A model for diffusive systems: Beyond the Arrhenius mechanism

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HIGHLIGHTS

- We study the non-Arrhenius process and propose an explanation about it.
- We propose a diffusion coefficient that is proportional to the supercooled-liquid concentration.
- The proposed model allows us to explain the anomalous behavior of the diffusivity robustly.
- We demonstrate that this new approach is consistent with experimental patterns.

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ABSTRACT

Diffusivity in supercooled liquids was observed to exhibit a non-Arrhenius behavior near the glass-transition temperature. This process, which occurs where the activation energy depends on the temperature, suggests the possibility of a metastable equilibrium. This peculiar phenomenon cannot be explained using the usual Markovian stochastic models. Based on a non-linear Fokker–Planck equation, we propose a diffusion coefficient that is proportional to the supercooled-liquid concentration. The proposed model allows us to explain the anomalous behavior of the diffusivity robustly. We demonstrate that this new approach is consistent with experimental patterns. Besides, it could be applied to non-Arrhenius chemical kinetics.

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In the transport phenomena of many systems, such as solids and porous media, the temperature dependence of the diffusion coefficient $D(T)$, is currently assumed to exhibit Arrhenius-like behavior, i.e., a linear relationship $\log D \propto 1/T$. In certain systems, the linearity is not experimentally well-established. However, it can be enforced because the number and accuracy of experimental data points are usually not too high, and the accessible range of the $1/T$ variable is small. Currently, the improvement in experimental techniques to study the reaction mechanism and ionic transport has allowed measurements with high accuracy in a wide range of temperatures. Thus, the systems that exhibit a non-linear relationship with such dependence were clearly identified, such as the transport process in supercooled liquid under focus here. However, the diffusion barrier or activation energy is usually assumed to be constant, and there is no well-defined model that correctly characterizes these phenomena in the nonlinear Arrhenius framework. In particular, for the transport mechanism

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in supercooled liquid, there is increasing evidence from various recent studies on the temperature dependence of diffusivity processes that notice the deviations from the Arrhenius mechanism [1–7].

According to IUPAC rules the activation energy in dynamic equilibrium is defined as Eq. (1). The activation energy is temperature dependent and it is also often described as Arrhenius law [8]. According to Tolman's theorem [9], the Arrhenius activation energy is a phenomenological quantity defined in terms of the slope of an Arrhenius plot, i.e.,

$$\frac{\partial (\ln(k))}{\partial \left(\frac{1}{T}\right)} = -\frac{E_a}{k_b} \tag{1}$$

where k is the rate constant, E_a is the activation energy, T is the temperature and k_b is the Boltzmann constant. According to Eq. (1), if E_a is constant, the rate coefficient k decays exponentially with the inverse of temperature. Within the Arrhenius regime, there are several interpretations for the activation energy [10–18,9,19]. Tolman [9] interpreted the activation energy as the difference between the average energy of the molecules that reacted and the average energy of all the particles of the system. However, based on a diffusion model for chemical reactions, Kramers [19] interpreted the activation energy using stationary temperature-dependent solutions of a Fokker–Planck equation [20]. We recall that a Fokker–Planck equation may be derived from the Langevin equation by using standard techniques.

In recent years, several systems were reported to significantly deviate from this law [1–7,21–23]. These approaches assumed a dependence between the activation energy and the temperature. Two different behaviors of the linearity deviation were identified in the plot $\ln k \times 1/T$ [24]: a *sub-Arrhenius* behavior, which is associated with dominance of tunneling quantum effects, and a *super-Arrhenius* behavior, which occurs when classical transport phenomena predominate. Nishiyama et al. [25] adopted a quadratic function to describe the nonlinear regimes. An alternative mathematical description was proposed by Aquilanti et al. [26], which had defined the rate constant in terms of the deformed exponential

$$k(T) = A \left(1 - d\frac{\epsilon}{k_b T}\right)^{\frac{1}{d}} \tag{2}$$

where A, ϵ and d are phenomenological parameters, and the limit $d \rightarrow 0$ recovers the conventional Arrhenius Law. However, it is worth noting that although this function properly fits the experimental data, no physical interpretation was given for the equation.

Recent experimental works [27,28] reported a non-Arrhenius-type behavior for diffusive processes in supercooled liquids near the glass transition temperature. In particular, using the procedure described by Smith and Kay [2], the diffusivity as a function of temperature provides an experimental curve that can be modeled by an exponential deformed by Aquilanti similar to that proposed in Eq. (2).

Considering the existing problems on this subject, our main objective in this letter is to propose an alternative model based on a nonlinear equation of Fokker–Planck type for diffusive systems beyond the Arrhenius mechanism. Furthermore, the present study provides new insights into the deviations from linearity in many non-Arrhenius phenomena such as VTF and non-exponential processes. This approach was successfully applied in a variety of physical systems such as astrophysical phenomena [29,30] and sunspots [31].

According to Frank [32], for the one-dimensional frame, Fokker–Planck-like equations correspond to the following general form

$$\frac{\partial}{\partial t} C(v, t) = -\frac{\partial}{\partial v}[F(v, t, C)C(v, t)] + \frac{\partial^2}{\partial v^2}[D(v, t, C)C(v, t)] \tag{3}$$

where v is the random variable that characterizes the stochastic process, and $C(v, t)$ is the probability density. The coefficients $F(v, t, C)$ and $D(v, t, C)$ are the probability density functionals, whose explicit forms depend on the dynamic evolution of the stochastic process to be modeled. If Eq. (3) describes a diffusion process, $C(v, t)$ corresponds to the diffusing substance concentration, and the functionals $F(v, t, C)$ and $D(v, t, C)$ correspond to the drag coefficients and widespread dissemination, respectively.

In this context, the nonlinear functional forms that we suggest for the coefficients $F(v, t, C)$ and $D(v, t, C)$ correspond to the proposed forms in Plastino and Plastino [33] and Schwämmle et al. [34], so that,

$$F(v, t, C) = -\left(\frac{dU}{dv}\right) C^{\sigma-1} \tag{4}$$

and

$$D(v, t, C) = \Gamma C^{\alpha-1} \tag{5}$$

where $U(v)$ is a generalized potential, Γ is a temperature-dependent parameter and the exponents σ and α (both $\neq 1$) define nonlinear processes in the dissemination and drift. Thus, for a stationary regime with regularity conditions for $v \rightarrow \pm\infty$, it is straightforward to verify that using Eqs. (4) and (5), the solution of Eq. (3) is,

$$C_S(T) = C_0 \left[1 - (\alpha - \sigma)f(T)E\right]^{\frac{1}{\alpha-\sigma}} \tag{6}$$