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Model-dependent nature of blowtorch effect on the escape and equilibration rates

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Abstract. We analyze the relaxation behavior of a bistable system when the background temperature profile is inhomogeneous due to the presence of a localized hot region (blowtorch) on one side of the potential barrier. Since the diffusion equation for inhomogeneous medium is model-dependent, we consider two physical models to study the kinetics of such system. Using a conventional stochastic method, we obtain the escape and equilibration rates of the system for the two physical models. For both models, we find that the hot region enhances the escape rate from the well where it is placed while it retards the escape rate from the other well. However, the value of the escape rate from the well where the hot region is placed differs for the two models while that of the escape rate from the other well is identical for both. This work, for the first time, gives a detailed report of the similarities and differences of the escape rates and, hence, exposes the common and distinct features of the two known physical models in determining the way the bistable system relaxes.

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1 Introduction

A system in contact with a uniform thermal bath settles around its equilibrium state or, in general, around its competing equilibrium states determined by the Boltzmann factor $\exp(-E/k_BT)$. This simple fact does not hold when the bath temperature is nonuniform and was explicitly argued by Landauer in his now influential paper [1] on relative stability, i.e. relative occupation, of the competing local energy minima for a system far from equilibrium. He pointed out the globally determining role played by the nonequilibrium kinetics of the unstable intermediate states even as these are very rarely populated. In particular, for a system with two unequally competing equilibrium states, i.e. an asymmetric bistable potential, he showed that the application of localized heating at a point on the reaction coordinate lying between the lower energy minimum and the potential barrier maximum can raise the relative population of the higher-lying energy minimum above that given by the Boltzmann factor. This is the so-called blowtorch effect [1] that arises due to the nonuniform thermal bath. It generalizes the problem of escape of a Brownian particle over a potential barrier under the influence of equilibrium thermal fluctuations, studied originally by Kramers [2], to the case of nonuniform temperature along the reaction coordinate.

It is known that the diffusion equation describing motion of a Brownian particle in a homogeneous medium with temperature T and under an external potential $V(x)$ is given by

$$
\frac{\partial}{\partial t}P(x,t) = \mu \frac{\partial}{\partial x} \left(V'(x)P(x,t) \right) + D \frac{\partial^2}{\partial x^2} P(x,t), \quad (1)
$$

where $P(x, t)$ is the probability density of the particle at position x at time t, μ is the mobility, D is the diffusion coefficient such that $D = k_B T \mu$ (k_B is Boltzmann constant), and $V' \equiv \frac{dV}{dx}$. However, when one wants to investigate the blowtorch effect, the medium is inhomogeneous due to the temperature nonuniformity. Accordingly, one has to generalize the diffusion equation, equation (1), to account for effects arising from inhomogeneous temperature or more generally inhomogeneous medium. Unfortunately, the diffusion equation describing motion of a Brownian particle in an inhomogeneous medium has been controversial for a long time [3]. The controversy was whether one should take the diffusion term to be

or

$$
\frac{\partial}{\partial x}\left(D(x)\frac{\partial}{\partial x}P(x,t)\right),\,
$$

 $\frac{\partial}{\partial x^2} (D(x)P(x,t)),$

 ∂^2

or something else. It was more or less settled after van Kampen, taking three different physical models with inhomogeneous media, arrived at three different diffusion equations [4–6]. This exposed the model-dependent nature

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of the diffusion equation for inhomogeneous media [3]. For the same reason, one should anticipate the results of studies on the blowtorch effect to be model-dependent.

