TD 14: Out-of-Equilibrium Arrhenius Law - Solutions

Baptiste Coquinot & Antonio Costa

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The Arrhenius law has been demonstrated in TD 12 using the Fokker-Planck equation. In this exercise, we revisit this result using path integrals and prove it in the more general case of non-conservative forces. We consider a particle at position $\mathbf{x}$ with dynamics $\dot{\mathbf{x}} = \mathbf{F} + \eta$ where $\mathbf{F}$ is a force, a priori non-conservative and η is a Brownian noise $\langle \eta_\alpha(t)\eta_\beta(t')\rangle = 2T\delta(t-t')\delta_{\alpha\beta}$. The force $\mathbf{F}$ has three equilibrium points, two stable points S_1 and S_2 and one unstable point U. The space is separated in three regions: the basin of attraction of S_1, the basin of attraction of S_2 and the point U.

1. Write the Fokker-Planck equation associated with this dynamics.
2. Writing a stationary solution as $\mathbb{P}_s = \frac{e^{-\phi/T}}{Z}$ where Z is a normalisation factor, show that in the small T limit, ϕ is solution of the equation

$$\nabla\phi \cdot (\mathbf{F} + \nabla\phi) + O(T) = 0. \tag{1}$$

3. If $\mathbf{F}$ is a conservative force $\mathbf{F} = -\nabla V$, what is the pseudo-potential ϕ?

Action and path integral: the Martin-Siggia-Rose formalism. To describe this dynamics we can use a path integral formulation

$$\mathbb{P}(\mathbf{x}_f, t_f|\mathbf{x}_0, t_0) = \int_{\mathbf{x}_0}^{\mathbf{x}_f} \mathcal{D}\mathbf{x}\mathcal{D}\mathbf{y}\, e^{-S(\mathbf{x},\mathbf{y})} \tag{2}$$

where $\mathbf{y}$ is an auxiliary field. This problem can then be written using the Martin-Siggia-Rose action

$$S(x,y) = \int_{t_0}^{t_f} \mathrm{d}t\, i\mathbf{y}(t) \cdot [\dot{\mathbf{x}}(t) - \mathbf{F}(\mathbf{x}(t)) - iT\mathbf{y}(t)]\,. \tag{3}$$

4. Changing $\hat{\mathbf{y}} = T\mathbf{y}$, write the action in canonical form.
5. Discuss the several terms in the action and explain why we can make a saddle-point approximation in the low temperature limit.
6. Deduce the equations of motion (Euler-Lagrange equations) in the saddle-point approximation.
7. Show that $(\dot{\mathbf{x}} = \mathbf{F}(\mathbf{x}), \mathbf{y} = 0)$ is a solution.
8. In the case of a conservative force, show that $(\dot{\mathbf{x}} = -\mathbf{F}(\mathbf{x}), i\mathbf{y} = -\mathbf{F}/T)$ is a solution. In the non-conservative case, this generalises with the solution $(\dot{\mathbf{x}} = \mathbf{F}(\mathbf{x}) + 2\nabla\phi, i\mathbf{y} = \nabla\phi/T)$.

Arrhenius Law. The Arrhenius law is an estimate of the probability to go from S_1 to S_2. Since we restrict to the most probable paths, we follow the path $(\dot{\mathbf{x}} = -\mathbf{F}(\mathbf{x}), i\mathbf{y} = -\mathbf{F}/T)$ from S_1 to U then the path $(\dot{\mathbf{x}} = \mathbf{F}(\mathbf{x}), \mathbf{y} = 0)$ from U to S_2.

9. Using the fact that the path integral is normalised, estimate the probability to go from U to S_2 in the low temperature limit.
10. Show that the probability to go from S_1 to U in the low temperature limit is proportional to $e^{-\frac{\Delta\phi}{T}}$ where $\Delta\phi = \phi(U) - \phi(S_1)$.
11. Deduce the Arrhenius law: the transition time from S_1 to S_2 is

$$\tau_{S_1\to S_2} \propto e^{\frac{\Delta\phi}{T}}. \tag{4}$$

Correction

1. The Fokker-Planck equation writes

$$\partial_t \mathbb{P}(\mathbf{x},t) = \nabla \cdot (-\mathbf{F} + T\nabla)\mathbb{P}(\mathbf{x},t) \tag{5}$$

2. Injecting $\mathbb{P}_s$ in the Fokker-Planck equation we derive

$$-\nabla \cdot \mathbf{F} - \nabla^2\phi + (\mathbf{F} + \nabla\phi) \cdot \frac{\nabla\phi}{T} = 0 \tag{6}$$

where we have used that $\partial_t \mathbb{P}_s = 0$. Taking the main order in T leads to the result.

3. If $\mathbf{F} = -\nabla V$ we see that $\phi = V$. Thus, ϕ is the generalisation of a potential we only fulfil a weaker equation.

