Tale 10 on theory of activated processes, Kramers' problem and the Wiener-Hopf method

I decided to tell this tale to show how the Wiener-Hopf method works on example of a physical problem.

Kramers' problem of escape from a potential well

Consider a particle moving in a potential well and interacting with a thermal bath. The equation of motion for such a particle has the form:

$$m\ddot{x} + m\gamma\dot{x} - U'(x) = \eta(t) \tag{1}$$

where γ is a damping rate, m is the particle's mass, and the random force is assumed to be distributed by the Gaussian law

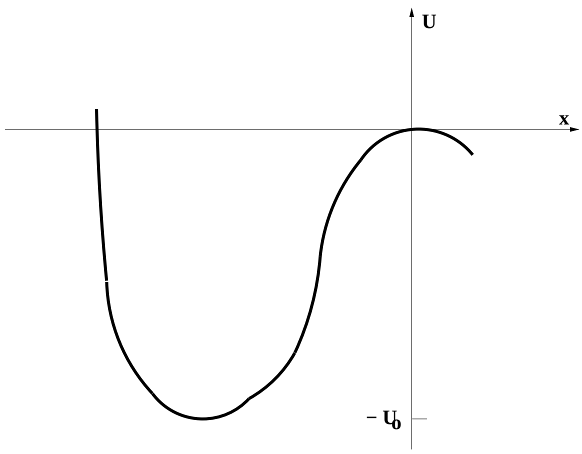

Figure 1: Potential well, from which the Brownian partcle escapes over the barrier, located at origin.

with the white-noise correlation function:

$$\langle \eta(t) \rangle = 0, \qquad \langle \eta(t)\eta(t') \rangle = 2m\gamma T\delta(t-t') \tag{2}$$

The distribution function $F(p,x,t)$ in the phase space p,x satisfies the Fokker-Planck equation:

$$\frac{\partial F}{\partial t} + \frac{p}{m}\frac{\partial F}{\partial x} - \frac{\partial}{\partial p}\left\{F\frac{dU}{dx} + \gamma\left[pF + mT\frac{\partial F}{\partial p}\right]\right\} = 0 \tag{3}$$

If the temperature of the bath T is low enough ($T \ll U_1$), then the rate of escape is low as well. So, the distribution function will come to approximate equilibrium:

$$F \propto N(t)\exp\left[-\frac{p^2}{2mT} - \frac{U(x)}{T}\right], \ -\epsilon = -\left(\frac{p^2}{2m} + U\right) \gg T \tag{4}$$

in a relatively short time, while the total number $N(t)$ changes slowly.

The normalization of the distribution function (4) is determined mainly by the shape of the potential near its minimum

$$U(x) = -U_1 + \frac{m\Omega_1^2}{2}(x - x_{min})^2,$$

which gives

$$F(x,p,T) = \frac{N(t)\Omega_1}{2\pi T}\exp\left\{-\frac{1}{T}\left[U_1 + U(x) + \frac{p^2}{2m}\right]\right\}, \tag{5}$$

where only the total number $N(t)$ depends on t. The total flux from the trap J may be expressed through the distribution function:

$$J = \frac{1}{m}\int dp\ p\ F(p).$$

Since J is proportional to N,

$$\dot{N} = -J = -\frac{N}{\tau},$$

where $1/\tau = J/N$ is the escape rate.
Thus, our purpose is to find τ. To do this we must solve the stationary FP-equation

$$\frac{p}{m}\frac{\partial F}{\partial x} - \frac{\partial}{\partial p}\{F\frac{dU}{dx} + \gamma[pF + mT\frac{\partial F}{\partial p}]\} = 0 \tag{6}$$

with the boundary conditions

$$F(x,p,T)|_{\epsilon} = \frac{N(t)\Omega_1}{2\pi T}\exp\left\{-\frac{1}{T}\left[U_1 + U(x) + \frac{p^2}{2m}\right]\right\}, \tag{7}$$

$$-\epsilon = -\left(\frac{p^2}{2m} + U\right) \gg T,\; x \to x_{\text{min}},\; F(x \to +\infty) \to 0. \tag{8}$$

