Quantum Mechanics for Classical Particles

Ben Vollmayr-Lee
Bucknell University

Dickinson College — February 2, 2010

Quantum Mechanics for Classical Particles

Dynamics of Stochastic Classical Particles

Examples: Decay, Hops, and Reactions

Reaction-Diffusion Systems

Mapping to Quantum Mechanics

Why Study Classical Particles ...

...when the world is quantum mechanical?

Answer: room temperature and molecular masses

- typical momentum given by $p^2/2m \sim kT \quad \Rightarrow \quad p \sim \sqrt{mkT}$
- de Broglie wavelength $\lambda = h/p \sim h/\sqrt{mkT}$
- For $T = 300\,\mathrm{K}$ and typical molecular masses, $\lambda \sim 10^{-11}\,\mathrm{m}$
- Typical molecular separations $10^{-10}\,\mathrm{m}$ and higher

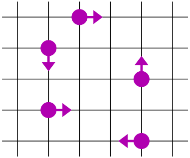
Conclusion:

Quantum interference effects negligible, classical models of molecular interactions work fine at 300 K.

Stochastic Particle Models

Diffusion:

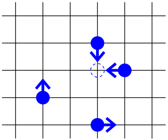
Particles on a lattice undergoing random walks.



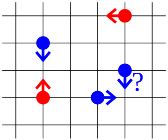
Diffusion-Limited Reactions:

One or more species of random-walking particles, with a reactions occuring when particles occupy the same lattice site

A+A→A

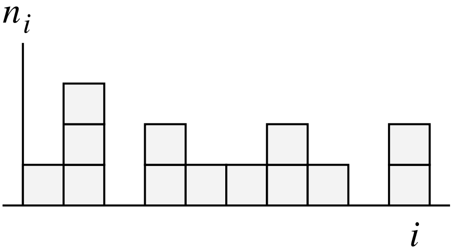


A+B→∅



Stochastic Classical Particles on a Lattice

Consider a set of lattice sites labeled $i = 1$, 2, 3, $\ldots$, and each site is occupied by n_1, n_2, n_3, $\ldots$ particles.



Define

- $\alpha =$ a particular state, i.e., $\alpha = \{n_1, n_2, n_3, \ldots\}$
- $P(\alpha, t) =$ the probability of obtaining state α at time t.

Probability Master Equation

Dynamical processes (hops, reactions, decays) will cause a change of state from α to β.

$$\boxed{w_{\alpha\to\beta} = \text{rate of transition from } \alpha \text{ to } \beta\text{, defines dynamics}}$$

Master Equation

$$\frac{d}{dt}P(\alpha,t) = \sum_\beta \Big[\underbrace{w_{\beta\to\alpha}P(\beta,t)}_{\text{flow into } \alpha} - \underbrace{w_{\alpha\to\beta}P(\alpha,t)}_{\text{flow out of } \alpha}\Big]$$

Note: $\sum_\alpha P(\alpha,t) = 1$ preserved by the master equation

Quantum Mechanics for Classical Particles

Dynamics of Stochastic Classical Particles

Examples: Decay, Hops, and Reactions

Reaction-Diffusion Systems

Mapping to Quantum Mechanics

Example: Radioactive Decay

Consider identical particles at a single site that undergo radioactive decay at rate λ.

The rate for a transition from n to m particles is

$$w_{n\to m} = \begin{cases} 0 & \text{for } m \neq n-1 \\ n\lambda & \text{for } m = n-1 \end{cases}$$

and the master equation is

$$\frac{d}{dt}P(n,t) = \lambda\Big[(n+1)P(n+1,t) - n\,P(n,t)\Big]$$

Example: Radioactive Decay

Consider identical particles at a single site that undergo radioactive decay at rate λ.

The rate for a transition from n to m particles is

$$w_{n\to m} = \begin{cases} 0 & \text{for } m \neq n-1 \\ n\lambda & \text{for } m = n-1 \end{cases}$$

and the master equation is

$$\frac{d}{dt}P(n,t) = \lambda\Big[(n+1)P(n+1,t) - n\,P(n,t)\Big]$$

Wait! That doesn't look like exponential decay ...

