Characterization of the non–Arrhenius behavior of supercooled liquids by modeling non–additive stochastic systems

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I. INTRODUCTION

The dynamical response of a wide class of materials can be achieved by the so-called Arrhenius law [1–5]. Basically, it consists of an exponential decay with the inverse of the temperature characterized by the so-called temperature independent activation energy [1, 4]. The search for a physical interpretation for the activation energy established the fundamentals of the transition state theory [6–8] since it associates an Arrhenius-like behavior with diffusive processes in several systems [4, 9–12].

However, from the development of new technologies and advances in materials preparation techniques, a wide variety of new compounds could be synthesized, leading to the improvement of experimental techniques for the study of chemical reactions and diffusive processes. In this scenario, several systems have revealed deviations from Arrhenius behavior, evidenced through the temperature dependence of the activation energy [1]. In the last years, the characterization of non-Arrhenius behaviors has received considerable attention, since it was observed in water type models SPC/E (extended simple point charge) [13, 14], food systems [15], diffusivity in supercooled liquids near glass transition [2, 10, 11, 16, 17], chemical reactions [8, 18, 19] and several biological processes [20, 21]. Therefore, modeling these non-Arrhenius systems becomes a large avenue for research and an actual challenge to overcome. The non-Arrhenius behaviors manifest themselves as concave curves (sub-Arrhenius behavior), associated with non-local quantum effects [8, 19, 22], or convex curves (super-Arrhenius behavior), associated with the predominance of classical transport phenomena [3, 20, 22, 23].

Despite much effort by the scientific community, there are only a few phenomenological relationships proposed to model non-Arrhenius processes, such as the Vogel-Tamman-Fulcher equation [24, 20] and the Aquilanti-Mundim d-Arrhenius model [3, 19, 20, 22, 23, 27, 28]. Recently, other phenomenological expressions have been proposed [5, 10, 17]. However, there is a need to establish a wide class of equations that characterize non-Arrhenius processes in a consistent theoretical basis for the physical interpretation of the characteristic non-Arrhenius behavior of several diffusive processes.

Nevertheless, Aquilanti-Mundim equation can be derived from the stationary regime of the non-linear Fokker-Planck equation, and the diffusivity dependence with the temperature is consistent with experimental results [5]. Non-linear Fokker-Planck equations, especially equations whose stationary solutions maximizes non-additive entropies [29], such as the Tsallis entropy [30], has been successfully employed for modeling non-Markovian processes [31, 32], anomalous diffusion [33, 34], astrophysical systems [35], sunspots [36] and pitting corrosion [37], suggesting that this class of equations can also be an alternative way to describe the non-Arrhenius behavior of non-additive stochastic systems.

In this context, we show in this letter a class of non-homogeneous continuity equations whose the generalized coefficient allow us to model a wide range of non-Arrhenius processes. We modeling the characteristic super-Arrhenius behavior of diffusivity and viscosity in supercooled liquids, where we determine a characteristic threshold temperature associated with the discontinuities in its dynamical properties, such as the viscosity and the activation energy. In addition, we define a generalized exponent which characterizes the non-Arrhenius process and serves as an indicator of the level of fragility in glass-forming systems, whereas the threshold temperature indicates a fragile–to–strong transition, a general behavior of metallic glass–forming liquids [38]. We also derive from our model a generalized version for the Stokes-Einstein equation, where we obtain a characteristic tem-
temperature independent behavior (at low temperatures) for sub-Arrhenius processes, and a sudden death behavior around the threshold temperature for super-Arrhenius processes. Our results paves the way to the characterization of the breakdown of the standard Stokes-Einstein relation, mainly in supercooled liquids, leading to the establishment of a theoretical interface between a macroscopic and microscopic point of view of the matter through a non-equilibrium statistical mechanics.

II. GENERALIZED MODEL FOR REACTION–DIFFUSION PROCESSES

Let us consider the concentration $\rho(r, t)$ of a substance measured in volume $V$ at time $t$, the total amount of substance for the same volume is given by the non-homogeneous continuity equation. In this context, we propose the following conditions:

(i) $f(r, t) = \nabla \cdot \mathbf{\eta}(r, t)$ is a volumetric density per unit time associated with dissipative processes and $\mathbf{\eta}(r, t)$ is a field of non-zero divergence;

(ii) $\mathbf{\eta}(r, t) = -\kappa_m^{-1}\rho^n \nabla \phi$, where $\kappa_m$ is a positive constant parameterized by the exponent $m$ and $\phi$ is a generalized potential;

(iii) for the steady state $\mathbf{\eta}(r, t) \rightarrow \mathbf{\eta}_S(r)$, where is a field of zero divergence;

(iv) $\mathbf{J} = -D(r, t; \rho) \nabla \rho$ is a diffusion flux, for a generalized version of Fick’s first law in which $D(r, t; \rho)$ is a generalized diffusion coefficient;

(v) $D(r, t; \rho) = (\Gamma/2)\rho^{n-1}$, where $\Gamma$ is a positive definite parameter, related to a class of nonlinear equations associated with anomalous diffusive processes.

