88 5.3. Fock space representation, Hamiltonian structure

chemical reactions on d-dimensional lattice, sites $i, j \dots$

fully characterized by occupation numbers $\{n_i, m_i \dots\}$ of

particle species $A, B, \dots$, $n_i, m_i, \dots = 0, 1, \dots$ integer

reactions alter these numbers by integer amounts

→ employ "second-quantized", bosonic Fock space representation

with annihilation / creation operators a_i, a_i^+ obeying the algebra

$$[a_i, a_j] = 0 = [a_i^+, a_j^+], \quad [a_i, a_j^+] = \delta_{ij}$$

and similarly for b_i, b_i^+, with $[a_i, b_j] = 0 = [a_i, b_j^+]$

as for quantum harmonic oscillator, construct particle number eigenstates

$$a_i |n_i\rangle = n_i |n_i - 1\rangle, \quad a_i^+ |n_i\rangle = |n_i + 1\rangle, \quad a_i^+ a_i |n_i\rangle = n_i |n_i\rangle$$

with integer eigenvalues $n_i = 0, 1, \dots$, vacuum state: $a_i |0\rangle = 0$

note: normalization different from quantum mechanics

→ Fock product state $|\{n_i, m_i, \dots\}\rangle = \prod_i (a_i^+)^{n_i} (b_i^+)^{m_i} \dots |0\rangle$

introduce formal state vector via linear combination of all Fock

states weighted with configurational probabilities:

$$|\Phi(t)\rangle = \sum_{\{n_i, m_i \dots\}} P(\{n_i, m_i \dots\}; t) \, |\{n_i, m_i, \dots\}\rangle$$

since time evolution from master equation is linear,

one can write $\dfrac{\partial |\Phi(t)\rangle}{\partial t} = -H |\Phi(t)\rangle$

with non-Hermitean stochastic pseudo-Hamiltonian, really

Liouville time evolution operator, H

example: $kA \xrightarrow{\lambda} \ell A$ $(k > \ell \geqq 0)$, reactions on-site

master equation: $\frac{\partial P(n_i;t)}{\partial t} = \lambda \left[\frac{(n_i+k-\ell)!}{(n_i-\ell)!} P(n_i+k-\ell;t) - \frac{n_i!}{(n_i-k)!} P(n_i;t) \right]$

for state vector (site i): first term: shift index $n_i \to n_i+\ell-k$

$$\frac{\partial|\phi_i(t)\rangle}{\partial t} = \lambda \sum_{n_i=\max(0,k-\ell)}^{\infty} P(n_i;t) \overbrace{n_i(n_i-1)\dots(n_i-k+1)\,|n_i-k+\ell\rangle}^{=(a_i^+)^\ell a_i^k |n_i\rangle}$$
$$- \lambda \sum_{n_i=k}^{\infty} P(n_i;t)\, \underbrace{n_i(n_i-1)\dots(n_i-k+1)\,|n_i\rangle}_{=(a_i^+)^k a_i^k |n_i\rangle}$$

$\to H_i = \lambda \left[(a_i^+)^k - (a_i^+)^\ell \right] a_i^k$

on-site reactions: <u>local</u> operators $H = \sum_i H_i(\{a_i^+ \dots\},\{a_i \dots\})$ normal-ordered

- positive contribution: from loss term in master equation, indicates "order" k of chemical reaction: $:(a_i^+ a_i)^k: = (a_i^+)^k a_i^k$
- negative contribution, from gain term: encodes reaction process, k particles destroyed, ℓ recreated: $(a_i^+)^\ell a_i^k$

$\to$ "cookbook recipe" for construction of pseudo-Hamiltonians, e.g.

