SECOND-QUANTISED APPROACH
to
REACTION-DIFFUSION SYSTEMS

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Outline.

1. Review of 2nd-quantised formalism [`Doi, Peliti`]
2. Langevin equation
3. Example: $A + A \rightleftharpoons C$ [`P-A Rey, JC`]

Second-quantised formalism

Master equation:

$$(d/dt)p(\alpha;t) = \sum_\beta R(\alpha \leftarrow \beta)p(\beta) - \sum_\beta R(\beta \leftarrow \alpha)p(\alpha)$$

Reaction-diffusion system: particles of species $j = A, B, \ldots$ diffuse on a lattice $\{\mathbf{r}\}$ and undergo single-site reactions. $\{\alpha\} = \{n_j(r)\}$.

Similarities to relativistic QFT:

- time-evolution equation is linear (like Schrödinger equation)
- particle number is not conserved

Suggests *second-quantised* formalism:

- operators $[\hat{a}_j(\mathbf{r}), \hat{a}^\dagger_{j'}(\mathbf{r}')] = \delta_{jj'}\delta_{\mathbf{r},\mathbf{r}'}$
- 'vacuum' $\hat{a}_j(\mathbf{r})|0\rangle = 0$
- many-particle state

$$|\Psi(t)\rangle \equiv \sum_{\{n_j(\mathbf{r})\}} p(\{n_j(\mathbf{r})\};t) \prod_j \prod_{\mathbf{r}} (\hat{a}^\dagger_j(\mathbf{r}))^{n_j(\mathbf{r})}|0\rangle$$

Then master equation $\Leftrightarrow$

$$(d/dt)|\Psi\rangle = -\hat{H}|\Psi\rangle$$

where $\hat{H} = \hat{H}(\{\hat{a}_j(\mathbf{r}); \hat{a}^\dagger_j(\mathbf{r})\})$.

Example : $\quad A + A \xrightarrow{\lambda} \emptyset$

$\hat{H} = \hat{H}_{\text{diff}} + \hat{H}_{\text{react}}$ where

$$\hat{H}_{\text{diff}} \propto \sum_{\text{n.n.}} \left(\hat{a}^\dagger(\mathbf{r}')\hat{a}(\mathbf{r}) - \hat{a}^\dagger(\mathbf{r})\hat{a}(\mathbf{r})\right) \to D\int(\nabla\hat{a}^\dagger.\nabla\hat{a})d^dr$$

$$\hat{H}_{\text{react}} = \lambda\int(\hat{a}^2 - \hat{a}^{\dagger 2}\hat{a}^2)d^dr$$

Differences from many-body quantum mechanics:

- no i
- expectation values given by

$$\begin{aligned} \overline{\mathcal{O}} &= \sum_{\{n(\mathbf{r})\}} p(\{n(\mathbf{r})\};t)\mathcal{O}(\{n(\mathbf{r})\}) \\ &= \langle 0|e^{\sum_{\mathbf{r}}\hat{a}(\mathbf{r})}\hat{\mathcal{O}}|\Psi(t)\rangle \\ &\neq \langle\Psi(t)|\hat{\mathcal{O}}|\Psi(t)\rangle \end{aligned}$$

– move $e^{\sum_{\mathbf{r}}\hat{a}(\mathbf{r})}$ to right $\Leftrightarrow$ shift $\hat{a}^\dagger(\mathbf{r}) \to \hat{a}^\dagger(\mathbf{r}) + 1$

$$\hat{H}_{\text{react}} \to -\lambda\int(2\hat{a}^\dagger\hat{a}^2 + \hat{a}^{\dagger 2}\hat{a}^2)d^dr$$

Path integral formulation: $(\hat{a}^\dagger(\mathbf{r}), \hat{a}(\mathbf{r})) \to (\bar{a}(\mathbf{r},t), a(\mathbf{r},t))$ and

$$\langle 0|\ldots|0\rangle = \int \mathcal{D}\bar{a}\mathcal{D}a \ldots e^{-S}$$

where

$$S = \int (\bar{a}\partial_t a + D\nabla\bar{a}\nabla a + \lambda(2\bar{a}a^2 + \bar{a}^2 a^2))dt d^d r + S_{t=0}$$

- starting point for Feynman diagram expansion and RG analysis [Lee]
- *OR...*

Langevin equation

- $$e^{-\lambda\bar{a}^2 a^2} = \langle e^{\eta\bar{a}}\rangle_\eta$$
  where $\langle\eta\rangle = 0$, $\langle\eta^2\rangle = -2\lambda a^2 = -2\lambda\langle a^2\rangle$;
- $$\int e^{(\text{expression})\bar{a}} d\bar{a} = \delta(\text{expression})$$

Langevin-type equation:

$$\partial_t a = D\nabla^2 a - 2\lambda a^2 + \eta(\mathbf{r},t)$$

where

$$\langle\eta(\mathbf{r},t)\eta(\mathbf{r}',t')\rangle = -2\lambda\langle a(\mathbf{r},t)^2\rangle\delta(\mathbf{r}-\mathbf{r}')\delta(t-t')$$

