

BEYOND THE LANGEVIN THEORY

Contents

1	General setting	1
2	Onsager's regression hypothesis	2
3	Linear response	4
4	Kubo formula	7
5	The generalized Langevin equation	9
6	Scaling limits	10

1 General setting

Let us now turn to the general framework of which the Theory of Langevin is an approximation: a Brownian particle interacting with the particles of a fluid, whose motion is governed by an Hamiltonian of the form

$$H^0(X, P, q, p) = \frac{P^2}{2M} + H_F(q, p) + H_I(X, q) \quad (1)$$

where X and P are the canonical coordinates of the Brownian particle, $q = (q_1, \dots, q_N)$ and $p = (p_1, \dots, p_N)$ those of the fluids particles; H_F is the Hamiltonian of the fluid and H_I is the interaction energy between the Brownian particle and the fluid.

2 Onsager's regression hypothesis

Proposition 1 (Onsager's regression hypothesis (1931))

The average regression of fluctuations of a macroscopic variable will

obey the same laws as the corresponding macroscopic irreversible process.

The macroscopic irreversible process of the motion of a particle in a fluid is given by Stokes' law

$$M \frac{d\mathbf{V}}{dt} = -\gamma \mathbf{V}, \quad \gamma = 6\pi\eta a \quad (2)$$

According to Onsager's hypothesis

$$R(t) \equiv \langle \mathbf{V}_t \mathbf{V}_0 \rangle \quad (3)$$

has to obey Stokes' law, hence

$$R(t) = R(0) e^{-\gamma t/M}$$

with $R(0)$ fixed by equipartition:

$$R(0) = \langle \mathbf{V}_0^2 \rangle = \frac{k_B T}{M},$$

whence

$$R(t) = \langle \mathbf{V}_t \mathbf{V}_0 \rangle = \frac{k_B T}{M} e^{-\gamma|t|/M} \quad (4)$$

in agreement with the prediction of Langevin's theory.

Can one prove Onsager's hypothesis?

3 Linear response

Let us probe the Brownian particle by adding to the Hamiltonian a small term, possibly depending on time, so that the Hamiltonian is

$$H = H^0 + \varepsilon H^1(t), \quad H^1 = B(X, P)g(t) \quad (5)$$

where, H^0 is given by eq. (1), B is a function only of the phase variables of the Brownian particle and $g(t)$ is a given function of time.

Let $A = A(X, P)$ any quantity pertaining the Brownian particle, e.g. its velocity. Then A evolves according to the law

$$\frac{dA^\varepsilon}{dt} = -\{H, A^\varepsilon\}, \quad (6)$$

where $\{f, g\}$ is the Poisson bracket of the functions on phase space f and g . It is convenient to introduce the linear operator (Liouvillian)

$$iL f = \{H, f\} = i\{H^0, f\} + i\varepsilon\{H^1(t), f\} \equiv i [L^0 + \varepsilon L^1(t)] f$$

so that the above equation can be rewritten as

$$i\frac{dA^\varepsilon}{dt} = L^0 A^\varepsilon(t) + \varepsilon L^1(t) A^\varepsilon(t).$$

By time dependent perturbation theory (Dyson series), at the lowest order in ε , one finds

$$A^\varepsilon(t) = A^0(t) + \varepsilon A^1(t)$$

where

$$A^0(t) = e^{-iL^0 t} A(0) \tag{7}$$

and

$$\begin{aligned} A^1(t) &= -e^{-iL^0 t} \int_0^t ds e^{iL^0(s)} (iL^1(s)) e^{-iL^0 s} A(0) \\ &= -e^{-iL^0 t} \int_0^t ds \{B(X^0(s), P^0(s), A(X, P))\} g(s) \\ &= \int_0^t \{A(X^0(t), P^0(t)), h(X^0(s), P^0(s))\} g(s) ds \end{aligned}$$

The result becomes more transparent if we set $\delta A(t) = A^0(t) + \varepsilon A^1(t)$, drop all indices and stipulate that the time dependence is always understood with respect to the unperturbed Hamiltonian. Then

$$\delta A(t) = \int_0^t \{A(t), B(s)\} g(s) ds \quad (8)$$

Consider for example the case $A = B = V$. Then

$$\delta V(t) = \int_0^t \{V(t), V(s)\} g(s) ds \quad (9)$$

at equilibrium

$$\int_0^t \{V(t), V(s)\} g(s) ds = \int_0^t \langle \{V(t), V(s)\} \rangle g(s) ds$$

This is almost Onsager hypothesis; instead of the correlation function we have a propagator (Poisson bracket), but this is not an essential difference

With a bit more work one can establish Onsager hypothesis (at least, to the extent that linear response is trustable). In doing so one meets:

- The dispersion relations of Kramers-Kronig (1926-1927)
- The fluctuation-dissipation theorem of Callen-Welton (1951)

TO BE WRITTEN ... In the mean while see the beautiful book: ***D. Forster. "Hydrodynamic Fluctuations, Broken Symmetry, And Correlation Functions."***

