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I. Santamaría-Holek^{1,a)}  and A. Pérez-Madrid^{2,b)} 

AFFILIATIONS

¹UMDI-J, Facultad de Ciencias, Universidad Nacional Autónoma de México, Campus Juriquilla, 76230 Querétaro, Mexico

²Departament de Física de la Matèria Condensada, Universitat de Barcelona, 08028 Barcelona, Spain

^{a)} Author to whom correspondence should be addressed: isholek.fc@gmail.com

^{b)} agustiperezmadrid@ub.edu

ABSTRACT

Understanding and managing the influence that either external forces or non-equilibrated environments may have on chemical processes is essential for the current and future development of theoretical chemistry. One of the central questions to solve is how to generalize the transition state theory in order to make it applicable in far from equilibrium situations. In this sense, here we propose a way to generalize Eyring's equation based on the definition of an effective thermal energy (temperature) emerging from the coupling of both fast and slow dynamic variables analyzed within the generalized Langevin dynamics scheme. This coupling makes the energy distribution of the fast degrees of freedom not equilibrate because they have been enslaved to the dynamics of the corresponding slow degrees. However, the introduction of the effective thermal energy enables us to restore an effective adiabatic separation of timescales leading to a renormalization of the generalized fluctuation–dissipation theorem. Hence, this procedure opens the possibility to deal with systems far away from equilibrium. A significant consequence of our results is that Eyring's equation is generalized to treat systems under the influence of strong external forces.

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I. INTRODUCTION

The Arrhenius law and the transition state theory¹ constitute a fundamental theoretical framework for describing and predicting the kinetic aspects of chemical reactions. The aim of the transition state theory (TST) formulated by Eyring was to determine the chemical reaction rates and other transport coefficients from the knowledge of the partition functions of the molecules involved, calculated by using quantum and equilibrium statistical mechanics. The great achievement of the TST was that it gave enormous elasticity to theoretical chemistry in which both quantum mechanics and statistical thermodynamics became the very solid cornerstones. However, interest in the influence that external forces and non-equilibrated environments or heat baths may have on chemical processes has recently emerged.^{2–4} An excellent exposition of the general situation was recently provided by Matyushov⁵ and studied in the case of electron transfer reactions by Craven and Nitzan.⁶

The critical point is that, at the nanoscale, the temperature (pressure or chemical potential) gradients are enormous even for

small differences of their values, and therefore, the assumptions of local equilibrium⁷ or linear regression laws⁸ seem to be no longer valid.⁵ Nonetheless, this drastic situation does not disqualify previous use of thermodynamics in order to tackle this fundamental problem.

On the nanoscale level of description, the influence of these strong forces, or gradients, may introduce non-linear corrections to the value of the aforementioned intensive parameters.⁹ The critical ingredient is associated with the fact that external forces or gradients are sources of extra energy that is supplied to the system and dissipated into the heat bath. Thus, the thermal energy giving rise to spontaneous fluctuations becomes enhanced. This extra energy introduces a coupling between the dynamics of slow and fast degrees of freedom, violating the adiabatic separation of their corresponding dynamics.

The aforementioned coupling introduces theoretical and methodological complications, as the information about the dynamics of the fast degrees of freedom is not frequently available in practice. It is thus of interest to renormalize the dynamical description

so that the forces leading to the coupling of degrees of freedom are absorbed in an effective intensive variable, such as temperature or chemical potential.^{9,10} This renormalization of the intensive thermodynamic parameters enables us to perform a dynamic description in which the fluctuation–dissipation theorem incorporates the renormalized variables. In doing this, the second law of thermodynamics is still obeyed in a similar form as in a system at thermal equilibrium: the (effective) energy of the fluctuations is dissipated into the heat bath in a precise balance involving the effective temperature and the corresponding transport coefficient associated with energy dissipation (typically identified with friction). In the present work, we analyze these questions using the framework of the generalized Langevin equation (GLE).