- $A \xrightarrow{\mu} \emptyset$, $A \underset{\lambda}{\overset{\sigma}{\rightleftarrows}} A+A$: $H_i = (a_i^+ - 1)(\mu - \sigma a_i^+ + \lambda a_i^+ a_i) a_i$

generalization to multiple species straightforward, for example

- $kA + \ell B \underset{\sigma}{\overset{\lambda}{\rightleftarrows}} mC$: $H_i = \left[(a_i^+)^k (b_i^+)^\ell - (c_i^+)^m \right] (\lambda a_i^k b_i^\ell - \sigma c_i^m)$
- Lotka-Volterra predator-prey dynamics: $A \xrightarrow{\mu} \emptyset$, $B \xrightarrow{\sigma} B+B$,

  $A+B \xrightarrow{\lambda} A+A$: $H_i = \mu(a_i^+ - 1)a_i - \sigma b_i^+(b_i^+ - 1)b_i + \lambda a_i^+(b_i^+ - a_i^+)a_i b_i$
- non-local processes such as hopping from site i to site j, rate D:

  treat different sites as distinct species $\to H = D \sum_{\langle ij \rangle} (a_i^+ - a_j^+)(a_i - a_j)$

note: if occupation numbers are restricted to $0 \leqq n_i \leqq 2S+1$:

representation in terms of spin S operators possible/useful formal solution of time evolution equation: $|\phi(t)\rangle = e^{-Ht}|\phi(0)\rangle$

initial configuration e.g. uncorrelated Poisson distribution:

$P(\{n_i\};0) = \prod_i P_0(n_i)$, $P_0(n_i) = \frac{\bar{n}_0^{\,n_i}}{n_i!} e^{-\bar{n}_0}$, $\langle n_i\rangle = \bar{n}_0$ on site

→ initial state vector $|\phi(0)\rangle = \prod_i \frac{(\bar{n}_0 a_i^+)^{n_i}}{n_i!} e^{-\bar{n}_0}|0\rangle = e^{\bar{n}_0 \sum_i (a_i^+ - 1)}|0\rangle$

→ borrow methods from many-particle quantum mechanics for further analysis.

however: no interference terms, probabilities, not amplitudes

to compute expectation value of observable $A(\{n_i\})$:

$\langle A(t)\rangle = \sum_{\{n_i\}} A(\{n_i\}) P(\{n_i\};t)$ (function of site occupation numbers)

use projection state $\langle \mathcal{P}| = \langle 0| \prod_i e^{a_i}$, $\langle \mathcal{P}|0\rangle = 1$

with $[e^{a_i}, a_j^+] = e^{a_i}\delta_{ij}$: $\langle \mathcal{P}|a_i^+ = \langle \mathcal{P}|$

then: $\langle \mathcal{P}|A(\{a_i^+ a_i\})|\phi(t)\rangle = \langle \mathcal{P}|A(\{a_i^+ a_i\})\, e^{-H(\{a_i^+\},\{a_i\})t}|\phi(0)\rangle$

$= \sum_{\{n_i\}} \langle 0|\prod_i e^{a_i} \overset{\to A(\{n_i\})}{A(\{a_i^+ a_i\})} \underbrace{\prod_i (a_i^+)^{n_i}|0\rangle}_{|\{n_i\}\rangle} P(\{n_i\};t) = \langle A(t)\rangle$

↑ commute through

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set $A = 1$ → probability conservation $1 = \langle \mathcal{P}|e^{-Ht}|\phi(0)\rangle$

normalized initial state $\langle \mathcal{P}|\phi(0)\rangle = 1$ → $\langle \mathcal{P}|H(\{a_i^+\},\{a_i\}) = 0$

again, commute $\prod_i e^{a_i}$ through: → $H(\{a_i^+ \to 1\};\{a_i\}) = 0$

and rewrite observable averages : $A(\{a_i^+ a_i\}) := \tilde{A}(\{a_i^+\},\{a_i\})$

projection state from left yields $\tilde{A}(\{a_i^+ \to 1\},\{a_i\})$

e.g.: $a_i^+ a_i \to a_i$, $a_i^+ a_i\, a_j^+ a_j = a_i^+ a_i \delta_{ij} + a_i^+ a_j^+ a_i a_j \to a_i \delta_{ij} + a_i a_j$