Investigations on the blowtorch have been largely on studying the influence of position-dependent temperature on the steady-state relative populations of the energy minima. Kinetic aspects of such systems are just beginning to be addressed as they are related to the problem of molecular motors [7]. There has been only one previous work which explicitly studied the effect of blowtorch on the equilibration rate by taking one physical model [8]. Although their results illustrate the role of the various parameters describing the blowtorch, the supersymmetric method used in that work is not as transparent (due to the initial transformation used) as the conventional stochastic methods used in dealing with similar problems.The main purpose of this paper is to understand the extent to which the equilibration is model-dependent in a more transparent way using the standard method of first passage time. To this end, the kinetic aspects for the two physical models that used to be controversial – one originally suggested by Landauer [9] and the other by van Kampen $[4]$ – are considered leaving the third model for future analysis. As in the previous work [8], the blowtorch is mimicked by considering the inhomogeneity to arise from local heating in one of the potential wells. We use the Brinkman's method [10] to get analytic expressions not only for the equilibration rate but also for the individual escape rates from the two wells. This enables us to clearly see how these individual escape rates are affected by the blowtorch and are reported for the first time in this paper.

The rest of this paper is organized as follows. In Section 2, the rate equations that capture the late stage dynamics of the population in each well will be derived for two physical models, each described by their respective diffusion equations. In Section 3, considering a model bistable potential and a temperature profile that mimics a simple hot region, we derive analytic expressions for the escape and equilibration rates for both models. Section 4 discusses the results along with comparison to the previous work [8]. We summarize and conclude in Section 5.

2 Rate equations

Motion of a Brownian particle in a bistable potential at its late stage of evolution involves, beyond the local fluctuations about the minima, jumps of the particle from one well to the other. When the barrier height separating the two wells is high compared to the thermal energy, these jumps are rare and take place on timescales very much greater than the timescales for local fluctuations. Under these conditions, we can coarse-grain the spatial region into two, corresponding to the two wells of the potential, and keep track of the particle's probabilities in the leftand right-wells as time flows. This leads to the rate equations for these probabilities. We derive the rate equations starting from their corresponding diffusion equations for two inhomogeneous physical models.

2.1 van Kampen's model

This model, which we call van Kampen's model, considers motion of noninteracting Brownian particles in an inhomogeneous medium with a high friction. Starting from the one dimensional Kramers' equation and utilizing the general method for eliminating fast variables [11,12], van Kampen arrived at the diffusion equation for this system [4]. Later on, Jayannavar and Mahato [13] also arrived at the same diffusion equation for the same system starting from a microscopic treatment where they took the thermal bath as a set of harmonic oscillators. This diffusion equation is given by

$$
\frac{\partial P(x,t)}{\partial t} = \frac{\partial}{\partial x} \bigg[\mu(x) V'(x) P(x,t) + \mu(x) \frac{\partial}{\partial x} (k_B T(x) P(x,t)) \bigg]. \tag{2}
$$

Note that, in this model, the expression for the diffusion term is neither of the first nor of the second type as suggested above.

The steady state probability distribution for this diffusion equation, equation (2), is given by

$$
P_{ss}(x) = \frac{N}{T(x)} \exp\left[-\int^x \frac{V'(\tilde{x})}{k_B T(\tilde{x})} d\tilde{x}\right],\tag{3}
$$

where N is normalization constant. In the absence of external potential, the dependence of P_{ss} on the temperature, *i.e.* $P_{ss} \propto \frac{1}{T(x)}$, shows that at steady state a hot region is less populated than a relatively cold region of the same width. Such equilibration process can be seen to arise via pressure equilibration [14]. On the other hand, the effect of the external potential, $V(x)$, on the steady state distribution of the system is fully accounted for by the exponential factor in the equation (Eq. (3)).

Consider a bistable potential where A and C designate the respective points of the left- and right-minima while B designates the barrier maximum and positioned so as to coincide with $x = 0$. The dynamics for van Kampen's model is governed by the diffusion equation, equation (2), given above which can be expressed as a continuity equation

$$
\frac{\partial P(x,t)}{\partial t} = -\frac{\partial J(x,t)}{\partial x} \tag{4}
$$

where $J(x, t)$ is the current density given by

$$
J(x,t) = -\mu(x) \left[V'(x)P(x,t) + \frac{\partial}{\partial x} (k_B T(x)P(x,t)) \right].
$$
\n(5)