Our involvement with this situation traces back to a series of papers dealing with the Fokker–Planck dynamics of a system under strong internal constraints or external forces.^{9–14} Among other situations, we have found that in far from equilibrium systems, the reaction constants of diffusion-controlled chemical reactions are modified by the existence of a “mean-field temperature,” which incorporates the non-equilibrium constraints. Although restricted to the application of Kramer’s transition state theory,⁹ the proof of the emergence of a non-equilibrium or effective temperature provides a sound theoretical approach for the reformulation of the traditional TST as it is seen to be needed at the nanoscale.^{5,6} Our approach to the effective temperature has been tested through the comparison with several experiments on tracer diffusion in dense colloidal media already cited in one of our previous works¹³ and computer simulations on active non-linear rheology in glassy systems.^{14–17}

Our results allow us to reformulate the TST to describe systems in the presence of far from equilibrium heat baths. The results go in a spirit similar to that of Craven and Nitzan⁶ but with larger implications. In particular, this renormalization introduces in a natural way non-linear effects in the external forces, which are hidden in the intensive parameters of the corresponding distribution functions. These corrections become therefore included in the expression of the reaction rates.

This article is organized as follows: In Sec. II, by introducing a change of variables for the fast degree of freedom, we show how the effective temperature arises and how it depends on the external force. Section III is then devoted to calculating the probability distribution function of the fast degree of freedom and to showing how a generalization of the fluctuation–dissipation theorem of the system can be rewritten by introducing a scaling relation for the fast degree of freedom. This scaling relation allows us to rewrite the distribution function and the Langevin equation in such a form that the adiabatic separation of time scales can be recovered. In Sec. IV, this recovery allows us to establish a general formulation of the TST for systems far away from equilibrium, a result that is summarized by Eyring’s formula. Section V presents our concluding remarks.

II. EMERGENCE OF AN EFFECTIVE TEMPERATURE FROM THE GENERALIZED LANGEVIN DYNAMICS

Let us consider a system whose state can be characterized by two coupled Brownian degrees of freedom α and β in the presence of a heat bath at temperature T . The description of the time evolution of these variables follows the classical generalized Langevin scheme,¹⁸ and thus, by assuming that β is the fast variable and α the slow one,

the evolution of α obeys the following equation:

$$\frac{d\alpha}{dt} = \beta(t), \quad (1)$$

while the dynamics of the fast variable is governed by the Langevin equation

$$\frac{d\beta}{dt} = - \int_0^t \kappa(t-t')\beta(t')dt' + X_\alpha(t) + F(t), \quad (2)$$

where $\kappa(t-t')$ is the memory kernel related to the dissipative forces arising in the interaction between the heat bath and the Brownian degree of freedom β . The thermal random force $F(t)$ is assumed Gaussian, thus having zero average $\langle F(t) \rangle = 0$ and second moment¹⁹

$$\langle F(t)F(t') \rangle = k_B T \kappa(t-t'), \quad (3)$$

where the brackets indicate an average over the realizations of the noise. In addition, as usual we assume that

$$\langle \beta(0)F(t) \rangle = 0. \quad (4)$$

Here, α can be understood as a configurational variable in such a way that Eqs. (1) and (2) combine to give

$$\ddot{\alpha} = - \int_0^t \kappa(t-t')\dot{\alpha}(t')dt' + X_\alpha(t) + F(t), \quad (5)$$

where dots indicate the time derivative. In Eq. (2), we have introduced the time-dependent force $X_\alpha(t)$, which, in general, may depend on the state of the slow variable α .^{13,14} When this force is large enough, the dynamics of both the fast and slow variables become coupled in such a way that the adiabatic approximation is not valid because the variables have overlapping characteristic times.^{9,18} In contrast to what the long-time dynamics adiabatic hypothesis would require, this overlapping makes the joint probability distribution not factorizable as a product of two separated marginal probability distributions, the one corresponding to α and the other to β . Because of this, the long-time average of the kinetic energy, $\langle \beta^2 \rangle$, is no longer proportional to the heat bath temperature T . Thereby, in the following, we will derive the expression of the correction terms for a strong time-dependent force $X_\alpha(t)$.