Two regimes of escape

A particle, trapped in our potential well, escapes from it, what leads to depletion of the distribution function in the energy range of width T near the barrier top, where the potential may be represented as

$$U(x) = -\frac{m\omega^2 x^2}{2}, \quad \omega \sim \Omega,\; m\omega^2 x^2 \sim U_1.$$

The distribution function at smaller energies is largely unperturbed.
The damping rate γ has the same dimension as that of frequency. So, if $\gamma \gg \omega$, then our particle moves aperiodically. In the opposite limit $\gamma \ll \omega$ the particle moves almost periodically, losing

in every period of oscillation a relative part of its energy of the order of γ/ω. Thus, the energy loss per period δ_1 is given by

$$\delta_1 \sim \frac{\gamma U_1}{\omega}$$

There are, therefore, two regimes of under-damped motion:
i). $\delta_1 \gg T$ and
ii). $\delta_1 \ll T$.
In the case i). our particle comes to the escape energy range only once; in the case ii). it comes repeatedly.

Integral equation

We assume that under conditions of under-damping ($\gamma \ll \omega$, but $\delta_1 \ll T$ or $\delta_1 \gg T$) the escape rate is determined by energies close to zero. It is convenient to introduce new variables

$$p_{\pm}(\epsilon, x) = \pm\sqrt{2m[\epsilon - U(x)]}, \tag{9}$$

which allow to express the derivatives in the form:

$$\left(\frac{\partial}{\partial p}\right)_x = \frac{p_{\pm}}{m}\left(\frac{\partial}{\partial \epsilon}\right)_x \tag{10}$$

$$\left(\frac{\partial}{\partial x}\right)_p = \left(\frac{\partial}{\partial x}\right)_{\epsilon} + \frac{dU}{dx}\left(\frac{\partial}{\partial \epsilon}\right)_x \tag{11}$$

It is natural now to define distribution functions for left(right) moving particles

$$f^{R,L}(\epsilon, x) = \frac{1}{N} F[p_{\pm}, x, \epsilon] \tag{12}$$

We'll see that it is possible to set $\epsilon = 0$ into $p_{\pm}(\epsilon, x)$. Under this assumption, the FP equations take the form

$$\frac{\partial f^{R,L}}{\partial x} = \pm\sqrt{-2mU(x)}\,\frac{\partial}{\partial \epsilon}\left[f^{R,L} + T\frac{\partial f^{R,L}}{\partial \epsilon}\right] \tag{13}$$

subject to the boundary conditions

$$
\begin{aligned}
f^R(\epsilon, x_1(\epsilon)) &= f^L(\epsilon, x_1(\epsilon)), \quad \epsilon - U[x_2(\epsilon)] = 0, && (14)\\
f^R(\epsilon, x_2(\epsilon)) &= f^L(\epsilon, x_2(\epsilon)), \quad \epsilon < 0,\ \epsilon - U[x_2(\epsilon)] = 0, && (15)\\
f^L(\epsilon, 0) &= 0, \qquad \epsilon > 0. && (16)
\end{aligned}
$$

Here $x_{1(2)}(\epsilon)$ denote stoping points at left(right) side of potential well and Eq (16) shows that there is no flux from the right at $\epsilon > 0$. The FP equations could be simplified if we introduce the action $S(x, \epsilon)$ instead of x, using the relations:

$$\frac{dS}{dx} = \pm\sqrt{2m[\epsilon - U(x)]}, \quad \frac{dS}{dx} = \pm\sqrt{-2mU(x)}, \ \epsilon = 0. \qquad (17)$$

Therefore, the FP equation has the form

$$\frac{\partial f^{R,L}}{\partial S} = \gamma \frac{\partial}{\partial \epsilon} [f^{R,L} + T\frac{\partial f^{R,L}}{\partial \epsilon}] \qquad (18)$$