From Master Equation to Differential Equation

Let $\rho(t) = \langle n \rangle = \sum_n n\, P(n,t)$ be the average number of particles at time t. Then

$$\dot{\rho} = \sum_n n \dot{P}(n,t) = \sum_n n \Big[\lambda(n+1)P(n+1,t) - \lambda n P(n,t) \Big]$$

From Master Equation to Differential Equation

Let $\rho(t) = \langle n \rangle = \sum_n n\, P(n,t)$ be the average number of particles at time t. Then

$$\dot{\rho} = \sum_n n\dot{P}(n,t) = \sum_n n\Big[\lambda(n+1)P(n+1,t) - \lambda n P(n,t)\Big]$$

$$= \lambda \sum_n n(n+1)P(n+1,t) - \lambda \sum_n n^2 P(n,t)$$

$$= \lambda \sum_m (m-1)mP(m,t) - \lambda \sum_n n^2 P(n,t)$$

From Master Equation to Differential Equation

Let $\rho(t) = \langle n \rangle = \sum_n n\, P(n,t)$ be the average number of particles at time t. Then

$$\dot{\rho} = \sum_n n\dot{P}(n,t) = \sum_n n\Big[\lambda(n+1)P(n+1,t) - \lambda n P(n,t)\Big]$$

$$= \lambda \sum_n n(n+1)P(n+1,t) - \lambda \sum_n n^2 P(n,t)$$

$$= \lambda \sum_m (m-1)mP(m,t) - \lambda \sum_n n^2 P(n,t)$$

$$= -\lambda \sum_m mP(m,t)$$

$$= -\lambda\rho$$

Example: $A + A \to 0$ Reaction

Again, consider a single lattice site, with the rule that a pair of particles may annihilate each other. The rates are

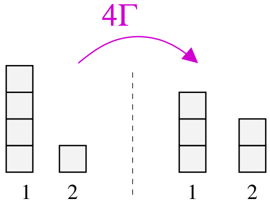
$$w_{n \to m} = \begin{cases} 0 & \text{for } m \neq n-2 \\ n(n-1)\lambda & \text{for } m = n-2 \end{cases}$$

and the master equation is

$$\frac{d}{dt} P(n,t) = \lambda \Big[(n+2)(n+1) P(n+2,t) - n(n-1) P(n,t) \Big]$$

Example: Hop

Now consider two sites, $i = 1$ and 2, with a rate Γ of hopping from site 1 to site 2.



$$w_{(n_1,n_2)\to(m_1,m_2)} = \begin{cases} 0 & \text{for } m_1 \neq n_1 - 1 \ \text{ or } \ m_2 \neq n_2 + 1 \\ n_1\Gamma & \text{for } m_1 = n_1 - 1 \text{ and } m_2 = n_2 + 1 \end{cases}$$

and the master equation is

$$\frac{d}{dt}P(n_1, n_2, t) = \Gamma\Big[(n_1 + 1)P(n_1 + 1, n_2 - 1, t) - n_1 P(n_1, n_2, t)\Big]$$

Dynamics of Stochastic Classical Particles

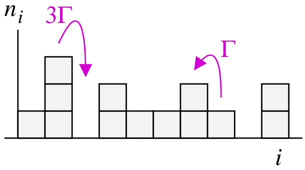
Examples: Decay, Hops, and Reactions

Reaction-Diffusion Systems

Mapping to Quantum Mechanics

Diffusion

Consider a one-dimensional chain of lattice sites $i = 1, 2, \ldots$ and let all particles hop left or right with rate Γ. The master equation is

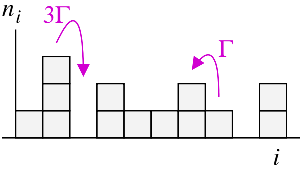


$$\frac{d}{dt}P(\alpha,t) = \Gamma \sum_{\langle ij \rangle} \Big[(n_i+1)P(n_i+1, n_j-1, \ldots, t) - n_i P(\alpha,t)$$

$$(n_j+1)P(n_i-1, n_j+1, \ldots, t) - n_j P(\alpha,t) \Big]$$

Diffusion

Consider a one-dimensional chain of lattice sites $i = 1, 2, \ldots$ and let all particles hop left or right with rate Γ. The master equation is



$$\frac{d}{dt}P(\alpha, t) = \Gamma \sum_{\langle ij \rangle} \Big[(n_i + 1)P(n_i + 1, n_j - 1, \ldots, t) - n_i P(\alpha, t)$$

$$(n_j + 1)P(n_i - 1, n_j + 1, \ldots, t) - n_j P(\alpha, t) \Big]$$

Define $\rho(x, t) = \sum_\alpha n_i P(\alpha, t)$ where $x = i\Delta x$.