The standard Laplace transform procedure for solving the Langevin equation enables one to find the corrections to the long-time kinetic energy average. Hence, the solution of Eq. (2) is obtained by using Laplace transforms, giving

$$\beta(t) = \beta(0)R(t) + \int_0^t R(t-t')[X_\alpha(t') + F(t')]dt', \quad (6)$$

where we have introduced the memory function $R(t) = \mathcal{L}^{-1}\left\{\frac{1}{s+\hat{\kappa}(s)}\right\}$, with $\hat{\kappa}(s)$ being the Laplace transform of $\kappa(t)$. Moving now the contribution of the external force term, $X_\alpha(t)$, to the left-hand side of Eq. (6), we define the new characteristic variable $\tilde{\beta}(t)$,

$$\tilde{\beta}(t) \equiv \beta(t) - \int_0^t R(t-\tau)X_\alpha(\tau)d\tau, \quad (7)$$

which satisfies the equality

$$\tilde{\beta}(t) = \tilde{\beta}(0)R(t) + \int_0^t R(t-\tau)F(\tau)d\tau, \quad (8)$$

where by construction, $\tilde{\beta}(0) = \beta(0)$. From (8) and taking into account Eq. (4), it follows the equality

$$R(t) = \frac{\langle \tilde{\beta}(0)\tilde{\beta}(t) \rangle}{\langle \tilde{\beta}(0)^2 \rangle}, \quad (9)$$

which expresses the response function $R(t)$ defined above in terms of the two time correlation of the variable β . On the other hand, since Eqs. (8) and (6) are formally similar, we also infer that as Eq. (6) is the solution of Eq. (2), Eq. (8) must be the solution of

$$\frac{d}{dt}\tilde{\beta}(t) = -\int_0^t \kappa(t-\tau)\tilde{\beta}(\tau)d\tau + F(t), \quad (10)$$

this being an equation formally similar to (2). Moreover, in view of the properties of $F(t)$, already stated in the context of Eq. (2), we conclude that Eq. (10) describes a stationary Gaussian process.²⁰

The previous manipulations enables us to calculate the value of the (“kinetic”) energy by using Eqs. (7) and (8). From (7), it follows that

$$\langle \beta^2 \rangle = \langle \tilde{\beta}^2 \rangle + 2 \int_0^t R(t-\tau)\langle \tilde{\beta}(t)X_\alpha(\tau) \rangle d\tau + \int_0^t d\tau \int_0^t d\tau' R(t-\tau)R(t-\tau')\langle X_\alpha(\tau)X_\alpha(\tau') \rangle. \quad (11)$$

Substituting Eq. (8) into the second term at the right-hand side of (11), one finally obtains

$$\langle \beta(t)^2 \rangle = \langle \tilde{\beta}^2(t) \rangle + \int_0^t \int_0^t R(t-\tau)R(t-\tau')\langle X_\alpha(\tau)X_\alpha(\tau') \rangle d\tau d\tau', \quad (12)$$

where we have assumed that no correlation exists between both the initial velocity and thermal noise with the force X_α , that is, $\langle \tilde{\beta}(0)X_\alpha(\tau) \rangle = 0 = \langle F(t)X_\alpha(\tau) \rangle$.

The second moment of the characteristic variable $\tilde{\beta}$ can be explicitly evaluated by using Eqs. (3) and (8) and the fact that the response function and the memory function are connected by

$$\frac{d}{dt}R(t) = -\int_0^t \kappa(t-\tau)R(\tau)d\tau. \quad (13)$$

Taking the time derivative of $\langle \tilde{\beta}^2(t) \rangle$ obtained from Eq. (8) and using Eqs. (3) and (13), it follows that

$$\frac{d}{dt}\langle \tilde{\beta}(t)^2 \rangle = 2(k_B T - \langle \tilde{\beta}(0)^2 \rangle)R(t) + \int_0^t \kappa(t-\tau)R(\tau)d\tau, \quad (14)$$

which establishes that if initially the system is in equilibrium, $\langle \tilde{\beta}(0)^2 \rangle = k_B T$, one has $d\langle \tilde{\beta}(t)^2 \rangle/dt = 0$ and this system remains in equilibrium. Thus, under the assumption that

$$\langle \tilde{\beta}(t)^2 \rangle = k_B T, \quad (15)$$

the knowledge of the second moment of the original variable β enables us to define the effective nonequilibrium temperature through the equality

