Capture of Brownian particles and reaction theory

Fabrice Thalmann\textsuperscript{1}, Carlos M. Marques\textsuperscript{1}, Albert Johner\textsuperscript{1}, Nam-Kyung Lee\textsuperscript{2}

\textsuperscript{1}Institut Charles Sadron, CNRS & Université de Strasbourg - France
\textsuperscript{2}Department of Physics, Sejong University, Seoul, South Korea

15/01/2010
Capture of Brownian particles

Application: Time resolved association kinetics of colloids

Membrane adhesion

Second quantization formalism

References
Capture of Brownian particles

Application: Time resolved association kinetics of colloids

Membrane adhesion

Second quantization formalism

References

1. Introduction: capture of Brownian particles
2. Adhesion kinetics of magnetic colloids
3. Other interesting situations
4. Algorithms with non conserved number of particles
Capture of Brownian particles

Application:
Time resolved association kinetics of colloids
Membrane adhesion
Second quantization formalism
References
(Colloidal) particle physics

Capture of Brownian particles

Application: Time resolved association kinetics of colloids

Membrane adhesion

Second quantization formalism

References

Particles  Atoms  Molecules  (colloidal) Particles

fm  Å  nm  10–1000 nm
Will the Brownian particle hit the upper boundary or the lower boundary first?
The Brownian particle disappears as soon as it hits a boundary. ⇒ absorbing boundary conditions

- first passage time
- diffusive barrier crossing
Probability of presence $c(r, t)$ obeys:

$$ (\partial_t - D\Delta) c(r, t) = 0; $$

$$(1)$$

$$ c(r, t)|_{r \in \partial D} = 0; $$

$$(2)$$

$$ c(r, t = 0) = \delta(r - r_M). $$

$$(3)$$

Diffusion equation + Dirichlet (absorbing) BC.
Single absorbing wall; diffusion coefficient $D$. Source image, probability of presence $c(r, t)$ reads:

$$c(r, t) = \frac{e^{-x^2+y^2/4Dt}}{(4\pi Dt)^{3/2}} \left[ e^{(z-d)^2/4Dt} - e^{(z+d)^2/4Dt} \right]$$
Operator $-\Delta$ has strictly positive eigenvalues $\lambda_1 \leq \lambda_2 \leq \ldots$. Survival probability $\phi(t) \sim e^{-D\lambda_1 t}$

Are there semiclassical estimates of $\lambda_1$?
Two diffusive colloidal particles, radius $R_A$ and $R_B$, diffusivity $D_A$ and $D_B$, “reaction” (aggregation) upon first encounter.

Capture radius $R_c = R_A + R_B$, Relative diffusion constant $D_c = D_A + D_B$, $B$ disappears when touching $A$. 
Capture of Brownian particles

Application: Time resolved association kinetics of colloids

Membrane adhesion

Second quantization formalism

References

Smoluchovsky reaction rate (2)
Electrostatic analogy

- Put A at the origin
- Assume (mean-field) stationary diffusion state, concentration of B reads:

\[
c_B(r) = \left(1 - \frac{R_c}{r}\right)c_B(\infty)
\]

- Average total flux of B around A: \(\vec{j} = -\vec{\nabla}c_B\)

\[4\pi D_c R_c \rightarrow \text{rate}\]
Capture of Brownian particles

Application: Time resolved association kinetics of colloids

Membrane adhesion

Second quantization formalism

References

Smoluchovsky reaction rate (4)

\[ \frac{\text{d}[C]}{\text{d}t} = -k_{on}[A][B]; \quad k_{on} = 4\pi(D_A + D_B)(R_A + R_B) \]

Association constant \( A + B \rightarrow C \)

Important for enzyme kinetics: if \( R_A \sim R_B \), \( k_{on} \) almost size independent

see e.g. D.Shoup and A.Szabo. Biophys.J. 40 (1982),
Non mean-field behaviours as expected for reacting and diffusing species in low dimensions.