4 Kubo formula

(1957) From the relation between the position and velocity

$$X_t - X_0 = \int_0^t V_s ds \quad (10)$$

we can also get a general Kubo formula

$$D = \int_0^\infty \langle V_t V_0 \rangle dt \quad (11)$$

where V_t is the **stationary** velocity process. In fact, for a stationary process, eq. (10) gives

$$\begin{aligned}
\langle (X_t - \langle X_t \rangle)^2 \rangle &= \int_0^t du \int_0^t dv \langle V_u V_v \rangle \\
&= \int_0^t du \int_0^u dv \langle V_u V_v \rangle + \int_0^t du \int_u^t dv \langle V_u V_v \rangle \\
&= \int_0^t du \int_0^u dv \langle V_{u-v} V_0 \rangle + \int_0^t du \int_u^t dv \langle V_{u-v} V_0 \rangle \\
&= 2 \int_0^t \int_0^t ds \int_0^s du \langle V_u V_0 \rangle = 2 \int_0^t du \langle V_u V_0 \rangle \int_u^t ds \\
&= 2 \int_0^t du (t - u) \langle V_u V_0 \rangle
\end{aligned}$$

For $t \rightarrow \infty$ we then find (in the Cesaro sense)

$$D = \lim_{t \rightarrow \infty} \frac{\langle (X_t - \langle X_t \rangle)^2 \rangle}{2t} = \int_0^\infty du \langle V_u V_0 \rangle \quad (12)$$

Applying Kubo formula to the Langevin approximation,

$$\langle V_t V_s \rangle = \frac{k_B T}{M} e^{-\alpha|t-s|}$$

one gets immediately

$$\int_0^\infty \langle V_t V_0 \rangle dt = \frac{k_B T}{\alpha M} = \frac{k_B T}{\gamma} = D$$

5 The generalized Langevin equation

(Mori 1965, Kubo 1966). Exact equation at equilibrium (no approximations!):

$$\dot{V}(t) = - \int_{t_0}^t \gamma(t-s) V(s) ds + \frac{1}{M} R(t) \quad (13)$$

with

$$\langle R(t) \rangle = 0$$

Let (Fourier-Laplace transform)

$$\tilde{\gamma}(\omega) = \int_0^{\infty} e^{-i\omega t} \gamma(t) dt$$

Then

$$M \tilde{\gamma}(\omega) = \frac{1}{\langle V^2 \rangle} \int_0^{\infty} \langle R(t_0) R(t_0 + t) \rangle e^{-i\omega t} dt \quad (14)$$

Under the assumptions:

- Equipartition: $M \langle V^2 \rangle = k_B T$
- $\langle V(t_1) R(t_2) \rangle = 0$ for $t_1 < t_2$

6 Scaling limits

.....

By considering the rescaled process

$$X^\varepsilon(t) = \varepsilon X \left(\frac{t}{\varepsilon} \right) \quad (15)$$

we extract the mean motion by letting $\varepsilon \rightarrow 0$. Since

$$X^\varepsilon(t) = \varepsilon \int_0^{t/\varepsilon} V(s) ds \approx \frac{1}{N} \sum_{k=1}^N \Delta V_k,$$

letting $\varepsilon \rightarrow 0$ in eq. (16) is nothing but the law of large number.

Central limit Diffusive scale:

$$X^\varepsilon(t) = \varepsilon X \left(\frac{t}{\varepsilon^2} \right) \tag{16}$$

$$X^\varepsilon(t) = \varepsilon \int_0^{t/\varepsilon^2} V(s) ds \approx \frac{1}{\sqrt{N}} \sum_{k=1}^N \Delta V_k,$$

We have

$$\dot{X}^\varepsilon(t) = \frac{1}{\varepsilon} \dot{X} \left(\frac{t}{\varepsilon^2} \right) \tag{17}$$

$$\ddot{X}^\varepsilon(t) = \frac{1}{\varepsilon^3} \ddot{X} \left(\frac{t}{\varepsilon^2} \right) \tag{18}$$

For the Ornstein-Uhlenbeck process

$$M\ddot{X}(t) = -\gamma\dot{X}(t) + \sigma\dot{W}(t) \quad (19)$$

we have (recalling the scaling property of white noise)

$$M\ddot{X}^\varepsilon(t) = M\frac{1}{\varepsilon^3}\ddot{X}\left(\frac{t}{\varepsilon^2}\right) = \frac{1}{\varepsilon^3}\left[-\gamma\dot{X}\left(\frac{t}{\varepsilon^2}\right) + \sigma\dot{W}\left(\frac{t}{\varepsilon^2}\right)\right] \quad (20)$$

$$= \frac{1}{\varepsilon^3}\left[-\gamma\varepsilon\dot{X}^\varepsilon(t) + \sigma\varepsilon\dot{W}(t)\right] \quad (21)$$

$$= \frac{1}{\varepsilon^2}\left[-\gamma\dot{X}^\varepsilon(t) + \sigma\dot{W}(t)\right] \quad (22)$$

whence

$$\varepsilon^2 M\ddot{X}^\varepsilon(t) = -\gamma\dot{X}^\varepsilon(t) + \sigma\dot{W}(t) \quad (23)$$

For $\varepsilon \rightarrow 0$, $\dot{X}^\varepsilon(t) \rightarrow \dot{X}^0(t)$ such that

$$0 = -\gamma\dot{X}^0(t) + \sigma\dot{W}(t) \quad \Rightarrow \quad \dot{X}^0(t) = \frac{\sigma}{\gamma}\dot{W}(t)$$

whence

$$X^\varepsilon(t) \rightarrow \int_0^t \frac{\sigma}{\gamma}\dot{W}(s)ds = \frac{\sigma}{\gamma}W(t)$$

That is to a Wiener process with diffusion constant

$$D = \frac{1 \sigma^2}{2 \gamma^2} = \frac{2 \gamma k_B T}{\gamma^2} = \frac{2 k_B T}{\gamma}$$

(THIS IS NOT A MATHEMATICAL PROOF!)