



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.,

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

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

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

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

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

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,

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

and

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

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,

$$C_s(T) = C_0 [1 - (\alpha - \sigma)f(T)E]^{\frac{1}{\alpha-\sigma}} \quad (6)$$

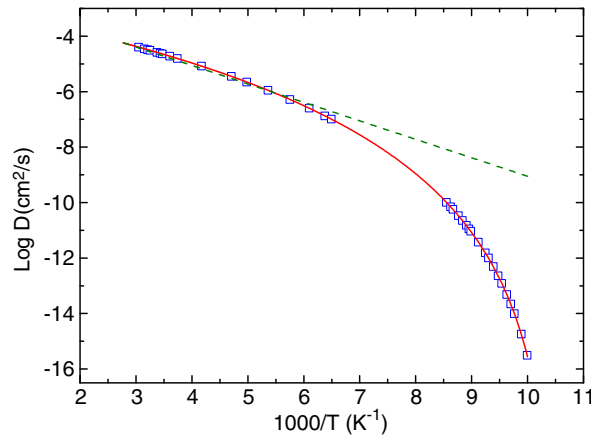


Fig. 1. Arrhenius plot of the supercooled-liquid diffusivity (open squares) and the diffusivity from Kr permeation (open circles). The dashed line is the fit using the usual Arrhenius model. The solid line is the fit using the proposed model (Eq. (9)), for the supercooled liquid and Kr permeation data.

where C_0 corresponds to a normalization constant and it is parameterized by temperature, $f(T) = C_0^{\sigma-\alpha}/(\alpha\Gamma)$, and $E = U(v) - U(v_0)$. If Eq. (6) describes the stationary regime of a diffusive substance, E represents a potential barrier related to the necessary energy to lead the substance from the maximum concentration state, which is related to the initial condition, to the dynamical equilibrium regime.

To ensure the robustness of the model, the boundary condition $\alpha \rightarrow \sigma$ should recover the classical form of the Arrhenius equation which implies three conditions: $\alpha = 2$, which provides a diffusion coefficient that is directly proportional to the concentration, $D_0 = \Gamma C_0$ is independent of temperature and $f(T) \propto 1/T$. For such conditions, it is easy to see that the rate of change of the diffusion coefficient with temperature corresponds to expression

$$\frac{1}{D_S} \frac{dD_S}{dT} = \frac{E}{\kappa T^2} \left(\frac{D_S}{D_0} \right)^{\sigma-2} \quad (7)$$

where κ is a proportionality constant. It is possible to rewrite Eq. (7) in the form,

$$\kappa \frac{\partial}{\partial \left(\frac{1}{T}\right)} [\ln D_S] = -E \left(\frac{D_S}{D_0} \right)^{\sigma-2}. \quad (8)$$

The left-hand side of Eq. (8) defines the generalized activation energy E_G , which depends on temperature. It must be emphasized that in the limit $\sigma \rightarrow 2$, $\frac{E}{\kappa} \rightarrow \frac{E_a}{k_b}$. Finally, the explicit dependence of E_G on the temperature is given by

$$E_G = E \left[1 - (2 - \sigma) \frac{E}{\kappa T} \right]^{-1}. \quad (9)$$

The inverse activation energy versus inverse temperature linear dependence implied in Eq. (2) [26] is recovered, and the identification can be made $\sigma = 2 - d$.

To verify the applicability of the proposed methodology, we used the recently published experimental approaches [2] to characterize the activation energy and the diffusivity of the supercooled liquid, which was created when the film was heated above its glass transition temperature T_g . In one of these experiments [2], a thick monolayer of an inert gas is covered by a vapor-deposited amorphous film. The film is heated above its T_g temperature, whereupon it transforms into a supercooled liquid, which allows the inert gas to permeate through the film. The temperature and rate of permeation are used to determine the diffusivity of the supercooled liquid. Additionally, we calculated the diffusion activation energies E_a in the temperature range $100 < T < 350$ K, and the results are plotted in Figs. 1 and 2. In this case, E_a corresponds to the pseudo-activation energy that is associated with the diffusion process and is thought to represent a potential energy barrier that obstructs the structural rearrangement of the melt. The result shows that the activation energy is a nonlinear function of the absolute temperature.

As a second application we used the formalism to characterize the experiment proposed by Matthiesen et al. [1] where the permeation of krypton gas through initially amorphous overlayers was used to determine the diffusivity of the supercooled liquid, which was created when the film was heated above its glass transition temperature T_g . In this procedure, the main idea is that when the amorphous film is heated to temperatures near its T_g , it transforms into a supercooled liquid, and the inert gas can begin to diffuse through the overlayer. In this experiment, the authors applied this approach to investigate the temperature and composition dependence of the diffusivity of supercooled-liquid mixtures of methanol and ethanol. The results of this experiment prove that the diffusivity of krypton inert gas is directly and quantitatively related to the diffusivity of the supercooled-liquid overlayer. The final results are presented in Fig. 3, using the deformed Arrhenius plots

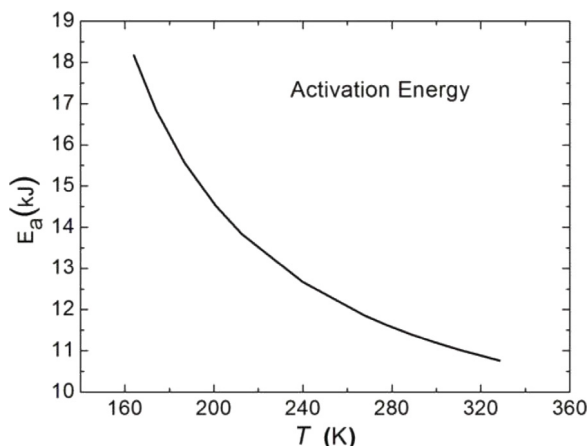


Fig. 2. Diffusion activation energy as a function of the absolute temperature using Eq. (9).