- Historical example by D. Toussaint and F. Wilczek (1983)

\[ A + \bar{A} \rightarrow \emptyset \]

- Many epidemic propagation models: \( H \) healthy, \( S \) sick

\[ S + H \rightarrow S + S \]

\[ S \rightarrow H \]

\[ S \rightarrow \emptyset \]
Capture of Brownian particles

Application: Time resolved association kinetics of colloids

Membrane adhesion

Second quantization formalism

References

\[ A + \overline{A} \rightarrow \emptyset \] (Toussaint and Wilczek)


- Naive mean-field scaling implies \([A] = [\overline{A}]\), \(\frac{d[A]}{dt} = -k[A]^2\) therefore \([A] \sim t^{-1}\).
- Accurate treatment shows that \([A] \sim t^{-d/4}\), mean field result recovered for \(d \geq d_c = 4\) only!
- Reaction restricted to \(A, \overline{A}\) domains boundaries.
$A + \overline{A} \rightarrow \emptyset$ (D. Toussaint and F. Wilczek)

**Reaction restricted to $A$, $\overline{A}$ domains boundaries.**

- "Foam" of particle-antiparticle domains

Usual mean-field chemical kinetics should not be assumed in low dimensional or restricted environment.
… which does not mean the same for everybody...

1. Diffusive, superdiffusive, Levy flight displacements (disease propagation, search strategies...)
2. Many-body correlations, anomalous scaling
3. Complex diffusive behaviours and configuration spaces (e.g. polymer or membrane dynamics)
4. Hydrodynamic interactions

Our focus is mainly on item 3 and 4
Capture of Brownian particles
Application: Time resolved association kinetics of colloids
Membrane adhesion
Second quantization formalism
References

Polymer bridging and cyclization problems
Barrier crossing

Polymer bridging similar to a Kramers reaction path across an activated state, but

<table>
<thead>
<tr>
<th>Dynamics</th>
<th>Bridging</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>many internal degrees of freedom</td>
<td>diffusive</td>
<td>inertial, damped few degrees of freedom</td>
</tr>
</tbody>
</table>

References

Capture of Brownian particles

Application: Time resolved association kinetics of colloids

Membrane adhesion

Second quantization formalism

Barrier crossing

Polymer bridging similar to a Kramers reaction path across an activated state, but

<table>
<thead>
<tr>
<th>Dynamics</th>
<th>Bridging</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>many internal degrees of freedom</td>
<td>diffusive</td>
<td>inertial, damped few degrees of freedom</td>
</tr>
</tbody>
</table>

References
And when it becomes difficult. . .

- Curved spaces (rotational diffusion)
- Large number of degrees of freedom (macromolecules)
- Inhomogeneous diffusion (ex: hydrodynamical interactions)

Configuration space: reaction zone defined by $S(r)$. 
Capture of Brownian particles

Application:
Time resolved association kinetics of colloids
Membrane adhesion
Second quantization formalism

Polymer bridging and cyclization problems

Wilemski-Fixman approach:

\[
(\partial_t - \hat{L}_D) G(r, r_i; t) = -qS(r) G(r, r_i; t)
\]  \hspace{1cm} (4)

Left: diffusion term, Right: reaction term

- \( S(r) \) sink (annihilation of particles)
- \( \hat{L}_D \) diffusion operator (geometry)
- \( G(r, r_i; t) \) Green function probability to reach \( r \) at time \( t \), starting from \( r_i \) without having reacted.
Wilemski-Fixman approach

Capture of Brownian particles

Application: Time resolved association kinetics of colloids

Membrane adhesion

Second quantization formalism

References

Free diffusion

\[
(\partial_t - \hat{L}_D) G_0(r, r_i; t) = 0
\]  \hspace{1cm} (5)

If \( G_0 \) known, then \( G \) is given by an integral equation

\[
G(r, r_i; t) = G_0(r, r_i; t) - q \int_0^t dt' \int dr' G_0(r, r'; t - t') S(r) G(r', r_i; t')
\]  \hspace{1cm} (6)

With a few assumptions, one deduces \( G \) from \( G_0 \).
Survival probability $\phi(t)$

- $\phi(t)$ monotonous, $1 \rightarrow 0$
- $-\phi'(t)$ distribution of reaction times
- $-\phi'(t)/\phi(t) = \text{reaction rate } \omega(t)$