We follow the Brinkman's method [10] to get the rate equations for the populations in the left- and rightwells. We introduce the coarse-grained variables, $n_A(t)$ and $n_C(t)$, that describe the populations in the left- and right-wells, respectively, defined as

$$
n_{A(C)}(t) = \int_{-\infty(0)}^{\infty} P(x, t) dx.
$$
 (6)

Here, the integral with the limits $\int_{-\infty}^{0}$ is for $n_A(t)$ while the integral with the limits \int_0^∞ is for $n(t)$. If $J(x, t)$ is multiplied by a quantity $Q(x)$ defined as

$$
Q(x) \equiv \exp\left[\int_{x_A}^{x} \frac{V'(\tilde{x})}{k_B T(\tilde{x})} d\tilde{x}\right]
$$
 (7)

and integrated from x_A to x_C , one obtains the relation

$$
P(x_C, t)k_BT(x_C)Q(x_C) - P(x_A, t)k_BT(x_A) = -\int_{x_A}^{x_C} \frac{J(x, t)Q(x)}{\mu(x)} dx.
$$
 (8)

For high barrier, the integral on the right side of equation (8) can be simplified by assuming that the major contribution to the integral arises from the region near the top of the barrier. On the other hand, $J(x, t)$ is very nearly constant in this region so that we can replace its value by $J(0, t)$. Hence, we get

$$
J(0,t) = \frac{P(A,t)T_A - P(C,t)T_CQ(C)}{\int_A^C \frac{Q(x)}{\mu(x)}dx}.
$$
 (9)

Here, $A(C)$ stands for $x_{A(C)}$ and k_B is set to unity from now onwards. During late stages of the evolution, *i.e.* beyond the time required for local equilibration in each well, $P(x, t)$ can be expressed as

$$
P(x,t) = \rho(t)P_{ss}(x) \tag{10}
$$

where $\rho(t)$ is essentially constant within each well, but keeps track of leakage across the barrier. Lastly, using equations $(3, 6)$ and (10) in equation (9) we get the rate equations for the two populations as

$$
\frac{dn_A}{dt} = -\lambda_A^V n_A(t) + \lambda_C^V n_C(t),
$$

$$
\frac{dn_C}{dt} = \lambda_A^V n_A(t) - \lambda_C^V n_C(t)
$$
(11)

where

$$
\lambda_{A(C)}^{\text{V}} = \frac{D_{A(C)}}{\int_{A}^{C} \frac{\mu_{A(C)}Q(x)}{\mu(x)} \, \mathrm{d}x \int_{-\infty(0)}^{0(\infty)} \frac{T_{A(C)}}{T(x)Q(x)} \, \mathrm{d}x} \,. \tag{12}
$$

The superscript 'V' above the λ 's is used to denote van Kampen's model while superscript 'L' will be used later to denote another model called Landauer's model. λ_A and λ_C are the *escape rates* of the particles from left-well to right-well and vice versa, respectively. The eigenvalues of the coefficient matrix for the rate equations, equation (11), are 0 and $-(\lambda_A^V + \lambda_C^V)$. Therefore, the relaxation or the *equilibration rate*, λ_{eq}^V , is just the sum of the two escape rates; *i.e.*, $\lambda_{eq}^V = \lambda_A^V + \lambda_C^V$.

2.2 Landauer's pipe model

This model, originally suggested by Landauer [9], consists of a very narrow pipe, radius ϵ , filled with Knudsen gas. As the molecules of the gas move through the pipe they get thermalized by colliding with the wall whose temperature varies along the pipe. They are also under an external potential field, $V(x)$. Starting from the Kramers equation for the distribution function of the molecules and taking the limit $\epsilon \to 0$, van Kampen [5] used singular perturbation method to arrive at the corresponding diffusion equation, which is given by

$$
\frac{\partial P(x,t)}{\partial t} = \frac{\partial}{\partial x} \left[\mu(x) V'(x) P(x,t) + \frac{\partial}{\partial x} (D(x) P(x,t)) \right],\tag{13}
$$

where $\mu(x) = \frac{8\epsilon}{3\sqrt{2\pi T(x)}}$ is the mobility of the molecules. In this model, it is worth noting that the diffusion term is of the first type as suggested above. The stationary solution of equation (13) is

$$
P_{ss}(x) = \frac{N}{\sqrt{T(x)}} \exp\left[-\int^x \frac{V'(\tilde{x})}{T(\tilde{x})} d\tilde{x}\right].
$$
 (14)