$$k_B\theta(t) \equiv \langle \beta(t)^2 \rangle = k_B T + \int_0^t \int_0^t R(\tau)R(\tau')\langle X_\alpha(t-\tau)X_\alpha(t-\tau') \rangle d\tau d\tau', \quad (16)$$

obtained from Eq. (12). When the force X_α is sufficiently slow (for instance, due to the application of a low-frequency field), Eq. (16) reduces to

$$k_B\theta(t) = k_B T + \gamma(t)^2 X(t)^2, \quad (17)$$

where

$$\gamma(t) = \int_0^t R(\tau)d\tau \quad (18)$$

is a time-dependent friction coefficient and $X^2 = \langle X_\alpha^2 \rangle$ (see Refs. 9 and 14).

III. ROLE OF THE EFFECTIVE TEMPERATURE IN THE PROBABILITY DISTRIBUTIONS: RECOVERING THE ADIABATIC APPROXIMATION

The results obtained in Sec. II show that the dynamics of $\tilde{\beta}(t)$ constitutes a Gaussian process whose probability distribution may be written in the following form:

$$P(\tilde{\beta}) = \left(\frac{1}{2\pi A(t)} \right)^{1/2} e^{-[\tilde{\beta}-\beta(0)R(t)]^2/2A(t)}, \quad (19)$$

where $A(t) = k_B T[1 - R^2(t)]$ [see Eq. (10) and Refs. 14, 21, and 22]. After using Eq. (7), the probability distribution for $\beta(t)$ is given by

$$f_\alpha(\beta) = \left(\frac{1}{2\pi A(t)} \right)^{1/2} e^{-[\beta-\beta(0)R(t)-\int_0^t R(t-\tau)X_\alpha(\tau)d\tau]^2/2A(t)}. \quad (20)$$

This is an expression that explicitly depends on the external force X_α and, therefore, reveals the involvement of the slow variable in the dynamics of the fast degree of freedom. In fact, the stochastic dynamics of the coupled system of both fast and slow degrees of freedom can be described by the joint distribution function $F(\alpha, \beta, t) = \psi(\alpha, t)f_\alpha(\beta, t)$, with $f_\alpha(\beta, t)$ being the conditional distribution. Since α and β are coupled, we cannot write the previous relation as the product of two independent marginal distributions $\psi(\alpha, t)f(\beta, t)$ in general.

However, in view of the role played by the mean-square value of the fast variable for Gaussian processes [see Eq. (19) and the result (16)], an adiabatic separation of time scales between the slow and fast degrees of freedom can be established by introducing the scaling relation,

$$\frac{\rho^2(t)}{\theta(t)} = \frac{\beta^2(t)}{T}, \quad (21)$$

which defines the scaled fast variable $\rho(t) = \beta(t)\sqrt{\frac{\theta(t)}{T}}$. Using this relation in Eq. (20), one obtains

$$f_{\alpha, \langle X^2 \rangle}(\rho) = \left(\frac{1}{2\pi\mathcal{M}(t)} \right)^{1/2} e^{-[\rho - \rho(0)R_\rho(t) - \int_0^t R_\rho(t-\tau)X_\alpha(\tau)d\tau]^2/2\mathcal{M}(t)}, \quad (22)$$

where now the variance is given by $\mathcal{M}(t) = k_B\theta(t)[1 - R^2(t)] = A(t)(\theta/T)$, which introduces the effective temperature $\theta(t)$. Since $\rho(0) = \beta(0)$, we note that the response function of the new variable, R_ρ , is given by

$$R_\rho(t) = \frac{\langle \rho(0)\rho(t) \rangle}{\langle \rho^2(0) \rangle} = \sqrt{\frac{\theta}{T}} R(t). \quad (23)$$