→ $\langle A(t)\rangle = \langle 0|\tilde{A}(\{1\},\{a_i\})\, e^{-H(\{1+a_i^+\},\{a_i\})t}|\tilde{\phi}(0)\rangle$

with initial state vector $|\tilde{\phi}(0)\rangle = e^{\bar{n}_0 \sum_i a_i^+}|0\rangle$

connection with <u>generating functions</u>:

$$g(x,t) = \sum_n x^n P_n(t)\,, \quad g(1,t) = 1\,, \quad \langle n(t)\rangle = \frac{\partial g(x,t)}{\partial x}\Big|_{x=0}\,, \text{ etc.}$$

e.g., for $kA \xrightarrow{\lambda} lA$: $\quad \frac{\partial g(x,t)}{\partial t} = -H(x,p)\,g(x,t)$

with "<u>momentum</u>" $p = \frac{\partial}{\partial x}$, $[p,x] = 1$

and Hamiltonian $H(x,p) = \lambda(x^k - x^l)\,p^k$

or, for $A \xrightarrow{\mu} \emptyset$, $A \xrightarrow{\sigma} A+A$: $\quad H(x,p) = (x-1)(\mu - \sigma x)\,p$

probability conservation: $g(1,t) = 1$ satisfied if $H(1,p) = 0$

$\rightarrow$ correspondence $x \leftrightarrow a^+$, $p \leftrightarrow a$

<u>"classical trajectories"</u>, c.f. method of characteristics:

$$\underbrace{\frac{dx(t)}{dt}}\, = \frac{\partial H(x,p)}{\partial p}\,, \quad \frac{dp(t)}{dt} = -\frac{\partial H(x,p)}{\partial x} \qquad \text{Hamilton's equations of motion}$$

always solved by $x = 1$, owing to probability conservation

insert into $\frac{dp(t)}{dt}$, identifying $p(t) = \langle n(t)\rangle \rightarrow$ <u>mean-field rate equations</u>

e.g. $kA \xrightarrow{\lambda} lA$: $\quad \frac{\partial H(x,p)}{\partial x} = \lambda(kx^{k-1} - lx^{l-1})\,p^k \xrightarrow[x=1]{} (k-l)\,\lambda\,p^k$

$A \xrightarrow{\mu} \emptyset$, $A \xrightarrow{\sigma} A+A$: $\quad \frac{\partial H(x,p)}{\partial x} = \mu p + \sigma(1-2x)\,p \xrightarrow[x=1]{} (\mu - \sigma)\,p$

<u>absorbing state</u>: $\quad \frac{dp(t)}{dt} = 0$ if $p = 0 \rightarrow H(x,0) = 0$

"phase space" trajectories $\{x(t), p(t)\}$ confined to hypersurfaces

$H = H(x(0), p(0))$, and can only intersect where $H = 0$

$\rightarrow$ starting point for <u>"semi-classical" treatments</u> of fluctuation effects in reaction systems (for example, WKB method)

5.4. Coherent-state path integral, Doi-Peliti field theory

coherent states: eigenstates of annihilation operators $a_i |\phi\rangle = \phi_i |\phi\rangle$

expand $|\phi\rangle = \sum_{\{n_i\}} \phi_{\{n_i\}} |\{n_i\}\rangle = \ldots = e^{\sum_i \phi_i a_i^\dagger} |0\rangle$

adjoint: $\langle\phi| a_i^\dagger = \phi_i^* \langle\phi|$, $\langle\phi|\phi'\rangle = e^{\sum_i \phi_i^* \phi_i'}$

$\rightarrow$ expectation values of normal-ordered products:

$$\langle\phi| A(\{a_i^\dagger\},\{a_i\}) |\phi'\rangle = A(\{\phi_i^*\},\{\phi_i'\})\, e^{\sum_i \phi_i^* \phi_i'}$$

closure relation: $\displaystyle\int \prod_i \frac{d\phi_i^* d\phi_i}{2\pi i}\, e^{-\sum_i \phi_i^* \phi_i} |\phi\rangle\langle\phi| = 1$

$\rightarrow$ "over complete"

goal: compute $\langle A(t)\rangle = \langle 0| \prod_j e^{a_j} A(\{a_i^\dagger a_i\})\, e^{-H(\{a_i^\dagger\},\{a_i\})t} |\phi(0)\rangle$

$$= \langle 0| \tilde{A}(\{1\},\{a_i\})\, e^{\sum_i a_i}\, e^{-H(\{a_i^\dagger\},\{a_i\})t}\, e^{\bar{n}_0 \sum_i (a_i^\dagger - 1)} |0\rangle$$

discretize time interval $[0,t_f]$ into infinitesimal time steps $t_\ell = \ell\tau$,