$\omega$ constant $\rightarrow$ exponential relaxation
$\omega(t)$ $\rightarrow$ non exponential relaxation
Limit of strong reaction rate

Capture of Brownian particles

Application: Time resolved association kinetics of colloids

Membrane adhesion

Second quantization formalism

References

Determination of survival function $\phi(t)$ reduces to the relaxation function $h(t)$

$$h(t) \simeq \frac{\int d\mathbf{r} S(\mathbf{r}) G_0(\mathbf{r}, \mathbf{r}_R; t)}{\int d\mathbf{r} S(\mathbf{r}) G_0(\mathbf{r}, \mathbf{r}_R; \infty)} - 1$$

$$\hat{\phi}(s) = \frac{\hat{h}(s)}{1 + s\hat{h}(s)}$$

In particular

$$\langle t \rangle = \int_0^\infty dt \ h(t)$$
Application: Time resolved association kinetics of colloids
Magnetic colloids...

- **Magnetic colloids** (⌀ : 200 nm) ⇒ alignment under field ($B \sim 1$ mT).
- Repulsion (charge stabilization, polymer brush) vs induced dipolar interaction ⇒ tunable distance.

J.Bibette team at ESPCI Paris

Magnetic colloids...

J. Bibette team at ESPCI Paris


- Magnetic colloids (⌀: 200 nm)
  ⇒ alignment under field ($B \sim 1$ mT).
- Repulsion (charge stabilization, polymer brush) vs induced dipolar interaction
  ⇒ tunable distance.

FIG. 1. Superparamagnetic beads (optical microscope, ×40)
Highly specific and stable pair of ligand and receptor
Noncovalent binding (H-bonds) $\Delta G \sim 30 \, k_B T$
Beads + streptavidin, $n_R$ receptors / bead (average).
A few biotinylated beads, $n_L = 0$ or 1 ligand / bead.
Possibility of spacer 1-10 nm

Figure: Initial state
Capture of Brownian particles

Application: Time resolved association kinetics of colloids

Membrane adhesion

Second quantization formalism

References

... for adhesion kinetics...

- Beads + *streptavidin*, $n_R$ receptors / bead (average).
- A few *biotinylated* beads, $n_L = 0$ or 1 ligand / bead.
- Possibility of spacer 1-10 nm

No ligand

Figure: Applied field
Capture of Brownian particles

Application: Time resolved association kinetics of colloids

Membrane adhesion

Second quantization formalism

References

Beads + streptavidin, \( n_R \) receptors / bead (average).

A few biotinylated beads, \( n_L = 0 \) or 1 ligand / bead.

Possibility of spacer 1-10 nm

Figure: Return to initial state
Capture of Brownian particles

Application: Time resolved association kinetics of colloids

Membrane adhesion
Second quantization formalism
References

... for adhesion kinetics...

- Beads + streptavidin, $n_R$ receptors / bead (average).
- A few biotinylated beads, $n_L = 0$ or 1 ligand / bead.
- Possibility of spacer 1-10 nm

With ligand

![Figure: Initial state](image-url)
Beads + *streptavidin*, $n_R$ receptors / bead (average).
- A few *biotinylated* beads, $n_L = 0$ or 1 ligand / bead.
- Possibility of spacer 1-10 nm

**With ligand**

Figure: Applied field

References
Beads + **streptavidin**, $n_R$ receptors / bead (average).
A few **biotinylated** beads, $n_L = 0$ or 1 ligand / bead.
Possibility of spacer 1-10 nm

**With ligand**

![Diagram of beads and receptors](image)

**Figure:** “Reaction” take place
Capture of Brownian particles

Application: Time resolved association kinetics of colloids

Membrane adhesion

Second quantization formalism

References

... for adhesion kinetics...

- Beads + streptavidin, $n_R$ receptors / bead (average).
- A few biotinylated beads, $n_L = 0$ or 1 ligand / bead.
- Possibility of spacer 1-10 nm

**With ligand**

**Figure:** Formation of remnant doublets
Capture of Brownian particles

Application: Time resolved association kinetics of colloids

Membrane adhesion

Second quantization formalism

References

... for adhesion kinetics...