Furthermore, Eq. (22) is concomitant with the stochastic equation

$$\rho(t) = \rho(0)R_\rho(t) + \int_0^t R_\rho(t-t')X_\alpha(t')dt' + \int_0^t R(t-t')\xi(t')dt', \quad (24)$$

where now the stochastic force ξ satisfies the fluctuation–dissipation relation

$$\langle \xi(t)\xi(t') \rangle = k_B\sqrt{\theta(t)\theta(t')} \kappa(t-t') \quad (25)$$

and therefore permits us to write the rescaled Langevin equation

$$\frac{d\rho}{dt} = - \int_0^t \kappa_\rho(t-t')\rho(t')dt' + X_\alpha(t) + \sqrt{\frac{T}{\theta}}\xi(t), \quad (26)$$

which is equivalent to write $F(t)/T^{1/2} = \xi(t)/\theta^{1/2}$, and where $\kappa_\rho(t) = \mathcal{L}^{-1}\{\hat{\kappa}_\rho(s)\}$ with $\hat{\kappa}_\rho = \frac{1}{R_\rho(s)} - s$. It should be mentioned that Eq. (25) is fully compatible with previous results obtained from microscopic models.^{23–25} It is interesting to express Eq. (25) in terms of the new time variables,

$$t_0 = \frac{t+t'}{2} \text{ and } \Delta = t-t', \quad (27)$$

such that $t = t_0 + \Delta/2$ and $t' = t_0 - \Delta/2$. Therefore, up to order one in Δ , Eq. (25) becomes

$$\langle \xi(t)\xi(t') \rangle = k_B\theta(t_0) \kappa(t-t'). \quad (28)$$

This last one constitutes a result that strengthens our previous assumption given through Eq. (22).

Likewise, the introduction of Eqs. (25) and (26) implies that, as it is required in the crude adiabatic approximation, the probability distribution of the fast variable can be separated from that of the slow variable if we neglect the time derivative of Eq. (26),

$$F(\alpha, \rho, t) \simeq \psi(\alpha, t)f_{\langle X^2 \rangle}(\rho), \quad (29)$$

yielding the approximated quasi-equilibrium Maxwellian distribution for the fast variable

$$f_{\langle X^2 \rangle}(\rho) = \left(\frac{1}{2\pi k_B\theta(t)} \right)^{1/2} e^{-\rho^2/2k_B\theta(t)}. \quad (30)$$

Therefore, both the generalized Langevin equation (26) and the modified fluctuation–dissipation theorem (25) or (28) provide a description of far from equilibrium systems in which the adiabatic timescale separation between the slow and fast degrees of freedom remains valid within the present pseudo-equilibrium approximation. Additionally, both Eqs. (25) and (26) describe a non-stationary Gaussian process.^{23–25}

The significance of our results can be made more clear by means of the Laplace transformation of Eq. (28). In this sense, by defining $\langle \xi(t)\xi(t') \rangle \equiv C_\xi(t_0, \Delta)$, we introduce

$$\hat{C}_\xi(\omega; t_0) \equiv \int_0^\infty e^{-t\Delta\omega} C_\xi(t_0, \Delta)d\Delta, \quad (31)$$

obtaining

$$\hat{C}_\xi(\omega; t_0) = k_B\theta(t_0)\hat{\kappa}(\omega). \quad (32)$$

These results have enormous importance, since they open the possibility to generalize, at least in an approximate form, many near-equilibrium statistical mechanics results to systems far away from equilibrium without incorporating complicated mathematical or numerical computations. The existence of the effective temperature or, at least, of the convenience of introducing it in the form shown here, was corroborated in a series of results listed in Refs. 13–17.

IV. EYRING EQUATION IN FAR FROM EQUILIBRIUM SYSTEMS

One of the most relevant applications of the new approach proposed here concerns the realm of chemical reactions, in particular, to the calculation of the Eyring formula for the reaction-rate constants in reactions that take place under strong non-equilibrium conditions.^{5,6} The effect that external forces might have on the reaction rates led by diffusion processes, that is, in the Kramers approximation, was previously studied in Ref. 9. Here, however, we will deal with the absolute rate theory.