$\ell = 0,\ldots,M$, $t_M = t_f$; insert closure relations at $t_1,\ldots,t_{M-1}$

$$\rightarrow \langle A(t)\rangle = \lim_{\substack{\tau\to 0\\ M\to\infty}} \int \prod_i \prod_{\ell=0}^{M} \frac{d\phi_i^*(t_\ell)\, d\phi_i(t_\ell)}{2\pi i}\, \tilde{A}(\{1\},\{\phi_i\})\, e^{\sum_i \phi_i(t_f)} \cdot$$
$$\cdot\, e^{-\tau \sum_{\ell=1}^{M} \left[\sum_i \phi_i^*(t_\ell) \frac{\phi_i(t_\ell) - \phi_i(t_{\ell-1})}{\tau} + H(\{\phi_i^*(t_\ell)\},\{\phi_i(t_{\ell-1})\})\right]}$$
$$\cdot\, e^{\sum_i (\bar{n}_0 [\phi_i^*(0) - 1] - |\phi_i(0)|^2)}$$

formally, take continuum limit in time:

$$\langle A(t)\rangle = \int \prod_i \mathcal{D}[\phi_i^*, \phi_i]\, \tilde{A}(\{1\},\{\phi_i\})\, e^{-\mathcal{A}[\phi_i^*, \phi_i]}$$

path (functional) integral representation with Doi-Peliti action

$$\mathcal{A}[\phi_i^*, \phi_i] = \int_0^{t_f} \left[\sum_i \phi_i^*(t) \frac{\partial \phi_i(t)}{\partial t} + H(\{\phi_i^*(t)\},\{\phi_i(t)\})\right] dt$$
$$\underbrace{- \sum_i \phi_i(t_f)}_{\text{from projection state at final time}} + \underbrace{\sum_i \left(|\phi_i(0)|^2 - \bar{n}_0 [\phi_i^*(0) - 1]\right)}_{\text{from initial time}}$$

e.g., "bulk" action for $kA \xrightarrow{\lambda} \ell A$, with unbiased hopping:

$$\mathcal{A}[\phi_i^*,\phi_i] = \int_0^{t_f} dt \Big(\sum_i \phi_i^*(t)\,\frac{\partial \phi_i(t)}{\partial t} + \lambda \sum_i \left[\phi_i^*(t)^k - \phi_i^*(t)^\ell\right] \phi_i(t)^k$$
$$+ D \sum_{\langle i j\rangle} \left[\phi_i^*(t) - \phi_j^*(t)\right]\left[\phi_i(t) - \phi_j(t)\right]\Big)$$

→ faithful representation of stochastic particle processes, including all "internal" reaction noise

Spatial continuum limit: $\sum_i \to \frac{1}{a_0^d}\int d^dx$ with lattice constant a_0

let $\phi_i^*(t) \to \hat\psi(\vec{x},t)$, $\phi_i(t) \to a_0^d\, \psi(\vec{x},t)$

→ action $$\mathcal{A}[\hat\psi,\psi] = \int d^dx \Big(\int_0^{t_f} \Big[\hat\psi(\vec{x},t)\,\frac{\partial \psi(\vec{x},t)}{\partial t} + \mathcal{H}\big(\hat\psi(\vec{x},t),\psi(\vec{x},t)\big)\Big]\, dt$$
$$- \psi(\vec{x},t_f) + \hat\psi(\vec{x},0)\,\psi(\vec{x},0) - \bar{n}_0\left[\hat\psi(\vec{x},0) - 1\right]\Big)$$

with pseudo-Hamiltonian density $\mathcal{H}$, for example for $kA \to \ell A$:

$$\mathcal{H}\big(\hat\psi(\vec{x},t),\psi(\vec{x},t)\big) = a_0^{(k-1)d}\,\lambda\left[\hat\psi(\vec{x},t)^k - \hat\psi(\vec{x},t)^\ell\right]\psi(\vec{x},t)^k$$
$$- a_0^2 D\, \hat\psi(\vec{x},t)\, \nabla^2 \psi(\vec{x},t)$$