In the absence of external potential, the dependence of $P_{ss}(x)$ on the temperature, *i.e.* $P_{ss} \propto \frac{1}{\sqrt{T}}$ $\frac{1}{T(x)}$, explains the fact that the speed of the molecules is proportional to $\sqrt{T(x)}$. Such equilibration process can be seen to arise via temperature equilibration [15] and tells us that the molecules in the hot region are weakly depleted compared to those of van Kampen's model.

Following identical procedures as in the previous subsection, the rate equations for Landauer's pipe model are

$$
\frac{dn_A}{dt} = -\lambda_A^{\text{L}} n_A(t) + \lambda_C^{\text{L}} n_C(t),
$$

$$
\frac{dn_C}{dt} = \lambda_A^{\text{L}} n_A(t) - \lambda_C^{\text{L}} n_C(t)
$$
(15)

where

$$
\lambda_{A(C)}^{\mathcal{L}} = \frac{D_{A(C)}}{\left(\int_A^C Q(x)dx\right)\left(\int_{-\infty(0)}^{0(\infty)} \frac{\sqrt{T_{A(C)}}}{\sqrt{T(x)}Q(x)}dx\right)}\tag{16}
$$

Hence, the equilibration rate is once again the sum of the individual escape rates.

3 Escape rates for model potential with a hot region

Now, by using the general expressions for the escape and equilibration rates and taking a specific model potential with a hot region, we will obtain closed form expressions for the rates. This will allow us to understand the extent to which the effect of the hot region on these rates is modeldependent.

Our model potential is a symmetric W-potential of barrier height V_0 and having the same magnitude in slope everywhere. The distance between the minima is 2L (see Fig. 1a). The temperature profile is piece-wise constant 372 The European Physical Journal B

Fig. 1. Plots of $V(y)$ and $T(y)$ versus y are, respectively, shown in (a) and (b). Note that y is a dimensionless variable such that $x = yL$.

with the hot region placed somewhere between the barrier maximum and the right minimum of the potential (see Fig. 1b), and given by the relation

$$
T(x) = T_0 + sT_0 [\Theta(x - (p - 0.5w)L)
$$

- $\Theta(x - (p + 0.5w)L)].$ (17)

Here $\Theta(x)$ is the Heaviside function, T_0 is the background (constant) temperature and sT_0 is the excess temperature such that the temperature, T , in the hot region is $T =$ $T_0(1 + s)$. In addition to the parameter s that quantifies the *strength* of the hot region (in units of T_0), parameters w and p quantify, respectively, its *width* and *position* of its mid-point from the barrier top (in units of L).

The previous blowtorch work on the kinetic aspect of a bistable system [8] used van Kampen's model. In addition, it considered the mobility to be the same everywhere. Here also, for the sake of comparison, we will confine to the constant mobility case for the van Kampen model.

For such a case, the expressions for the escape rate from the left-well for both models, λ_A^V and λ_A^L given, respectively, in equations (12, 16), will be identical. On the other hand, the expressions for the escape rate from the right-well for the two models are different from each other. In order to clearly see the effect of the hot region on the escape and equilibration rates, we define a quantity, $\Lambda_{A(C)}$, called enhancement factor for each escape rate from left- (right-)well as

$$
A_{A(C)} = \frac{\lambda_{A(C)}}{\lambda_{A(C)}^0} \,. \tag{18}
$$

Here $\lambda_{A(C)}^0$ stands for escape rate from left-(right-)well in the absence of the hot region. For the symmetric Wpotential, $\lambda_A^0 = \lambda_C^0$, and is given by

$$
\lambda_A^0 = \lambda_C^0 = D_0 \left(\frac{v}{2L}\right)^2 e^{-v},\tag{19}
$$

where $v \equiv \frac{V_0}{T_0}$ and D_0 is the diffusion coefficient outside (or in the absence of) the hot region. The corresponding enhancement factor for the equilibration rate