For this purpose, let us assume the existence of the quasi-equilibrium distribution function $f_{qeq}(\alpha; t)$ for the slow variable α ,

$$f_{qeq}(\alpha; t) = \frac{1}{Z[\theta(t)]} e^{-H(\alpha; t)/k_B\theta(t)}, \quad (33)$$

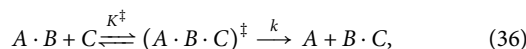
where $Z[\theta(t)] = \int f_{qeq}d\alpha$ is the partition function. In addition, the Hamiltonian $H(\alpha; t) \equiv H_t$, which contains the contribution of the force $X_\alpha(t)$, enters the Liouvillian

$$\mathcal{L}_t = i \left(\frac{\partial H_t}{\partial p} \frac{\partial}{\partial q} - \frac{\partial H_t}{\partial q} \frac{\partial}{\partial p} \right) \quad (34)$$

such that

$$\mathcal{L}_t f_{qeq}(\alpha; t) = 0. \quad (35)$$

Thus, by using the classical scheme of the transition state theory for a bimolecular reaction,¹



we can start our analysis by establishing that, in quasi-equilibrium, the relation between the chemical potential of the activated complex $(A \cdot B \cdot C)^\ddagger$, denoted by μ_{abc} , and that of the reactants is

$$\mu_{abc} - \mu_{ab} - \mu_c = 0. \quad (37)$$

The above condition comes from the fact that, in equilibrium at constant temperature and pressure, the condition $dG_\theta = 0$ must be satisfied. The chemical potential is related to the partition function by

$$\mu_\theta = -k_B \theta \ln |Z(\theta)|. \quad (38)$$

For a dilute mixture, the total partition function of the reactants $Z_r(\theta)$ is given as the product of the corresponding molecular partition functions $z_i(\theta)$ in the following form:

$$Z_r(\theta) = \frac{z_{ab}^{N_{ab}} z_c^{N_c}}{N_{ab}! N_c!}, \quad (39)$$

whereas for the activated complex, we have

$$Z_{abc}(\theta) = \frac{z_{abc}^{N_{abc}}}{N_{abc}!}. \quad (40)$$

Here, N_{ab} , N_c , and N_{abc} are the numbers of molecules of the reactants and of the activated complex. Using Eqs. (38)–(40) and Stirling's approximation, one may obtain the relation between the equilibrium constant and the partition functions,

$$K^\ddagger(\theta) = \frac{N_{abc}}{N_{ab} N_c} = \frac{z_{abc}}{z_{ab} z_c}, \quad (41)$$

where $K^\ddagger(\theta)$ is the equilibrium constant of the reaction. Taking into account that the energy difference of basal states between the reactants and the activated state is E_a , as shown in the classical Fig. 1,

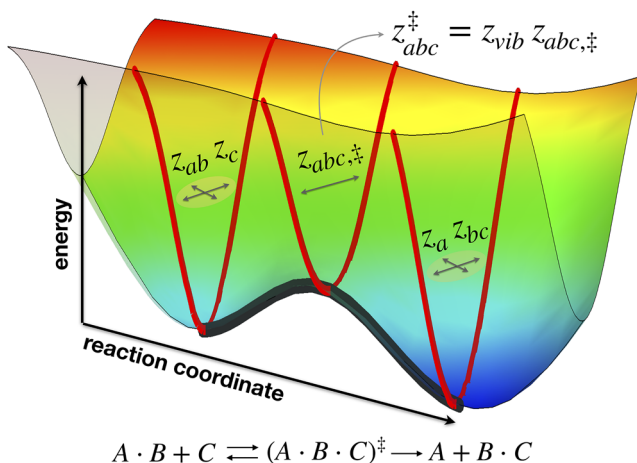


FIG. 1. Schematic representation of the reaction path (black line) along the reaction coordinate and of the partition functions associated with the degrees of freedom orthogonal to the reaction coordinate in the reactants, activated complex, and product states (red lines).

Eq. (41) can be written in the more convenient way,

$$K^\ddagger(\theta) = \frac{N_{abc}}{N_{ab} N_c} = \frac{z_{abc}^\ddagger}{z_{ab} z_c} e^{-E_a/k_B \theta}, \quad (42)$$

where now z_{abc}^\ddagger is the partition function of the activated complex with vanishing basal energy.