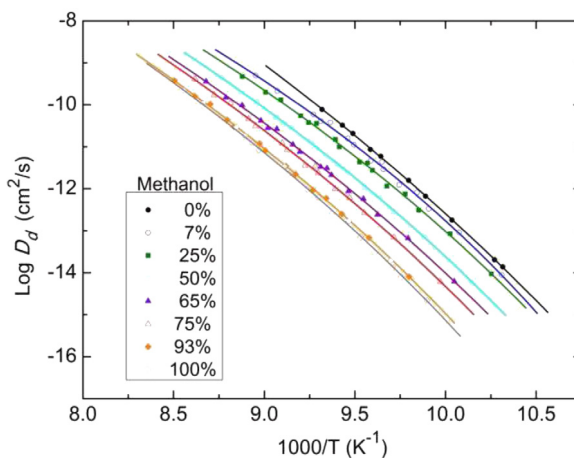


Fig. 3. Deformed Arrhenius plot of the diffusivity obtained from Kr permeation through overlayers with various compositions of methanol in ethanol, pure methanol and ethanol. The points represent the experimental data and the solid lines are our model fits to the measured diffusivity. At $T_g = 103$ K, the diffusivity is $D(T_g) = 1.3910^{(-14)} \text{ cm}^2/\text{s}$.

of the diffusivities obtained from Kr permeation through the overlayers with various compositions of ethanol in methanol, pure methanol and pure ethanol.

Using Eq. (9), we plotted E_a versus the absolute temperature for the following compositions of methanol in ethanol: 25%, 50%, 65%, 75% and 93%. The final results are plotted in Fig. 4. The value of the chi-square fit is $\chi^2 \approx 10^{-5}$, which guarantees the excellent consistency between the diffusivities obtained from the experimental data and those fitted using our model.

As previously mentioned, Kramers [19] proposed a model based on the Fokker–Planck equation for the usual modeling of chemical reactions, which properly verified the Arrhenius equation. The formalism proposed here is a generalization of the Kramers model, which corresponds to the limiting case $\sigma \rightarrow 2$, to reproduce the frameworks of nonlinearities modeled by the empirical equation proposed by Aquilanti et al. (see Eq. (2)). The stationary solution described in Eq. (6) can be interpreted as the concentration of chemical equilibrium, and the connection with the rate constant is established using the equilibrium constant. Eq. (8) becomes a generalization of Eq. (1).

It is important to highlight that the other methodologies or mathematical models in the references have their merits, as does the generalized Tolman model, which provides somewhat higher flexibility and enables extrapolation to more extended ranges of temperature. This result is particularly evident in Figs. 2 and 4, where the activation energy decreases with the temperature, whereas an asymptotically correct behavior is described using the new approach (see Eq. (9)). It is noteworthy that the success of this fitting procedure is partially because due to the flexibility of the deformed exponential function that coincides with the usual exponential function according to the well-known limit due to Euler. We recall that Landau and Lifshitz [35] used this definition to describe fluctuations in statistical mechanics. In the recent scientific literature, there are a variety of deformed algebras with applications in different areas of science [36–39]. Such a deformation of the exponential function occurs in the non-Boltzmann distribution of non-extensive Statistical Mechanics [40].

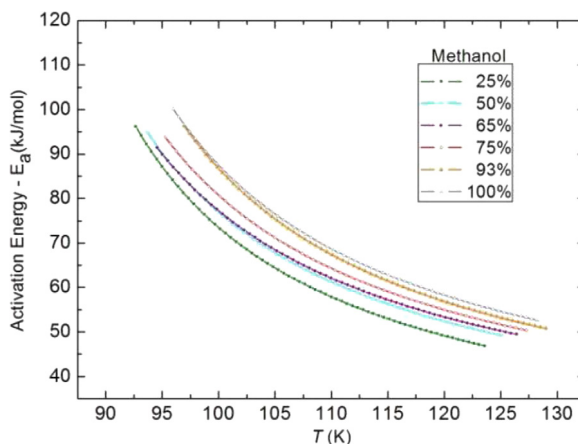


Fig. 4. Activation energy in kJ/mol is calculated using Eq. (9). The value of the chi-square fit is $\chi^2 < 10^{(-5)}$.

In summary, we note that (i) the diffusivity and the activation energy are power laws of the absolute temperature; (ii) for the diffusion mechanism and at the limit of $\sigma \rightarrow 2$ the usual Arrhenius law and Tolman's activation energy are recovered, which can be understood as a particular case of the proposed methodology; (iii) this case studies only the method to address a phenomenological description of deviations from the Arrhenius law. This observation suggests that many molecules cooperatively move regardless of the activation energy that is overcome in the key relaxation processes. Furthermore, the differential equation (Eq. (8)) provides insights into the deviations from linearity in many non-Arrhenius phenomena such as non-exponential processes. In this context, this model appears to be an alternative tool to understand the processes that occur when a supercooled liquid is cooled to temperatures near T_g , whereupon it forms a glass.

We conclude that the proposed formalism guarantees a physical interpretation of the observed super-Arrhenius behavior of diffusive processes in supercooled liquid near the glass transition temperature. The diffusion coefficient, which is represented in Eq. (6), satisfactorily fits the experimental data. Despite the emphasis on cases of super-Arrhenius behavior (convex), sub-Arrhenius (concave) cases can be interpreted from the proposed formalism, where the deformation parameter is the exponent $2 - \sigma$.

For a recent examples of convexity, see [41–43]. A case of anti-Arrhenius behavior (rate decreasing with temperature) is described in [44].

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