- Rotational diffusion limited reaction
- Doublet formation
- Optical measure of number of doublets (turbidity, light absorption)
Capture of Brownian particles

Application: Time resolved association kinetics of colloids

Membrane adhesion

Second quantization formalism

References

- Reaction time = Duration of applied magnetic field
- Repeated experiments ... or incremental measure of the reaction rate
- Turbidity \( \propto \) reaction advancement \( \xi(t) \), point per point
... time resolved

- Exponential experimental curve

First order kinetics \( \exp(-t/\tau) \).

Characteristic time \( \tau \approx \tau_1/n_R \), \( \tau_1 \) reaction time.
Case n° 1: bead saturated with receptors


Everything is reduced to a patch capture radius $r_c$

Reaction rate limited by the ligand diffusion:

$$\tau_1 = \tau_{\text{rot}} \ln(a/r_c)$$

$r_C$: capture radius, $a$ colloïd radius.
Case n° 2: two beads saturated with receptors

Time $\tau_2$ halves $\tau_1$ only in the limit $r_c/a \to 0$.

Relative corrections:

$$\frac{2\tau_2}{\tau_1} \sim \frac{1}{\ln(a/r_c)}$$
Case n° 3: one ligand and one receptor

The most interesting case:

\[ \tau_1 = \tau_{\text{rot}} \frac{4a^2}{r_C r_S} \left[ \left( \frac{r_C}{r_S} + \frac{r_S}{r_C} \right) \ln \left( \frac{r_C}{r_S} + \frac{r_S}{r_C} \right) + \left( \frac{r_S}{r_C} - \frac{r_C}{r_S} \right) \ln \left( \frac{r_C}{r_S} \right) \right] \]

Symetrical case \( r_C = r_S \):

\[ \tau_1 = 8 \ln(2) \tau_{\text{rot}} \frac{a^2}{r_C^2} \]

a bead radius, \( r_C \) capture radius.
Orders of magnitudes:

- $\tau_1$ (experimental) $\simeq 10^4$ s.
- $\tau_{\text{rot}} \simeq 5$ ms.
- Aspect ratio $a/r_c$ of order between $10^3$ and $10^4$
- Reasonable capture radius $r_c \simeq 1$ Å
- Capture radius correlates with spacer length if any
Other applications

Capture of Brownian particles
Application: Time resolved association kinetics of colloids
Membrane adhesion
Second quantization formalism
References
The problem of membrane adhesion (if any)

How to predict the distribution of the first adhesive patch creation times?
The problem of membrane adhesion

- Adhesion is a nucleation problem
- Hydrodynamic flow cannot be disregarded (unlike polymer bridging)
- Membrane dynamics harder than polymer dynamics
Reaction time between two spheres diverge if sticking boundary conditions are enforced


Distance cut-off or slippery condition needed, does that control the nucleation time?
The problem of membrane adhesion (if any)

- Lipidic bilayers in liquid phase $\Rightarrow$ free diffusion of ligands.
- Receptors grafted on the surface $\Rightarrow$ irreversible reaction
- Modeling (simulation, calculation) of the adhesion kinetics of the membrane onto the surface
- Velocity, membrane tension, hydrodynamics, homogeneous anchoring?
Second quantization formalism

Capture of Brownian particles

Application: Time resolved association kinetics of colloids

Membrane adhesion

Second quantization formalism

References
Master equation for reaction-diffusion $X \rightarrow \emptyset$

$$\partial_t n(r, t) = D \nabla^2 n(r, t) - \mu \nabla (n(r, t)f(r, t)) - S(r)n(r, t),$$

- diffusion + drift + reaction
- $n(r, t)$ probability of presence
- $f(r, t)$ drift force
- $S(r)$ sink (disappearance rate)