In this context, the non-homogeneous continuity equation becomes a particular class of nonlinear Fokker–Planck equations whose non-linearity of the generalized drag coefficient involves the information of the dissipative or exchange processes, such as phase transitions or chemical reactions. It is important to highlight that the equations are defined in such a way that leads to the generation of solutions that compose a class of rapidly decreasing functions that maximizes non-additive entropies, such as the Tsallis entropy, since this guarantees the possibility of fundamental solutions for the diffusion equation. From these conditions we obtain an alternative way to describe the non-Arrhenius behavior of the diffusion processes of non-additive stochastic systems such as supercooled liquids, from a consistent theoretical basis.

In order establish a wide class of equations that characterize non–Arrhenius behavior of supercooled liquids in a theoretical point of view, we define the diffusion coefficient in (v) for the particular case $n = 2$. In this context, the generalized potential $\phi$ can be reinterpreted as a potential energy $U(r)$ associated to a conservative force field, in dynamic equilibrium. Thus, we obtain the non-homogeneous continuity equation:

$$\frac{\partial \rho(r, t)}{\partial t} = \kappa_m^{-1} \nabla \cdot \left[ \left( \nabla U(r) \right) \rho^m \right] + \frac{\Gamma}{2} \nabla^2 \left[ \rho^2 \right].$$

III. DIFFUSIVITY, VISCOSITY AND FRAGILITY OF GLASS-FORMING LIQUIDS

Glasses are usually formed from a process called glass transition, in which the liquid substance is subjected to a rapid cooling process, reaching temperatures below the liquid-solid phase transition temperature without solidifying, which characterizes a state so-called supercooling. The characterization of diffusivity and viscosity in supercooled liquids are effective for the understanding of the glass transition and the formation mechanisms of amorphous solids.

Due to the fact that the stationary solution of Eq. (1) is a generalized exponential, the dependence of the generalized diffusion coefficient with temperature can be written as,

$$D(T) = D_0 \left[ 1 - (2 - m) \frac{E}{k_B T} \right]^{\frac{1}{2m}},$$

where $D_0 = \Gamma C_0$ (where $C_0$ is a normalization constant of the stationary concentration), $E = -\int \nabla U(r) \cdot r$ is a generalized energy and $C_0^{2-m} \kappa_m \Gamma = k_B T$.

From Eq. (2), recovered the Arrhenius standard behavior when $m \rightarrow 2$ and the energy $E$, in this limit, corresponds to a temperature independent activation energy.

Figure 1 shows the diffusivity of a supercooled liquid as function of reciprocal temperature. As we can see, for the condition $m < 2$ the proposed model encompasses a class of super-Arrhenius diffusive processes, associated with the predominance of classical transport phenomena, predominantly according to the experimental reports. In addition, the model also covers a wide class of sub-Arrhenius diffusive processes, characterized by the condition $m > 2$, associated with non-local quantum effects, and less sensitive to the exponential variations than the super-Arrhenius processes.

Moreover, it is also possible to verify the existence of a threshold temperature for super-Arrhenius processes, from which the diffusivity goes to zero, given by

$$T_t = \frac{(2 - m) E}{k_B}.$$ 

From Eq. (2) we can obtain the temperature dependence of the activation energy as

$$E_A(T) = \frac{E}{1 - (2 - m) \frac{E}{k_B T}}.$$
Figure 1. Monolog plot of the diffusivity as a function of reciprocal temperature. The curves $m > 2$ characterizes a class of sub-Arrhenius processes, while the curves $m < 2$ characterizes a class of super-Arrhenius processes. The $m = 2$ curve corresponds to the usual Arrhenius plot. The curves were simulated for $E/k_B = 1000K$ condition.

The main feature of non-Arrhenius processes. Furthermore, from Eq. (4), for the $m \rightarrow 2$ the activation energy achieves a temperature independent behavior $E_A(T) \rightarrow E$ corresponding to the Arrhenius law, as mentioned before.

Figure 2 shows the activation energies, corresponding to the diffusivity curves shown in Figure 1, calculated from the Eq. (4). As can be seen, the activation energy is an increasing function of the reciprocal temperature for sub-Arrhenius processes and decreasing for super-Arrhenius processes. In addition, for the super-Arrhenius processes, when the threshold temperature, Eq. (3), is achieved the activation energy diverges to infinity, indicating that this temperature had relation to the viscosity divergence in the glass transition.

Form Eq. (4), we can define the viscosity from the generalized mobility of the fluid [50] as

$$\eta(T) = \alpha \kappa_m \rho^{1-m},$$

(5)

where $\alpha$ is a positive definite constant. From Eq. (5) the Arrhenius model from viscosity is recovered for the limit case $m \rightarrow 2$.