$\phi_i - \phi_j \to a_0^{d+1}\vec\nabla\phi$, integrate by parts

classical field equations: $\frac{\delta \mathcal{A}[\hat\psi,\psi]}{\delta \psi(\vec{x},t)} = 0$ always solved by $\hat\psi(\vec{x},t) =$ (probability conservation)

inserted into $\frac{\delta \mathcal{A}[\hat\psi,\psi]}{\delta \hat\psi(\vec{x},t)} = 0$ then yields reaction-diffusion equations,

e.g. $$\frac{\partial \psi(\vec{x},t)}{\partial t} = a_0^2 D\, \nabla^2 \psi(\vec{x},t) - (k-\ell)\, a_0^{(k-1)d}\, \underbrace{\lambda\, \psi(\vec{x},t)^k}_{\text{note mean-field mass action factorizatio}}$$

shift $\hat\psi(\vec{x},t) = 1 + \tilde\psi(\vec{x},t)$, i.e., expand about mean-field solution:

→ action $$\mathcal{A}[\tilde\psi,\psi] = \int d^dx \Big(\int_0^{t_f} \Big[\tilde\psi(\vec{x},t)\,\frac{\partial \psi(\vec{x},t)}{\partial t} + \mathcal{H}\big(1+\tilde\psi(\vec{x},t),\psi(\vec{x},t)\big)\Big]\, dt$$
$$+ \tilde\psi(\vec{x},0)\, \underbrace{\left[\psi(\vec{x},0) - \bar{n}_0\right]}_{\text{imposes constraint fixing initial density}}\Big)$$

reverse procedure: given dynamical field theory, find equivalen

Langevin dynamics representation

Doi-Peliti field theory for at most $\underline{\text{binary}}$ $\underline{\text{reactions}}$:

$$\mathcal{A}[\tilde{\psi},\psi] = \int d^d x \int dt \left[\tilde{\psi}(\vec{x},t)\frac{\partial\psi(\vec{x},t)}{\partial t} + \mathcal{H}\big(\underbrace{1+\tilde{\psi}(\vec{x},t)}_{\text{at most quadratic}}, \psi(\vec{x},t)\big)\right]$$

e.g. $kA \to \ell A$; $k,\ell = 0,1,2$

$$\mathcal{H}(\hat{\psi},\psi) = \lambda(\hat{\psi}^k - \hat{\psi}^\ell)\psi^k + D\nabla\hat{\psi}\nabla\psi$$

$$\to \mathcal{H}(1+\tilde{\psi},\psi) = \lambda\left[(k-\ell)\tilde{\psi} + \frac{k(k-1)-\ell(\ell-1)}{2}\tilde{\psi}^2\right]\psi^k - D\tilde{\psi}\nabla^2\psi$$

$\underline{k=\ell}$: just diffusion, no reactions; $\underline{\text{no}}$ Brownian random walk noi

$\underline{k=1,\ \ell=0}$: $A \xrightarrow{\mu} \emptyset$; $\underline{k=0,\ \ell=1}$: $\emptyset \xrightarrow{\tau} A$ → also no reaction noise

$$\to \frac{\partial\psi(\vec{x},t)}{\partial t} = D\nabla^2\psi(\vec{x},t) - \mu\psi(\vec{x},t) + \tau$$

$\underline{k=0,\ \ell=2}$: $\emptyset \xrightarrow{\tau} A+A \to \frac{\partial\psi(\vec{x},t)}{\partial t} = D\nabla^2\psi(\vec{x},t) + 2\tau + \zeta(\vec{x},t)$

with $\langle\zeta(\vec{x},t)\zeta(\vec{x}',t')\rangle = 2\tau\,\delta(\vec{x}-\vec{x}')\delta(t-t')$ white noise "additive"

$\underline{k=1,\ \ell=2}$: $A \xrightarrow{\sigma} A+A \to \frac{\partial\psi(\vec{x},t)}{\partial t} = D\nabla^2\psi(\vec{x},t) + \sigma\psi(\vec{x},t) + \zeta(\vec{x},t)$

with $\langle\zeta(\vec{x},t)\zeta(\vec{x}',t')\rangle = 2\sigma\,\psi(\vec{x},t)\,\delta(\vec{x}-\vec{x}')\delta(t-t')$ (symbolic