- rate equation + noise, but if $a > 0$, noise is pure imaginary!
- necessary because $\overline{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')} < 0$ if $\mathbf{r} \neq \mathbf{r}'$
- possible because $a(\mathbf{r},t) \neq \rho(\mathbf{r},t)$:
  $$\overline{\rho(\mathbf{r},t)} = \langle a(\mathbf{r},t)\rangle \qquad \text{but} \qquad \overline{\rho(\mathbf{r},t)^2} \neq \langle a(\mathbf{r},t)^2\rangle$$

Application to $A + A \xrightarrow{\lambda} C, \quad C \xrightarrow{\mu} A + A$

Rate equations:

$$\begin{aligned}\partial_t \rho_a &= -2\lambda\rho_a^2 + 2\mu\rho_c \\ \partial_t \rho_c &= \lambda\rho_a^2 - \mu\rho_c\end{aligned}$$

$\Rightarrow (\rho_a(t), \rho_c(t)) \to (\rho_a(\infty), \rho_c(\infty))$ *exponentially* fast.

- this cannot be right, because $\rho_a + 2\rho_c$ is conserved, and any initial fluctuations should decay slowly, like $t^{-d/2}$.
- attempts to patch up the rate equations, by
  - adding diffusion terms $D\nabla^2\rho$ and assuming random initial conditions, and/or
  - adding real noise

  give unphysical results.

Second-quantised approach:

$$\begin{aligned} S_{\text{react}} &= \lambda(\bar{c}a^2 - \bar{a}^2a^2) + \mu(\bar{a}^2c - \bar{c}c) \\ \text{shift} &\to (\bar{c} - 2\bar{a})(\lambda a^2 - \mu c) - \bar{a}^2(\lambda a^2 - \mu c) \end{aligned}$$

$\Rightarrow$ Langevin-type equations

$$\begin{aligned} \partial_t a &= D\nabla^2 a - 2\lambda a^2 + 2\mu c + \eta \\ \partial_t c &= D\nabla^2 c + \lambda a^2 - \mu c \end{aligned}$$

where

$$\langle \eta(\mathbf{r}, t)\eta(\mathbf{r}', t')\rangle = \underbrace{2\langle \mu c - \lambda a^2\rangle}_{-2\langle \partial_t c\rangle} \delta(\mathbf{r} - \mathbf{r}')\delta(t - t')$$

- noise $\to 0$ as $t \to \infty \Rightarrow (a(\mathbf{r}, t), c(\mathbf{r}, t)) \to (a_\infty, c_\infty)$ where

$$\lambda a_\infty^2 = \mu c_\infty^2 \quad \text{and} \quad a_\infty + 2c_\infty = a_0 + 2c_0$$

- $\chi \equiv a + 2c$ is not strictly conserved:

$$\partial_t \chi = D\nabla^2 \chi + \eta$$

Solution:

$\chi(\mathbf{r},t) = \int_0^t dt' \int d^d r\, G_0(\mathbf{r}-\mathbf{r}'; t-t')\eta(\mathbf{r}',t') + \chi(t=0)$

so $\langle \chi(\mathbf{r},t)\rangle = \chi(t=0) = a_0 + 2c_0$, and

$$\begin{aligned}
\langle (\delta\chi)^2 \rangle &= -2 \int_0^t dt' (8\pi D(t-t'))^{-d/2} \partial_{t'} \langle c(t')\rangle \\
&\sim -2(8\pi D t)^{-d/2} \int_0^\infty dt' \partial_{t'} \langle c(t')\rangle \\
&= 2(c_0 - c_\infty)(8\pi D t)^{-d/2}
\end{aligned}$$

and higher cumulants vanish.

- now eliminate $a = \chi - 2c$ in the c-equation:

$$\partial_t c = D\nabla^2 c + \lambda(\chi - 2c)^2 - \mu c$$

  and solve for $\langle c\rangle$ in terms of $\langle (\delta\chi)^n\rangle$.

- leading term same as assuming *local* equilibrium:

$$\begin{aligned}
\lambda a(\mathbf{r},t)^2 &\approx \mu c(\mathbf{r},t) \\
a(\mathbf{r},t) + 2c(\mathbf{r},t) &= \chi(\mathbf{r},t)
\end{aligned}$$

  so

$$a \approx (-\mu + \sqrt{\mu^2 + 8\mu\lambda\chi})/(2\lambda)$$

  hence

$$\langle a\rangle = a_\infty + \text{const.} \langle (\delta\chi)^2\rangle + \cdots$$

Final result:

$$\langle c(t)\rangle - c_\infty \sim \frac{2\lambda\mu^2}{(4\lambda a_\infty + \mu)^2}(c_0 - c_\infty)(8\pi D t)^{-d/2}$$

Comments

- decay towards equilibrium is monotonic;
- correlations $\langle c(\mathbf{r},t)c(\mathbf{r}',t)\rangle$ can be treated similarly;
- unequal diffusivities $D_a \neq D_c$ also treatable but more difficult
- method generalises to more species when there are conservation laws

Summary

- general method gives a *systematic* way of computing the effects of fluctuations in reaction-diffusion systems, either by
  - renormalisation group, or
  - direct solution of the corresponding Langevin equation.
- complex noise is peculiar but leads to physical results.