This differential equation is already so similar to the diffusion equation, that we can rewrite it in the integral form without further explanation

$$f(\epsilon, S) = \int_{-\infty}^{+\infty} g(\epsilon - \epsilon', S - S') f(\epsilon', S') d\epsilon', \qquad (19)$$

where $g(\epsilon, 0) = \delta(\epsilon)$. The explicit form for $g(\epsilon, S)$ is

$$g(\epsilon, S) = \sqrt{\frac{1}{4\pi\gamma ST}} \exp\left[-\frac{(\epsilon + \gamma S)^2}{4\gamma ST}\right] \qquad (20)$$

The evolution of the distribution function, as a result of one oscillation, is

$$g(\epsilon) = g(\epsilon, S_1) = \sqrt{\frac{1}{4\pi\delta_1 T}} \exp\left[-\frac{(\epsilon + \delta_1)^2}{4\delta_1 T}\right]. \qquad (21)$$

Thus, the function, which was equal to $f_0(\epsilon)$ at the barrier's top will be transformed in one period of oscillation into

$$\int_{-\infty}^{0} d\epsilon' f_0(\epsilon') g(\epsilon - \epsilon`),$$

where it is taken into account that only $f(\epsilon)$ at $\epsilon < 0$ contribute to the evolution since $f(\epsilon)$ at $\epsilon > 0$ corresponds to escaping particles. Thus,

$$f(\epsilon) = \sqrt{\frac{1}{4\pi\delta_1 T}} \int_{-\infty}^{0} d\epsilon' f_0(\epsilon') \exp\left[-\frac{(\epsilon - \epsilon` + \delta_1)^2}{4\delta_1 T}\right]. \qquad (22)$$

After one oscillation the distribution is shifted by δ_1 and broadened with dispersion $\Delta = \langle\delta^2\rangle^{1/2} = (2\delta_1 T)^{1/2}$. Thus, if $\delta_1 \gg T$, then $\delta_1 \gg \Delta \gg T$. As $-\epsilon \gg T$,

$$f(\epsilon) = \frac{\Omega_1}{2\pi T} \exp\left(-\frac{\epsilon + U}{T}\right) \qquad (23)$$

The flux J can also be expressed through solution of the integral equation

$$\tau^{-1} = J = \int_{0}^{+\infty} f(\epsilon) d\epsilon$$

where the identity $d\epsilon = pdp/m$ is used. If $\delta_1 \ll T$, then $\delta_1 \ll \Delta \ll T$, and the kernel of the integral equation (22) may be expaned in energy difference. Upon the integration over energy ϵ' it yields a differential equation instead of an integral one:

$$\frac{d}{d\epsilon}\left(T\frac{df}{d\epsilon} + f\right) = 0. \qquad (24)$$

We can reduce its order to get the equation

$$T\frac{df}{d\epsilon} + f = J_\epsilon. \qquad (25)$$

The solution of Eq (25) compatible with the boundary conditions may be found in the form

$$f(\epsilon) = A\frac{\Omega_1}{2\pi T}\, e^{-U_1/T}(e^{\epsilon/T} - 1) \qquad (26)$$

which gives us the escape rate

$$\tau^{-1} = -\delta_1 T\frac{df}{d\epsilon}|_{\epsilon=0} = \frac{\Omega_1\delta_1}{2\pi T}e^{-U_1/T} \qquad (27)$$

We are looking for the expression for the escape rate in the form

$$\tau^{-1} = A\frac{\Omega_1}{2\pi}\, e^{-U_1/T} \qquad (28)$$

and see that A is linear in δ_1/T at $\delta_1 \ll T$. We will shortly see that $A = 1$ at $\delta_1 \gg T$. Thus, our purpose is to match these two asymptotes.