Following M. Doi J.of Physics, 9(9) p 1465 (1976), Mattis and Glasser, Rev.Mod.Phys. 70 p979 (1998)

\[ \hat{\mathcal{H}} = \int \mathbf{d} \mathbf{r} \left[ D (\nabla a^\dagger (\mathbf{r}) \cdot \nabla a(\mathbf{r})) - \mu (\mathbf{f}(\mathbf{r}) \cdot \nabla a^\dagger (\mathbf{r})) a(\mathbf{r}) \right. \\
\left. + S(\mathbf{r})(a^\dagger (\mathbf{r}) a(\mathbf{r}) - a(\mathbf{r})) \right] \tag{7} \]

\[ |\Phi(t)\rangle = \exp \left( - \hat{\mathcal{H}} t \right) a(\mathbf{r}_0) |0\rangle , \]

\[ n(\mathbf{r}, t) = \langle 0 | \exp \left( \int \mathbf{d} \mathbf{r}' a(\mathbf{r}') \right) a(\mathbf{r}) |\Phi(t)\rangle , \]
Trotter-Strang splitting → algorithm

Time evolution

$$|\psi(t)\rangle = e^{-(\hat{H}_D + \hat{H}_F + \hat{H}_R) t} |\psi(0)\rangle$$

$$e^{-(\hat{H}_D + \hat{H}_F + \hat{H}_R) t} = \left[ e^{-(\hat{H}_D + \hat{H}_F + \hat{H}_R) \Delta t} \right]^{t/\Delta t}$$

$$\simeq \left[ e^{-\frac{\Delta t}{2} \hat{H}_R} \cdot e^{-\frac{\Delta t}{2} \hat{H}_F} \cdot e^{-\Delta t \hat{H}_D} \cdot e^{-\frac{\Delta t}{2} \hat{H}_F} \cdot e^{-\frac{\Delta t}{2} \hat{H}_R} \right]^{t/\Delta t} .$$

(8)
Peliti integral functional

Functional integral expression of Doi’s evolution operator by L. Peliti.
Journal de Physique 46 p1469 (1985), J. Cardy cond-mat/1995

\[ \int \mathcal{D}[\eta](r, t)\mathcal{D}[\hat{\eta}](r, t) \]

\[ \exp \left[ - \int \text{d}r\text{d}t \left\{ \hat{\eta} \dot{\eta} - \hat{\eta} \Delta \eta + f(r)\hat{\eta} \nabla \eta + S(r)(\hat{\eta} \eta - \eta) \right\} \right] \tag{9} \]

Coherent state representation, \( \eta \) real, \( \hat{\eta} \) imaginary

...favorite starting point for studying many-body correlations.
Internal state switching

A (large steps) ↔ B (small steps)

The standard master equation of the process becomes:

\[ \partial_t n_A(r, t) = D \nabla^2 n_A(r, t) - \mu \nabla (\tilde{f}(r)n_A(r, t)) - S(r)n_A(r, t) + w_{AB}(r)n_B(r, t) - w_{BA}(r)n_A(r, t); \]

\[ \partial_t n_B(r, t) = D \nabla^2 n_B(r, t) - \mu \nabla (\tilde{f}(r)n_B(r, t)) - S(r)n_B(r, t) - w_{AB}(r)n_B(r, t) + w_{BA}(r)n_A(r, t). \]

Overlap between A and B populations...
Second quantization

\[ \hat{\mathcal{H}}_{\sigma} = \hat{\mathcal{H}}_{A,R} + \hat{\mathcal{H}}_{A,D} + \hat{\mathcal{H}}_{A,F} + \hat{\mathcal{H}}_{A,Ex} + \hat{\mathcal{H}}_{B,R} + \hat{\mathcal{H}}_{B,D} + \hat{\mathcal{H}}_{B,F} + \hat{\mathcal{H}}_{B,Ex}, \]

with components

\[
\begin{align*}
\hat{\mathcal{H}}_{A,R} &= \int dr \left[ S(r)(a^\dagger(r)a(r) - a(r)) \right]; \\
\hat{\mathcal{H}}_{A,D} &= \int dr \left[ D(\nabla a^\dagger(r) \cdot \nabla a(r)) \right]; \\
\hat{\mathcal{H}}_{A,F} &= \int dr \left[ -\mu(\tilde{f}(r) \cdot \nabla a^\dagger(r))a(r) \right]; \\
\hat{\mathcal{H}}_{A,Ex} &= \int dr \left[ w_{BA}(r) \left( a^\dagger(r)a(r) - b^\dagger(r)a(r) \right) \right]; \\
\hat{\mathcal{H}}_{B,R} &= \int dr \left[ S(r)(b^\dagger(r)b(r) - b(r)) \right]; \\
\hat{\mathcal{H}}_{B,Ex} &= \int dr \left[ w_{AB}(r) \left( b^\dagger(r)b(r) - a^\dagger(r)b(r) \right) \right].
\end{align*}
\]
Splitting