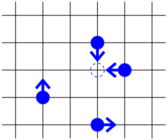
For small Δx this becomes the diffusion equation:

$$\frac{\partial \rho}{\partial t} = D \frac{\partial^2 \rho}{\partial x^2} \qquad D = \Gamma \Delta x^2 = \text{diffusion constant.}$$

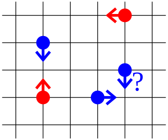
Reaction-Diffusion Systems

One or more species of particles undergoing random walks on a lattice, with a reactions occuring for particles on the same lattice site

A+A→A

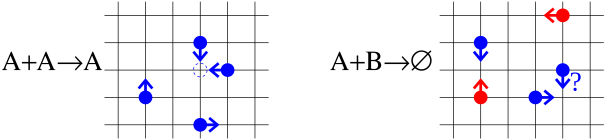


A+B→∅



Reaction-Diffusion Systems

One or more species of particles undergoing random walks on a lattice, with a reactions occuring for particles on the same lattice site



$A + A \to 0$: The density of particles decays as

$$\rho(t) = \begin{cases} Ct^{-1} & \text{for } d > 2 \\ \tilde{A} \ln t / Dt & \text{for } d = 2 \\ A(Dt)^{-d/2} & \text{for } d < 2 \end{cases}$$

where A and $\tilde{A}$ are universal numbers!

Reaction-Diffusion Master Equation

$$\frac{d}{dt}P(\alpha,t) = \frac{D}{\Delta x^2}\sum_{\langle ij\rangle}\Big[(n_i+1)P(n_i+1,n_j-1,\dots,t) - n_iP(\alpha,t)$$

$$+ (n_j+1)P(n_i-1,n_j+1,\dots,t) - n_jP(\alpha,t)\Big]$$

$$+ \lambda\sum_i\Big[(n_i+2)(n_i+1)P(\dots,n_i+2,\dots,t)$$

$$- n_i(n_i-1)P(\alpha,t)\Big]$$

Reaction-Diffusion Master Equation

$$
\begin{aligned}
\frac{d}{dt}P(\alpha,t) =& \frac{D}{\Delta x^2}\sum_{\langle ij\rangle}\Big[(n_i+1)P(n_i+1,n_j-1,\ldots,t)-n_iP(\alpha,t) \\
&\qquad + (n_j+1)P(n_i-1,n_j+1,\ldots,t)-n_jP(\alpha,t)\Big] \\
&+ \lambda\sum_i\Big[(n_i+2)(n_i+1)P(\ldots,n_i+2,\ldots,t) \\
&\qquad - n_i(n_i-1)P(\alpha,t)\Big]
\end{aligned}
$$

Yuck!

Dynamics of Stochastic Classical Particles

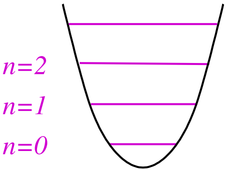
Examples: Decay, Hops, and Reactions

Reaction-Diffusion Systems

Mapping to Quantum Mechanics

Quantum Harmonic Oscillator

- Quantum harmonic oscillator eigenstates $|n\rangle$ are labeled by an integer $n \geq 0$.
- Eigenstate $|n\rangle$ has energy $E_n = \left(n + \frac{1}{2}\right)\hbar\omega$



- Raising and lowering operators $\hat{a}^\dagger$ and $\hat{a}$ step from one eigenstate to the next:

$$\hat{a}^\dagger|n\rangle = |n+1\rangle \qquad \hat{a}|n\rangle = n|n-1\rangle$$

- Ground state $|0\rangle$ obeys $\hat{a}|0\rangle = 0$, and $|n\rangle = (\hat{a}^\dagger)^n|0\rangle$.
- The raising and lowering operators do not commute:

$$[\hat{a}, \hat{a}^\dagger] \equiv \hat{a}\hat{a}^\dagger - \hat{a}^\dagger\hat{a} = 1$$

Doi Representation [Doi '76]

$$\text{integer } n \geq 0 = \begin{cases} \text{lattice site occupation number} \\ \text{label for QHO eigenstate} \end{cases}$$

Why not introduce a QHO at each lattice site?

Doi Representation [Doi '76]

$$\text{integer } n \geq 0 = \begin{cases} \text{lattice site occupation number} \\ \text{label for QHO eigenstate} \end{cases}$$

Why not introduce a QHO at each lattice site? Then state

$$\alpha = (n_1, n_2, \dots) \qquad \Leftrightarrow \qquad |\alpha\rangle = |n_1\rangle \otimes |n_2\rangle \otimes \dots$$

We'll need a pair of creation and annihilation operators $\hat{a}_i^\dagger$, $\hat{a}_i$ for each site. Then

$$|n_i\rangle = (\hat{a}_i^\dagger)^{n_i} |0\rangle$$

and we can write the state α as

$$|\alpha\rangle = \prod_i (\hat{a}_i^\dagger)^{n_i} |0\rangle$$

Doi Representation, part II

We can pack the probability function into a quantum state:

$$|\phi(t)\rangle = \sum_{\alpha} P(\alpha, t)|\alpha\rangle$$

and re-write the master equation in Schrödinger-like form:

$$\frac{d}{dt}|\phi(t)\rangle = -\hat{H}|\phi(t)\rangle$$

Doi Representation, part II

We can pack the probability function into a quantum state:

