt{\frac{\pi}{2|\tilde{U}_2''|}}$$

Solving Kramers Problem

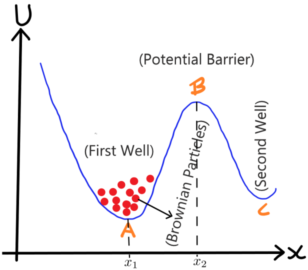


Figure: First well (A) with position x_1, potential barrier (B) with position x_2 and second well (C).

- Equation $\frac{J}{D} = \frac{e^{\tilde{U}(x_1)} f(x_1)}{\int_{x_1}^{x_2} e^{\tilde{U}} dx}$ now reads as

$$J = De^{-(\tilde{U}_2 - \tilde{U}_1)} \sqrt{\frac{2|\tilde{U}_2''|}{\pi}} f(x_1)$$

- Flux depends exponentially on the potential difference and also on the curvature $\tilde{U}_2''$ of the barrier
- Since the frictional force is strong enough, so the Brownian particle rapidly relaxed to the equilibrium.

Solving Kramers Problem

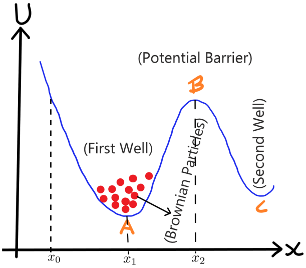


Figure: First well (A) with position x_1, potential barrier (B) with position x_2 and second well (C).

- So, the average phase space distribution at x_1 is given by equilibrium distribution i.e.

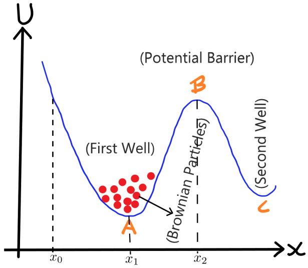
$$f(x_1) = \frac{e^{-\tilde{U}(x_1)}}{\int_{x_0}^{x_2} e^{-\tilde{U}(x)}\,dx}$$

- Expanding the potential around x_1 and ensuring potential well is always concave upward $\tilde{U}''(x_1) > 0$.

$$\tilde{U}(x) \approx \tilde{U}_1 + \frac{\tilde{U}_1''}{2}(x - x_1)^2$$

- which yields $f(x_1) \approx \frac{1}{\int_{-\infty}^{\infty} e^{-\frac{\tilde{U}_1''}{2}(x-x_1)^2}\,dx} \approx \sqrt{\frac{\tilde{U}_1''}{2\pi}}$

Solving Kramers Problem



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- So, the total flux

$$J = De^{-(\tilde{U}_2 - \tilde{U}_1)} \sqrt{\frac{2|\tilde{U}_2''|}{\pi}} f(x_1)$$

- becomes

$$J = \frac{D\sqrt{\tilde{U}_1''|\tilde{U}_2''|}}{\pi} e^{-(\tilde{U}_2 - \tilde{U}_1)}$$

Replacing the previously replaced notations

$$\therefore J = \frac{D\sqrt{U_1''|U_2''|}}{\pi K_B T} e^{-\Delta U / K_B T}$$

where, $\Delta U := U(x_2) - U(x_1)$

Closing Remarks

- Suppose we have two potential wells in such a way that one is at left and another one is at right of potential well A. So there is equally likely probability that particle can cross from A to any one of these potential wells.
- So, half of total flux of Brownian particles cross the barrier to go from A to C.
- Thus, the rate of crossing the barrier $\kappa = J/2$ and using $D = K_B T/\zeta$, we find

Closing Remarks

$$\kappa = \frac{D\sqrt{U_1''|U_2''|}}{2\pi K_B T} e^{-\Delta U/K_B T}$$

Thank You For Listening!
I Invite You To Ask Any Questions You May Have...

References

Kramers, H. (1940).
Brownian motion in a field of force and the diffusion model of chemical reactions.
Physica, 7(4):284 – 304.