TD 14: Out-of-Equilibrium Arrhenius Law

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January 13, 2022

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 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

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

Only when you have finished all the exercises

The Wikipedia Moment. HERBERT CALLEN (1919-1993).

A native of Philadelphia, Herbert Callen received his Bachelor of Science degree from Temple University. His graduate studies were interrupted by the Manhattan Project. He also worked on a U.S. Navy project concerning guided missiles (Project Bumblebee) at Princeton University in 1945. Callen subsequently completed his PhD in physics at the Massachusetts Institute of Technology (MIT) in 1947. He was supervised by the physicist László Tisza. His doctoral dissertation concerns the Kelvin thermoelectric and thermomagnetic relations, and Onsager's reciprocal relations; it was titled On the Theory of Irreversible Processes. Upon receiving his degree, Callen spent a year at the MIT Laboratory for Insulation Research and developed his theory of electrical breakdown for insulators.

In 1948, Callen joined the faculty of the Department of Physics at the University of Pennsylvania and became a professor in 1956. Specialists consider his most lasting contribution to physics to be the paper co-written with Theodore A. Welton presenting a proof of the fluctuation-dissipation theorem, an extremely general result describing how a system's response to perturbations relates to its behavior at equilibrium. This crucial result became the basis for the statistical theory of irreversible processes and explains how fluctuations dissipate energy into heat in general and the phenomenon of Nyquist noise in particular. Callen then pioneered the thermodynamic Green's functions for magnetism. With his students, he studied many-body problems involving spin operators. This led to the discovery of some useful methods of approximations.

The first edition of his classic text Thermodynamics and an Introduction to Thermostatistics was published in 1960. In it, he presents a rigorous axiomatic treatment of thermodynamics in which the state functions are the fundamental entities and the processes are their differentials. The postulates concern the existence of thermal equilibrium, and the properties of entropy. From them, he derives the fundamentals of thermodynamics, found in the first eight chapters. The much revised second edition, published in 1985, became a highly cited reference in the literature and an enduring textbook.

He was a successful teacher, noted for his ability to explain complicated phenomena in simple terms. He played a key role in the recruitment of promising solid-state physicists to the University of Pennsylvania in the late 1950s and continued to be active in the University's academic affairs till his retirement in 1985.

He was the recipient of a Guggenheim Fellowship for the academic year 1972-1973. In 1984, Callen received the Elliott Cresson Medal from the Franklin Institute. He retired in 1985. He was made a member of the National Academy of Sciences in 1990.

After battling Alzheimer's disease for eleven years, Herbert Callen died in the Philadelphia suburb of Merion in 1993. He was 73 years old. He was survived by his wife, Sara Smith, and their two children, Jed and Jill.