$$|\phi(t)\rangle = \sum_{\alpha} P(\alpha, t)|\alpha\rangle$$

and re-write the master equation in Schrödinger-like form:

$$\frac{d}{dt}|\phi(t)\rangle = -\hat{H}|\phi(t)\rangle$$

Why do this? Because it is a simpler description of the dynamics. For $A + A \to 0$ reaction diffusion we get

$$\boxed{\hat{H} = \frac{D}{\Delta x^2} \sum_{\langle ij \rangle} (\hat{a}_i^\dagger - \hat{a}_j^\dagger)(\hat{a}_i - \hat{a}_j) - \lambda \sum_i (1 - \hat{a}_i^{\dagger 2})\hat{a}_i^2}$$

$A + A \to 0$ on a Single Site

Master equation:

$$\frac{d}{dt}P(n,t) = \lambda\Big[(n+2)(n+1)P(n+2,t) - n(n-1)P(n,t)\Big]$$

Multiply by $|n\rangle$ and sum over n:

$$\frac{d}{dt}|\phi(t)\rangle = \lambda\sum_n P(n{+}2,t)\,(n+2)(n+1)|n\rangle - \lambda\sum_n P(n,t)\,n(n-1)|n\rangle$$

$A + A \to 0$ on a Single Site

Master equation:

$$\frac{d}{dt}P(n,t) = \lambda\Big[(n+2)(n+1)P(n+2,t) - n(n-1)P(n,t)\Big]$$

Multiply by $|n\rangle$ and sum over n:

$$\frac{d}{dt}|\phi(t)\rangle = \lambda\sum_n P(n{+}2,t)\,(n+2)(n+1)|n\rangle - \lambda\sum_n P(n,t)\,n(n-1)|n\rangle$$

$$= \lambda\sum_n P(n+2,t)\,\hat{a}^2|n+2\rangle - \lambda\sum_n P(n,t)\,\hat{a}^{\dagger 2}\hat{a}^2|n\rangle$$

$$= \lambda(\hat{a}^2 - \hat{a}^{\dagger 2}a^2)\sum_n P(n,t)\,|n\rangle$$

$$= \lambda(1 - \hat{a}^{\dagger 2})\hat{a}^2|\phi(t)\rangle = -\hat{H}|\phi(t)\rangle$$

Hop from Site 1 to Site 2

Master Equation

$$\frac{d}{dt}P(n_1,n_2,t) = \Gamma\Big[(n_1{+}1)P(n_1{+}1,n_2{-}1,t) - n_1 P(n_1,n_2,t)\Big]$$

Multiply by $|n_1,n_2\rangle$ and sum over n_1 and n_2:

$$\begin{aligned}\frac{d}{dt}|\phi(t)\rangle &= \Gamma\sum_{n_1,n_2} P(n_1{+}1,n_2{-}1,t)\,(n_1{+}1)|n_1,n_2\rangle \\ &\qquad - \Gamma\sum_{n_1,n_2} P(n_1,n_2,t)\,n_1|n_1,n_2\rangle \\ &= \Gamma\sum_{n_1,n_2} P(n_1{+}1,n_2{-}1,t)\,\hat{a}_2^\dagger\hat{a}_1\,|n_1{+}1,n_2{-}1\rangle \\ &\qquad - \Gamma\sum_{n_1,n_2} P(n_1,n_2,t)\,\hat{a}_1^\dagger\hat{a}_1\,|n_1,n_2\rangle \\ &= \Gamma(\hat{a}_2^\dagger - \hat{a}_1^\dagger)\hat{a}_1\,|\phi(t)\rangle\end{aligned}$$

Diffusion

- Hop from site 1 to site 2:

$$\hat{H}_{1\to 2} = \Gamma(\hat{a}_1^\dagger - \hat{a}_2^\dagger)a_1$$

- Allow for the reverse hop with the same rate:

$$\hat{H}_{1\leftrightarrow 2} = \Gamma(\hat{a}_1^\dagger - \hat{a}_2^\dagger)(\hat{a}_1 - \hat{a}_2)$$

- For hops between all neighboring lattice sites:

$$\boxed{\hat{H}_D = \frac{D}{(\Delta x)^2}\sum_{\langle ij\rangle}(\hat{a}_i^\dagger - \hat{a}_j^\dagger)(\hat{a}_i - \hat{a}_j)}$$

Summary

- Mapping to quantum description simplifies the master equation by getting rid of pesky factors involving n.
- Fock space description natural for identical particles acting independently, not restricted to quantum mechanics
- Solution for reaction diffusion system involves mapping the quantum hamiltonian to a quantum field theory and using Feynman diagrams . . . a lot of fun!