4. With this change of variables, the action becomes

$$\begin{aligned} S(x,y) &= \frac{1}{T}\int_{t_0}^{t_f} \mathrm{d}t\, i\mathbf{y}(t) \cdot [\dot{\mathbf{x}}(t) - \mathbf{F}(\mathbf{x}(t)) - i\mathbf{y}(t)] &(7)\\ &= \frac{1}{T}\int_{t_0}^{t_f} \mathrm{d}t \left(\left[\mathbf{y}(t) + i\frac{\dot{\mathbf{x}}(t) - \mathbf{F}(\mathbf{x}(t))}{2}\right]^2 + \left[\frac{\dot{\mathbf{x}}(t) - \mathbf{F}(\mathbf{x}(t))}{2}\right]^2 \right). &(8) \end{aligned}$$

which diverges when $T \to 0$.

5. We almost recognise our dynamics in the action: $\dot{\mathbf{x}}(t) - \mathbf{F}(\mathbf{x}(t)) + T\mathbf{y}(t)$. The auxiliary field $\mathbf{y}$ is actually a representation of the Brownian motion. The order in $\mathbf{y}$ corresponds to the Itô formalism: the Brownian motion appears in the second order. When going to canonical form we see that up to a linear change of variables for $\mathbf{y}$, the fields are decorrelated and then the auxiliary field disappears. Analytically its purpose if then to transform the second order in $\mathbf{x}$ in a first order which simplifies the calculations. Finally, for small T the action diverges so that the relevant terms minimise the action: we can perform a saddle-point approximation.

6. We have two fields and then two equations:

$$\begin{aligned} 0 &= \frac{\delta S}{\delta \mathbf{x}} = -i\dot{\mathbf{y}} - i\nabla\mathbf{F}(\mathbf{x}) \cdot \mathbf{y} \Longrightarrow \dot{\mathbf{y}} = -\nabla\mathbf{F}(\mathbf{x}) \cdot \mathbf{y} &(9)\\ 0 &= \frac{\delta S}{\delta \mathbf{y}} = i\dot{\mathbf{x}} - i\mathbf{F}(\mathbf{x}) - 2T\mathbf{y} \Longrightarrow \dot{\mathbf{x}} = \mathbf{F}(\mathbf{x}) - 2iT\mathbf{y} &(10) \end{aligned}$$

7. This is the trivial solution without thermal noise.

8. We only have to check

$$\dot{\mathbf{y}} = i\dot{\mathbf{x}} \cdot \nabla\mathbf{F}/T = -i\mathbf{F} \cdot \nabla\mathbf{F}/T = -\nabla\mathbf{F} \cdot \mathbf{y} \tag{11}$$

where we used that $\nabla_\alpha F_\beta = \nabla_\alpha \nabla_\beta V = \nabla_\beta \nabla_\alpha V = \nabla_\beta F_\alpha$ for a conservative force.

9. Imposing $(\dot{\mathbf{x}} = \mathbf{F}(\mathbf{x}), \mathbf{y} = 0)$ the action vanishes. Thus, the probability is

$$\mathbb{P}(U \to S_2) = \int \mathcal{D}\mathbf{x}\mathcal{D}\mathbf{y}\, e^{-S} \longrightarrow 1 \tag{12}$$

for $T \to 0$.

10. Imposing $(\dot{\mathbf{x}} = \mathbf{F}(\mathbf{x}) + 2\nabla\phi, i\mathbf{y} = \nabla\phi/T)$, the action becomes

$$S = \frac{1}{T}\int_{t_0}^{t_f} \mathrm{d}t\, \nabla\phi \cdot [2\nabla\phi - \nabla\phi] = \frac{1}{T}\int_{t_0}^{t_f} \mathrm{d}t\, (\nabla\phi)^2. \tag{13}$$

Furthermore, we have $\nabla\phi \cdot (\mathbf{F} + \nabla\phi) = 0$ *i.e.* $\nabla\phi \cdot (\dot{\mathbf{x}} - \nabla\phi) = 0$. Thus, the action is

$$S = \frac{1}{T}\int_{t_0}^{t_f} \mathrm{d}t\, (\nabla\phi)^2 = \frac{1}{T}\int_{t_0}^{t_f} \mathrm{d}t\, \dot{\mathbf{x}} \cdot \nabla\phi = \phi(U) - \phi(S_1). \tag{14}$$

Thus,

$$\mathbb{P}(S_1 \to U) \propto e^{-\frac{\Delta\phi}{T}}. \tag{15}$$

11. With the decomposition $S_1 \to U \to S_2$ we find

$$\mathbb{P}(S_1 \to S_2) = \mathbb{P}(S_1 \to U)\mathbb{P}(U \to S_2) \propto e^{-\frac{\Delta\phi}{T}} \tag{16}$$

and

$$\tau_{S_1 \to S_2} \propto \frac{1}{\mathbb{P}(S_1 \to S_2)} \propto e^{\frac{\Delta\phi}{T}}. \tag{17}$$