Fig. 2. Plot of Λ_{eq}^V as a function of position, p, of the hot region for $v = 20$, $w = 0.1$, and $s = 1$

will then be $\Lambda_{eq} = \frac{1}{2} (A_A + A_C)$. Using the particular Wpotential along with the temperature profile as given in equation (17), we get the following approximate closed form expressions for the enhancement factors, $\Lambda_{A(C)}$, for the corresponding models:

$$
A_A = A_A^V = A_A^L = \frac{1}{1 + sg(s, w)e^{-pv}},
$$
 (20)

$$
A_C^V = \frac{e^{2s\sigma}}{1 + sg(s, w)e^{-pv}} = e^{2s\sigma} A_A,
$$
 (21)

$$
A_C^{\mathcal{L}} = \frac{A_C^{\mathcal{V}}}{1 + (\sqrt{1 + s} - 1) g(s, w) e^{-(1 - p)v}},
$$
 (22)

where $\sigma \equiv \frac{wv}{2(1+s)}$ and

$$
g(s, w) = e^{s\sigma} \sinh(\sigma).
$$
 (23)

Note that the parameters w and p take values between 0 and 1 (in fact, $\frac{w}{2} \leq p \leq (1 - \frac{w}{2})$), while the parameter s takes positive values for a hot zone and negative values (but greater than -1) in case we have a *cold* zone.

4 Results and discussion

First of all, the enhancement factor for the equilibration rate for the van Kampen's model, $\Lambda_{eq}^{\text{V}} = \frac{1}{2} (\Lambda_A^{\text{V}} + \Lambda_C^{\text{V}})$, is given by

$$
A_{eq}^V = \frac{1 + e^{2s\sigma}}{2 + 2sg(s, w)e^{-pv}}.
$$
 (24)

This is exactly identical with the expression found in the previous work [8]. It is worth noting that the two different approaches to the problem give us exactly the same result. For the sake of completeness, we have shown a plot of Λ_{eq}^V versus p in Figure 2. It clearly shows that the equilibration rate saturates as the hot zone is placed further away from the barrier top as has been pointed out in the previous work [8].

Fig. 3. Plot of Λ_A as a function of strength, s, of the hot region for $w = 0.3$, $p = 0.15$ and $v = 10$.

Fig. 4. Plot of Λ_A as a function of width, w, of the hot region for $s = 1$, $p = 0.5w$ and $v = 10$.

Let us now see how the individual escape rates from each well are affected by the hot region which is placed in the right-well.

The value for the enhancement factor from the leftwell, Λ_A , which is identical for both models and given by equation (20), clearly shows that the presence of the hot zone diminishes the escape rate from the left-well. However; the hot zone's diminutive role becomes negligible when it is placed away from the barrier top because of the exponential term, e^{-pv} , appearing in the denominator. In fact, when the hot zone is placed at the top, *i.e.* $p = \frac{w}{2}$, $g(s, \sigma)$ tends to $\frac{1}{2}$ [16] so that Λ_A takes the smallest value of about $\frac{2}{2+s}$. On the other hand, when the hot zone is placed further away from the barrier top, Λ_A goes to unity. The decreasing effect of the hot zone on the escape rate from the left-well is illustrated by the plots of Λ_A as functions of s and w , respectively, shown in Figures 3 and 4. In Figure 4, the left-side of the hot zone is kept fixed touching the barrier top so that as w is varied p also varies such that $p = \frac{1}{2}w$.