In the quasi-equilibrium approximation, we know that the rate of formation of the products of (36) is

$$\frac{d}{dt} [B \cdot C](t) = \nu K^\ddagger [A \cdot B] [C]^\ddagger, \quad (43)$$

where ν is the characteristic frequency of the reaction and the symbol $[C]$ stands for the volumetric concentration of the species C. As is well known, the observable reaction rate k_{obs} can therefore be written in the following form:

$$k_{obs} \sim \nu \frac{z_{abc}^\ddagger}{z_{ab} z_c} e^{-E_a/k_B \theta}, \quad (44)$$

where we have used Eq. (42). Splitting the partition function of the activated complex as usually, $z_{abc}^\ddagger(\theta) = z_{abc,\ddagger} z_{vib}$, with z_{vib} being the partition function associated with the loose vibration of the activated complex along the reaction coordinate (see Fig. 1). In the vanishing limit for the frequency, one obtains $z_{vib}(\theta) \sim \frac{k_B \theta}{h \nu}$ and we recover the formal expression,

$$k_{obs} \simeq \frac{k_B \theta}{h} \frac{z_{abc,\ddagger}}{z_{ab} z_c} e^{-E_a/k_B \theta}. \quad (45)$$

Finally, defining the activated-state equilibrium constant for the stable states,

$$K_\ddagger \equiv \frac{z_{abc,\ddagger}}{z_{ab} z_c} e^{-E_a/k_B \theta}, \quad (46)$$

and using the well-known thermodynamic relation $\Delta G^\ddagger = -k_B \theta \ln K_\ddagger$ where $\Delta G^\ddagger(\theta)$ is the Gibbs energy of activation, Eq. (45) can be rewritten in the following form:

$$k_{obs} \sim \frac{k_B \theta}{h} e^{-\Delta G^\ddagger/k_B \theta}, \quad (47)$$

which is a generalization of the Eyring equation for systems far away from equilibrium. This generalization implies that all the thermodynamic quantities involved in, for instance, ΔG^\ddagger , are functions of the non-equilibrium temperature $\theta(t)$, defined in Eq. (16) or Eq. (17). Therefore, all thermodynamic quantities become non-linear functions of the applied force $X(t)$. It is interesting to write explicitly the dependence of Eq. (47) on the external force by using Eq. (17),

$$k_{obs} \sim \frac{k_B T}{h} \left(1 + \frac{\gamma(t)^2 X(t)^2}{k_B T} \right) \times \exp \left[-\frac{\Delta G^\ddagger}{k_B T} \left(1 + \frac{\gamma(t)^2 X(t)^2}{k_B T} \right)^{-1} \right], \quad (48)$$

which shows that the external field modifies not only the transition frequency but the energy barrier. At very low temperatures, the previous equation becomes

$$k_{obs} \sim \frac{\gamma(t)^2 X(t)^2}{h} \exp\left[-\frac{\Delta G^\ddagger}{\gamma(t)^2 X(t)^2}\right]. \quad (49)$$

When the standard Arrhenius form is used for the rate constant, the activation energy, E_a , is scaled with the effective temperature in the following form: $E_a/T = \Delta G^\ddagger/\theta$, which is consistent with Eq. (21). Then, it follows

$$E_a = \frac{T}{\theta} \Delta G^\ddagger. \quad (50)$$

An analogous expression for the activation barrier was written in Ref. 26.

The practical implications of Eq. (47) are wide. This equation constitutes the basis for studying many types of reaction and transport processes. In this sense, Ref. 1 is the first and ideal reference to look at to ascertain how the above-mentioned result is of great significance. References 13–15 present a recent illustration of the type of application of the present formalism in condensed matter problems involving diffusion and viscosity.

V. CONCLUSIONS

The introduction of effective kinetic temperatures in the robust framework of the generalized Langevin equation in the presence of strong forces driving the corresponding stochastic system away from equilibrium enables us to recover adiabatic timescale separation of near-equilibrium systems. In this quasi-equilibrium level of description, the fluctuation–dissipation theorem associated with the generalized Langevin equation that governs the evolution of the fast degree of freedom becomes modified by substituting the original heat bath temperature with the effective temperature that explicitly depends on the external forces.