Figure 3 shows the viscosity as a function of the reciprocal temperature. For super-Arrhenius processes ($m < 2$) the threshold temperature characterizes the regime from which the viscosity diverges to infinity. Due to this fact, the threshold temperature, Eq. (3), serves as an indicative of how close the system is of the glass transition region because it involves discontinuities in dynamic properties, such as the activation energy, Eq. (4), and viscosity, Eq. (5). The glass-liquid transition occurs for a range of temperatures for which viscosity take on a large value, but still does not diverge. In most glass-forming liquids, the glass transition temperature is established for the viscosity reference value of $10^{12}$ Pa.s, thus $T_i \leq T_g$.

On the other hand, from this model we can also calculate the level of fragility $M_\eta$ in glass-forming systems.
by our exponent $m$ as

$$M_\eta = \left( \frac{m - 1}{2 - m} \right) \left( \frac{1}{1 - \frac{T}{T_g}} \right),$$

(6)

For usual Arrhenius diffusive processes, the condition $m = 2$ characterizes a strong glass system, whereas for a wide class of super-Arrhenius diffusive processes the condition $m < 2$ characterizes a fragile glass system. In addition, another important feature that arises from our model is the distinguishability between strong and fragile systems for super-Arrhenius processes ($m < 2$), since how far further the glass transition temperature $T_g$ is from the threshold temperature, Eq. (3), more fragile the system will be. In this way, the ratio $T_i/T_g$ (Eq. 4) indicates a fragile–to–strong transition, usually found in some water and silica systems [54–57], where an initially fragile supercooled liquid can be transformed into a strong liquid upon supercooling toward $T_g$. Therefore, the dynamics around the glass transition region, characterized by Eq. (3), give us a measurement of how fragile a system is, establishing the theoretical basis for the understanding of the intrinsic features of the formation mechanisms of amorphous solids.

Moreover, an also remarkable result can be extracted from our model. The product between the generalized diffusion coefficient, Eq. (2) and the viscosity, Eq. (5), obtained from our generalized model for reaction–diffusion processes, provides a generalized Stokes-Einstein relation for any non–Arrhenius diffusion process, given by

$$D_\eta = \alpha_k BT \left[ 1 - (2 - m) \frac{E}{k_BT} \right]$$

(7)

Figure 4 shows the temperature dependence of the generalized Stokes-Einstein relation, Eq. (7), for different values of the coefficient $m$. For super-Arrhenius diffusive processes ($m < 2$) the relation gives an estimate of the glass transition temperature, since the generalized diffusion coefficient, Eq. (2), goes to zero faster than the viscosity, Eq. (5), diverges to infinity. Thus, the region in which the generalized Stokes-Einstein goes to zero is equivalent to the threshold temperature of glass transition, Eq. (6). In addition, as can be seen from the Figure 4, the usual form of the Stokes-Einstein relation is recovered from Eq. (7) for two conditions: (i) for any Arrhenius-like process ($m = 2$); and (ii) for the condition $E << k_BT$, i.e., thermal fluctuations predominate in the process, to the detriment of the concentration gradient.

On the other hand, for the sub-Arrhenius diffusive processes, it is worth noting that, from the condition $E >> k_BT$ the generalized Stokes-Einstein equation, Eq. (7), presents a temperature independent behavior, enabling the differentiation of the classical and quantum regimes, paving the way to the characterization of sub-Arrhenius processes through Eq. (7). Providing one path toward the understanding of the quantum effects in the dynamics of the non–additive stochastic systems.

IV. CONCLUSIONS

In summary, our main result was to provide to the literature an alternative way to describe the non–Arrhenius behavior of diffusive processes in glass-forming liquids. Our model was characterized by a generalized exponent $m$ which define the class of non-Arrhenius processes and serves as an indicator of the degree of the fragility in these systems. In addition, we determine the threshold temperature, Eq. (6), from which the dynamic properties, such as the activation energy and viscosity diverges, and gives us a reliable estimate of the degree of fragility, to the glass transition temperature, Eq. (6). In addition, as can be seen from the Figure 4, the usual form of the Stokes-Einstein relation is recovered from Eq. (7) for two conditions: (i) for any Arrhenius-like process ($m = 2$); and (ii) for the condition $E << k_BT$, i.e., thermal fluctuations predominate in the process, to the detriment of the concentration gradient.

On the other hand, for the sub-Arrhenius diffusive processes, it is worth noting that, from the condition $E >> k_BT$ the generalized Stokes-Einstein equation, Eq. (7), presents a temperature independent behavior, enabling the differentiation of the classical and quantum regimes, paving the way to the characterization of sub-Arrhenius processes through Eq. (7). Providing one path toward the understanding of the quantum effects in the dynamics of the non–additive stochastic systems.
Our results provide one path toward the differentiation of the super and sub-Arrhenius regimes leading to a better understanding of classical and quantum effects on the dynamics of non-additive stochastic systems, paving the way to the characterization of the formation mechanisms of amorphous solids through the study of non-Arrhenius diffusive processes in these systems.

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