"square-root" multiplicative noise, active regions cluster

$$\zeta(\vec{x},t) = \sqrt{\psi(\vec{x},t)}\,\eta(\vec{x},t),\quad \langle\eta(\vec{x},t)\eta(\vec{x}',t')\rangle = 2\sigma\,\delta(\vec{x}-\vec{x}')\delta(t-t')$$

beware: singularity, $\psi(\vec{x},t)$ in general complex field

$\underline{k=2,\ \ell=0 \text{ or } 1}$: $A+A \xrightarrow{\lambda} \emptyset, A \to \frac{\partial\psi(\vec{x},t)}{\partial t} = D\nabla^2\psi(\vec{x},t) - (2)\lambda\psi(\vec{x},t)$
$+ \zeta(\vec{x},t)$

$$\langle\zeta(\vec{x},t)\zeta(\vec{x}',t')\rangle = -2\lambda\,\psi(\vec{x},t)^2\,\delta(\vec{x}-\vec{x}')\delta(t-t')$$

"imaginary" multiplicative noise: $\zeta(\vec{x},t) = i\psi(\vec{x},t)\,\eta(\vec{x},t)$

active regions $\underline{\text{anti-correlated}}$ (depletion zones)

95 population dynamics:

- $A \xrightarrow{\mu} \emptyset$, $A \underset{\lambda}{\overset{\sigma}{\rightleftarrows}} A+A$ → noisy Fisher-Kolmogorov equation

$$\frac{\partial \psi(\vec{x},t)}{\partial t} = D\nabla^2\psi(\vec{x},t) + (\sigma-\mu)\psi(\vec{x},t) - \lambda\psi(\vec{x},t)^2 + \zeta(\vec{x},t)$$

$$\langle \zeta(\vec{x},t)\zeta(\vec{x}',t')\rangle = 2\psi(\vec{x},t)\left[\sigma - \lambda\psi(\vec{x},t)\right]\delta(\vec{x}-\vec{x}')\delta(t-t')$$

- Lotka-Volterra predator-prey dynamics: $A \xrightarrow{\mu} \emptyset$, $A+B \xrightarrow{\lambda} A+A$, $B \xrightarrow{\sigma} B+B$

$$\mathcal{A}[\tilde\varphi,\tilde\psi,\psi,\varphi] = \int d^d x \int dt \Big[\tilde\psi(\vec{x},t)\left(\frac{\partial}{\partial t} - D_A\nabla^2 + \mu\right)\psi(\vec{x},t)$$
$$- \lambda\left[1+\tilde\psi(\vec{x},t)\right]\left[\tilde\varphi(\vec{x},t) - \tilde\psi(\vec{x},t)\right]\psi(\vec{x},t)\varphi(\vec{x},t)$$
$$+ \tilde\varphi(\vec{x},t)\left(\frac{\partial}{\partial t} - D_B\nabla^2 - \sigma\right)\varphi(\vec{x},t) - \sigma\,\tilde\varphi(\vec{x},t)^2\varphi(\vec{x},t)\Big]$$

equivalent to coupled Langevin equations:

$$\frac{\partial \psi(\vec{x},t)}{\partial t} = (D_A\nabla^2 - \mu)\psi(\vec{x},t) + \lambda\psi(\vec{x},t)\varphi(\vec{x},t) + \zeta(\vec{x},t)$$

$$\frac{\partial \varphi(\vec{x},t)}{\partial t} = (D_B\nabla^2 + \sigma)\varphi(\vec{x},t) - \lambda\psi(\vec{x},t)\varphi(\vec{x},t) + \eta(\vec{x},t)$$

with noise (cross-) correlations $\langle \zeta(\vec{x},t)\rangle = 0 = \langle \eta(\vec{x},t)\rangle$

$$\langle \zeta(\vec{x},t)\zeta(\vec{x}',t')\rangle = 2\lambda\psi(\vec{x},t)\varphi(\vec{x},t)\,\delta(\vec{x}-\vec{x}')\delta(t-t')$$

$$\langle \zeta(\vec{x},t)\eta(\vec{x}',t')\rangle = -\lambda\psi(\vec{x},t)\varphi(\vec{x},t)\,\delta(\vec{x}-\vec{x}')\delta(t-t')$$

$$\langle \eta(\vec{x},t)\eta(\vec{x}',t')\rangle = 2\sigma\varphi(\vec{x},t)\,\delta(\vec{x}-\vec{x}')\delta(t-t')$$

→ prey cluster, predators cluster with predators and prey, prey and predators anti-correlated

$\varphi = 0$ absorbing state, $\psi = 0$ absorbing only for predators

ψ, φ both finite: species coexistence regime

→ essentially just Gaussian white noise, additive