This effective temperature interpreted as the energy necessary to perform fluctuations in the quasi-equilibrium state modify, in turn, the canonical probability distribution for the slow variable. This distribution retains the form of the equilibrium statistical mechanics but incorporates the corrected thermal energy. Given that this canonical distribution is the basis of the (molecular) transition state theory, we used it to generalize the Eyring equation in which all the thermodynamic parameters are functions of the effective temperature and, therefore, are non-linear functions of the externally applied force. This generalization is consistent with and goes far beyond our previous theoretical results on the subject; it⁹ can be of huge interest in the study of several fields, ranging from chemical reactions to transport processes in systems far away from equilibrium, as suggested recently by Craven and Nitzan⁶ and Matyushov.^{5,26} Here, we want to emphasize that after finishing this work, we have realized that our results also apply to photochemical processes [see Eq. (49)].

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DATA AVAILABILITY

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

REFERENCES

- 1 H. Eyring, *The Theory of Rate Processes* (McGraw-Hill, New York, 1941).
- 2 J. Lehmann, P. Reimann, and P. Hänggi, *Phys. Rev. Lett.* **84**, 1639 (2000).
- 3 G. T. Craven and R. Hernández, *Phys. Rev. Lett.* **115**, 148301 (2015).
- 4 M. Feldmaier, P. Schraft, R. Bardakcioglu, J. Reiff, M. Lober, M. Tschöpe, A. Junginger, J. Main, T. Bartsch, and R. Hernández, *J. Phys. Chem. B* **123**, 2070 (2019).
- 5 D. V. Matyushov, *Proc. Natl. Acad. Sci. U. S. A.* **113**, 9401–9403 (2016).
- 6 G. T. Craven and A. Nitzan, *Proc. Natl. Acad. Sci. U. S. A.* **113**, 9421 (2016).
- 7 D. Kondepudi and I. Prigogine, *Modern Thermodynamics: From Heat Engines to Dissipative Structures* (John Wiley and Sons, Chichester, 1999).
- 8 L. Onsager and S. Machlup, *Phys. Rev.* **91**, 1505 (1953).
- 9 I. Santamaría-Holek and A. Pérez-Madrid, *J. Phys. Chem. B* **115**, 9439 (2011).
- 10 I. Santamaría-Holek, A. Pérez-Madrid, and J. Rubí, *J. Non-Equilib. Thermodyn.* **41**, 123 (2016).
- 11 I. Santamaría-Holek, A. Pérez-Madrid, and J. Rubí, *J. Chem. Phys.* **120**, 002818 (2005).
- 12 J. M. Rubí, I. Santamaría-Holek, and A. Pérez-Madrid, *J. Phys.: Condens. Matter* **16**, S2047 (2004).
- 13 C. I. Mendoza, I. Santamaría-Holek, and A. Pérez-Madrid, *J. Chem. Phys.* **143**, 104506 (2015).
- 14 I. Santamaría-Holek and A. Pérez-Madrid, *J. Chem. Phys.* **145**, 134905 (2016).
- 15 D. Winter, J. Horbach, P. Virnau, and K. Binder, *Phys. Rev. Lett.* **108**, 028303 (2012).
- 16 C. F. E. Schroer and A. Heuer, *J. Chem. Phys.* **143**, 224501 (2015).
- 17 D. Winter and J. Horbach, *J. Chem. Phys.* **138**, 12A512 (2013).
- 18 R. Zwanzig, *Nonequilibrium Statistical Mechanics* (Oxford University Press, New York, 2001).
- 19 R. Kubo, *Rep. Prog. Phys.* **29**, 255 (1966).
- 20 R. F. Fox, *J. Math. Phys.* **18**, 2331 (1977).
- 21 S. Adelman, *Adv. Chem. Phys.* **44**, 143 (1980).
- 22 S. A. Adelman, *J. Chem. Phys.* **64**, 124 (1976).
- 23 J. J. Brey and J. Casado, *J. Stat. Phys.* **61**, 713 (1990).
- 24 L. Romero-Salazar and R. Velasco, *Rev. Mex. Fis.* **41**, 358 (1995), available at <https://rmf.smf.mx/ojs/rmf/article/view/2497/2465>.
- 25 R. Hernández and F. L. Somer, *J. Phys. Chem. B* **103**, 1064 (1999).
- 26 D. V. Matyushov, *J. Mol. Liq.* **266**, 361 (2018).