\[
\exp(-\mathcal{F}\hat{H}_\sigma \Delta t) = \left\{ e^{-\Delta t \hat{\mathcal{H}}_{B, Ex}/2} \left[ e^{-\Delta t \hat{\mathcal{H}}_{B, R}/2} e^{-\Delta t \hat{\mathcal{H}}_{B, F}/2} e^{-\Delta t \hat{\mathcal{H}}_{B, D}} \right] \right\}^{\mathcal{F}/2}
\]
\[
\times e^{-\mathcal{F}\Delta t \hat{\mathcal{H}}_{A, Ex}/2} \left[ e^{-\mathcal{F}\Delta t \hat{\mathcal{H}}_{A, R}/2} e^{-\mathcal{F}\Delta t \hat{\mathcal{H}}_{A, F}/2} e^{-\mathcal{F}\Delta t \hat{\mathcal{H}}_{A, D}} \right] e^{-\mathcal{F}\Delta t \hat{\mathcal{H}}_{A, Ex}/2}
\]
\[
\times \left\{ e^{-\Delta t \hat{\mathcal{H}}_{B, Ex}/2} \left[ e^{-\Delta t \hat{\mathcal{H}}_{B, R}/2} e^{-\Delta t \hat{\mathcal{H}}_{B, F}/2} e^{-\Delta t \hat{\mathcal{H}}_{B, D}} \right] \right\}^{\mathcal{F}/2}
\]

One recognizes occurrences of algorithm I in brackets \([\cdot]\).

Algebra dictates the algorithm!
Algorithm II: multiple time step algorithm

1. Repeat $\mathcal{F}/2$ times
   1.a. If the particle is $B$, consider changing its state during a time interval $\Delta t/2$, else do nothing.
   1.b. If the particle is still $B$, proceed with algorithm I during the time interval $\Delta t$.
   1.c. If the particle is still $B$, consider changing its state during a time interval $\Delta t/2$, else do nothing.

2. Do once
   2.a. If the particle is $A$, consider changing its state during a time interval $\mathcal{F}\Delta t/2$, else do nothing.
   2.b. If the particle is still $A$, proceed with algorithm I during the time interval $\mathcal{F}\Delta t$.
   2.c. If the particle is still $A$, consider changing its state during a time interval $\mathcal{F}\Delta t/2$, else do nothing.

3. Same as 1.
Application to rotating colloids

Capture of Brownian particles
Application: Time resolved association kinetics of colloids
Membrane adhesion
Second quantization formalism
References

Fully covered (sticking) colloid
Sticky patch

Θ_c
Θ_inf
Θ_sup
Capture of Brownian particles

Application: Time resolved association kinetics of colloids

Membrane adhesion

Second quantization formalism

References

Histories

no reaction

reaction

top to bottom $\mathcal{F} = 8, 16, 32$
Reaction time vs acceleration factor

Capture of Brownian particles
Application: Time resolved association kinetics of colloids
Membrane adhesion
Second quantization formalism

References
Capture of Brownian particles

Application: Time resolved association kinetics of colloids

Membrane adhesion

Second quantization formalism

References

Cpu time

one body

many body
Conclusion

This procedure leads to a **weak order two** reaction-diffusion algorithm.

Extension to many body interactions possible.

Internal state switching may also be used for **deterministic multiple time step algorithms**.
Further reading

- Measuring the kinetics of biomolecular recognition with magnetic colloids
  L. Cohen-Tannoudji et al, PRL 100(10), 108301 (2008)

- Ligand-receptor interactions in chains of colloids: When reactions are limited by rotational diffusion

- Fast algorithms for classical $X \rightarrow 0$ reaction diffusion problems
Special thanks

Pr. Nam-Kyung Lee, C.M. Marques, A. Johner