The Wiener-Hopf method

The right hand side of our equation has the form of convolution of two functions f and g on the negative half-axis:

$$f(\epsilon) = \int_{-\infty}^{0} d\epsilon' g(\epsilon - \epsilon')f(\epsilon')$$

Wiener and Hopf invented their method specially for solving the equations of exactly this kind. Following their prescription we introduce the two half-axis Fourier transformations

$$\phi_{\pm}(\mu) = \frac{2\pi}{\Omega_1}\exp\left(\frac{U_1}{T}\right)\int_{-\infty}^{+\infty} d\epsilon f(\epsilon)\; \theta(\pm\epsilon)\exp\left[\frac{(2i\mu+1)\epsilon}{2T}\right] \qquad (29)$$

Comparison with the normalization condition gives

$$A = \phi_+\left(\frac{i}{2}\right) \qquad (30)$$

The boundary condition

$$f(\epsilon) = \frac{\Omega_1}{2\pi T} \exp\left(-\frac{\epsilon + U_1}{T}\right)$$

as $\epsilon \to -\infty$ means that $\phi_-(\mu)$ has a pole at $\mu = i/2$ and $\phi_-(\mu) = -1(\mu + i/2)^{-1}$ at $|\mu + i/2| \ll 1$. The Fourier transform of the integral equation has the form

$$\phi_+(\mu) + \phi_-(\mu) = g(\mu)\phi_-(\mu), \tag{31}$$

$$g(\mu) = \exp\left[-\left(\mu^2 + \frac{1}{4}\right)\frac{\delta_1}{T}\right] \tag{32}$$

Thus,

$$\phi_+(\mu) = -\,G(\mu)\phi_-(\mu),$$

where

$$G(\mu) = 1 - \exp\left[-\left(\mu^2 + \frac{1}{4}\right)\frac{\delta_1}{T}\right] \tag{33}$$

It is important to note that $\phi_+(\mu)$ is a holomorphic function at $\mathrm{Im}\mu > -\alpha_+$ $(\alpha_+ > 0)$, and $\phi_-(\mu)$ is a holomorphous function at $\mathrm{Im}\mu < \alpha_- < 0$ with the only exception for its pole at $\mu = -i/2$. Thus there is a stripe where both these functions are holomorphous. The next step of the Wiener-Hopf procedure is to represent $G(\mu)$ in a factorised form $G(\mu) = G_+(\mu)\cdot G_-(\mu)$, where G_+ and G_- are entire functions which have no zeros the upper and lower half-planes respectively. If we manage to factorize G, then

$$\frac{\phi_+(\mu)}{G_+(\mu)} = -\,G_-(\mu)\phi_-(\mu). \tag{34}$$

It is a good idea to eliminate the pole of $\phi_-(\mu)$ at $\mu = -i/2$

$$\frac{\phi_+(\mu)}{G_+(\mu)}\,(\mu + \frac{i}{2}) = -\,G_-(\mu)\phi_-(\mu)\,(\mu + \frac{i}{2}) \tag{35}$$

Both sides of Eq (34) are holomorphous functions in certain areas and they coincide in the stripe where these areas overlap. Therefore, they are both holomorphous, equal in the whole plane including the infinity and, according to the Liouville theorem, they both are equal to a constant. Therefore,

$$\phi_-(\mu) = -\frac{i}{\mu + i/2} \frac{G_-(-i/2)}{G_-(\mu)} \tag{36}$$

$$\phi_+(\mu) = i \frac{G_-(-i/2) G_+(\mu)}{\mu + i/2} \tag{37}$$

As for the pre-exponential factor A, it is determined by Eq (30)

$$A = \phi_+(i/2) = |G_+(i/2)|^2$$

Thus, in order to find the escape rate, we don't need even to invert Furrier transform for $\phi_-(\mu)$. It is enough to split the kernel G into retarded and advanced parts. This problem of factorization may be reduced to the problem of an additive splitting by taking the logarithms

$$\log G(\mu) = \log G_+(\mu) + \log G_-(\mu)$$

Now we can express $\log G_\pm$ through $\log G$

$$\log G_\pm(\mu) = \pm \frac{1}{2\pi i} \int_{-\infty}^{+\infty} \frac{\log G(\mu')}{\mu' - \mu} \cdot d\mu' \tag{38}$$

and, finally,

$$G_\pm(\mu) = \exp\left(\pm \frac{1}{2\pi i} \int_{-\infty}^{+\infty} \frac{\log G(\mu')}{\mu' - \mu} d\mu' \right) \tag{39}$$