On the other hand, the enhancement factor from the right-well for van Kampen's model, Λ_C^V , given by equation (21) is composed of two products; *i.e.*, A_A and an exponential factor, $e^{2s\sigma}$. Taking note of the behavior of Λ_A discussed above, this means that the escape rate from the right-well gets enhanced by the exponential factor (of $e^{2s\sigma}$) when the hot zone is placed close to the bottom. However, if the hot zone is placed near the barrier top that (expo-

Fig. 5. Plots of Λ_C^V (solid line) and Λ_C^L (dashedline) as a function of position, p, of the hot region for $w = 0.3$, $s = 1$ and $v = 10.$

Fig. 6. Plots of Λ_C^V (solid line) and Λ_C^L (dashed line) as a function of width, w, of the hot region for $s = 1$, $p = 0.5$ and $v=10.$

nential) amount of the enhancement gets decreased by a factor of about $\frac{2}{2+s}$. Hence, the effect of the hot zone on Λ_C^V is maximum when it is placed at the bottom. Figure 5 illustrates this by plotting Λ_C^V versus p.

The same enhancement factor for Landauer's model, Λ_C^{L} , is a combination of two products: Λ_C^{V} and a diminutive term, $\frac{1}{1+(\sqrt{1+s}-1)g(s,w)e^{-(1-p)v}}$. This term takes a minimum value of about $\frac{2}{1+\sqrt{1+s}}$ when the hot zone is placed close to the bottom. On the other hand, when the hot zone is moved towards the barrier top it decays away to unity. (Note the exponential term $e^{-(1-p)v}$.) Hence, Λ_C^L behaves as Λ_C^V when the hot zone is placed away from the bottom but decays to a lower value when placed near the bottom. This leads to the existence of an intermediate position of the hot zone at which Λ_C^{L} takes an *optimum* value. In fact, the optimum value occurs at

$$
p = \frac{1}{2} + \frac{1}{2v} \left(\log(1 + \sqrt{1 + s}) \right), \tag{25}
$$

which, for high barrier, is practically at the mid-point between the barrier top and the right-minimum. To illustrate this further, we plot the dependence of $\Lambda_C^{\rm L}$ on p in the same figure above (Fig. 5) where we have plotted Λ_C^V versus p.

Figure 6 shows plots of Λ_C^V and Λ_C^L as a function of w. The exponential increase in the enhancement factor with

Fig. 7. Plots of Λ_C^V (solid line) and Λ_C^L (dashed line) as a function of strength, s, of the hot region for $w = 0.3$, $p = 0.5$ and $v = 10$.

increase in hot zone width, w , is clearly visible. Lastly, Figure 7 shows plots of Λ_C^V and Λ_C^L versus s where we get a monotonous increase of the enhancement factors with increase in s.

5 Summary and conclusion

The Brinkman's method has enabled us to calculate the individual escape rates as functions of the hot zone parameters in a direct and transparent way. In principle, one could use supersymmetric method to get these escape rates. To do so, however, one has to setup a single-well potential with a runaway on one side and place the hot zone within the well to calculate λ_C and then place the hot zone outside the well to calculate λ_A . This requires carrying out a separate calculation to obtain the individual escape rates. Hence, the Brinkman's method is better-suited and is also more transparent for calculating the escape rates.

The effect of the hot zone on the escape rates can be summarized by the value the corresponding enhancement factors take around the two extreme positions; i.e., top and bottom of the right-well. This is tabulated below.

As has been mentioned in the discussion above, the escape rates from the left-well are identical for the two physical models while the escape rates from the right-well show qualitatively different behavior from each other particularly as a function of the position of the hot zone.

In comparing the two models, we have limited ourselves to the constant mobility case for van Kampen's model. On the other hand, for Landauer's model mobility is *always* proportional to $T^{-\frac{1}{2}}$. It would be interesting to consider the general position-dependent mobility case for van Kampen's model and study the kinetic aspect of Landauer's blowtorch effect.

On the other hand, it is worth to look for actual systems where these theoretical results could be checked. We believe that microdevices such as Brownian heat engines [7] are possible candidates for checking these theoretical results. Even design of such devices that operate either efficiently or optimally demand knowledge of these results. One may need a hot reservoir, i.e. a hot region, of the right strength and width placed at an appropriate position to get an efficiently or optimally working Brownian heat engine instead of attaching one well to a hot and the other to a cold reservoir.

Lastly, we would like to mention that we do not yet have a convincing physical argument as to why the two models differ from each other.

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