Thus, as a result,

$$A = \exp\left\{ \frac{1}{2\pi} \int_{-\infty}^{+\infty} \frac{d\mu}{\mu^2 + \frac{1}{4}} \ln\left(1 - \exp\left(-\frac{\delta_1(\mu^2 + \frac{1}{4})}{T}\right)\right)\right\} \tag{40}$$

Now we are able to study the limiting cases. If $\delta_1 \ll T$, we can expand the exponent under the sign of the logarithm, and

$$\begin{aligned} A &= \exp\left\{\frac{1}{2\pi}\int_{-\infty}^{+\infty}\frac{d\mu}{\mu^2+\frac{1}{4}}\ \ln\left(\frac{\delta_1(\mu^2+\frac{1}{4})}{T}\right)\right\} = \\ &= \frac{\delta_1}{T}\exp\left\{\frac{1}{2\pi}\int_{-\infty}^{+\infty}\frac{d\mu}{\mu^2+\frac{1}{4}}\right\} = \frac{\delta_1}{T} \end{aligned} \tag{41}$$

As $\delta_1 \gg T$,

$$A = \exp\left\{-\frac{1}{2\pi}\int_{-\infty}^{+\infty}\frac{d\mu}{\mu^2+\frac{1}{4}}\ \exp\left(-\frac{\delta_1}{T}\left(\mu^2+\frac{1}{4}\right)\right)\right\} \tag{42}$$

Intermediate behavior is represented in the figure.

One more question which may intrigue the reader relates to the mean energy of an escaping particle. Since the distribution function near the barrier top has the form

$$f(\epsilon) = \frac{\Omega_1}{4\pi^2 T}\int_{-\infty}^{+\infty}\phi_+(\mu)\exp\left\{-\frac{\epsilon}{T}\left(-i\mu+\frac{1}{2}\right)\right\}d\mu \tag{43}$$

the mean energy may also be expressed through the Wiener-Hopf solution

$$\begin{aligned} <\epsilon> &= \frac{\int_0^{+\infty} f(\epsilon)\epsilon d\epsilon}{\int_0^{+\infty} f(\epsilon)d\epsilon} = T\left(\frac{d\log\phi_+(\mu)}{d\mu}\right)_{\mu=i/2} = \\ &= T\left\{1+\frac{2}{\pi}\int_0^{\pi/2}(1-2\cos^2 x)\ \ln\left(\frac{\delta_1}{4T\cos^2 x}\right)\right\} \end{aligned} \tag{44}$$

For $\delta_1 \gg T$ the integral in the brackets is negligible and $<\epsilon>= T$. For $\delta_1 \ll T$ we again can expand the exponent under the sign of logarithm and

$$\begin{aligned} \frac{<\epsilon>}{T} &= 1+\frac{2}{\pi}\int_0^{\pi/2}(1-\cos^2 x)\ \ln\left\{\frac{\delta_1}{4T\cos^2 x}\right\}dx = \\ &= \zeta(1/2)\sqrt{\frac{\delta_1}{\pi T}} = .82\sqrt{\frac{\delta_1}{T}} \end{aligned} \tag{45}$$

which is understandable since under conditions of very low viscosity the Langevine fluctuating force is weak as well and it does not accelerate a particle even to energy T over the top of the barrier.

Finally, we must emphasize that such a long and stressful work was absolutely necessary and led to complete success.