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On the One-Dimensional Transition State Theory and the Relation between Statistical and Deterministic Oscillation Frequencies of Anharmonic Energy Wells

Stefano Giordano,* Fabrizio Cleri, and Ralf Blossey

The transition state theory allows the development of approximated models useful to study the non-equilibrium evolution of systems undergoing transformations between two states (e.g., chemical reactions). In a simplified 1D setting, the characteristic rate constants are typically written in terms of a temperature-dependent characteristic oscillation frequency ν_s , describing the exploration of the phase space. As a particular case, this statistical oscillation frequency ν_s can be defined for an arbitrary convex potential energy well. This value is compared here with the deterministic oscillation frequency ν_d of the corresponding anharmonic oscillator. It is proved that there is a universal relationship between statistical and deterministic frequencies, which is the same for classical and relativistic mechanics. The independence of this relationship from the adopted physical laws gives it an interesting thermodynamic and pedagogical meaning. Several examples clarify the meaning of this relationship from both physical and mathematical viewpoints.

natural and engineered systems, such as chemical reactions, biological processes, combustion processes, and energy conversion devices.^[1–9] For instance, many different rate theories have been developed to describe how the rate of a chemical reaction depends on the properties of the reactants, such as their concentrations, temperature, pressure, and so on.^[10, 11] In these schemes, an ideal surface is introduced in phase space to separate the space into reactant and product regions, and trajectories passing through this surface generate products from reactants. Statistical analysis makes it possible to study these transitions, allowing the efficiency of transformation processes to be quantified. In addition to the mentioned theoretical developments, important numerical applications have been

1. Introduction

The dynamics of a thermodynamic system and the rate theories that describe its behavior are essential to understanding many


carried out, including molecular dynamics and rare event simulations.^[12] Moreover, transport theories are used to describe how the rate of heat or mass transfer depends on the properties of the system and the surrounding environment and how heat and mass transfer is coupled to chemical reactions.^[13, 14] In the physics and mechanics of solids, rate processes are important in the study of thermally activated creep or dislocations in crystals.^[15] Interestingly, rate theories have also been generalized to consider relativistic effects and, in particular, the effects of time dilation in chemical kinetics and the coupling effect between electronic states with different spin multiplicities.^[16–18] Interestingly, such effects seem to be observable at the macroscopic scale.^[16–18] For this reason, we adopt both classical and relativistic equations of motion in this work.

More in general, nowadays, statistical mechanics, thermodynamics, and rate theories play a crucial role in the description of several nanosystems and nanophysical phenomena, including folding and unfolding of two-state chains and macromolecules;^[19–23] molecular motors;^[24, 25] muscle behavior;^[26, 27] adhesion, cohesion, and fracture processes;^[28–31] friction and nanofriction;^[32–35] micro- and nano-heat engines;^[36–38] micro-magnetism and spintronics;^[39–43] as well as heat transfer in nanostructures,^[44–46] just to name a few. The most widely used methodologies adopted to study these systems are based on the Langevin and Fokker–Planck equations.^[47–53] For instance, we remember that the Kramers' classical solution to the Fokker–Planck equation for a bistable system^[4] is the basis of most rate theories.^[6]

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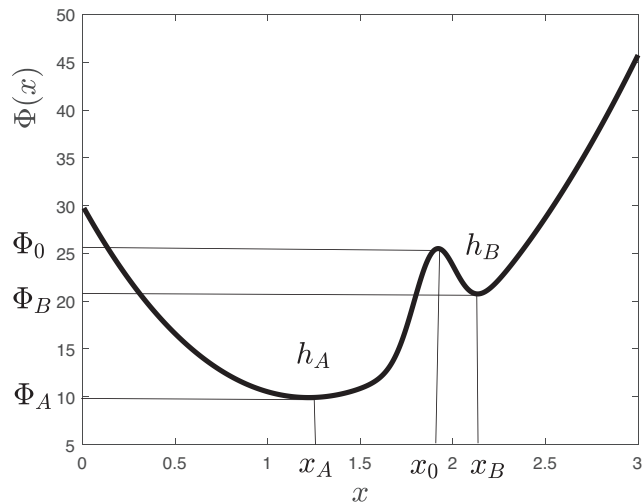


Figure 1. Example of bistable potential energy separating two regions A and B of the phase space.

One of the main ingredients of the transition rate theory is the frequency of transition between the two states A and B, calculated under thermodynamic equilibrium conditions. We denote it by ν_s^{AB} and it can be determined with Equation (10) discussed below, for a simple 1D case. It represents the number of transitions per second from state A to state B, induced simply by thermal fluctuations at thermodynamic equilibrium. It is the basic building block for determining the rate constants that appear in the rate equations, which are the fundamental outcome of transition rate theory. Although approximate, these equations are able to describe, at least qualitatively, the behavior of most of the systems mentioned above,^[6–9] in a regime out of equilibrium. The concept of transition frequency can be applied to the classical case of two energy wells separated by a barrier (as in **Figure 1**), and it provides the foundation for the classical results of the transition state theory (TST).^[54] In principle, the relationship that gives the statistical frequency is valid for any form of the potential energy of the system. Hence, it can also be applied to the simpler case of a single convex, generally anharmonic energy well (as in **Figure 2**). For this case, we denote the statistical frequency by ν_s , to distinguish it from the case with bistable energy. Although the convex case is less interesting for applications related to TST, it is important from a theoretical point of view because it allows to define a statistical, that is, thermally induced, oscillation frequency for an anharmonic oscillator. It is therefore of interest to compare the two types of frequencies associated with the anharmonic oscillator: statistical frequency and deterministic frequency. Moreover, this comparison can be drawn by a simple analytical procedure that emphasizes the physical interpretation, as discussed in the following sections of the paper. The statistical frequency refers to the frequency of oscillations when the oscillator is subjected to thermal fluctuation (at a temperature T). The statistical frequency $\nu_s(T)$ is a probabilistic quantity, and its determination requires the use of statistical methods, as described below. We use the Gibbs–Boltzmann distribution for the classical case and the Maxwell–Jüttner distribution for the relativistic case. On the other hand, the determin-

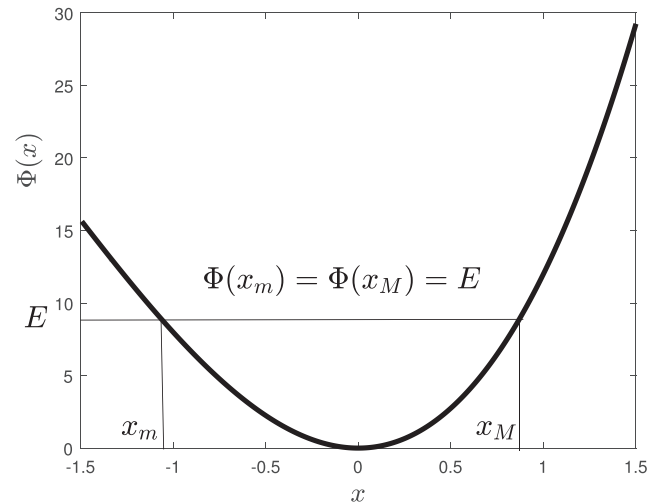


Figure 2. Example of potential energy well studied to compare the statistical and deterministic oscillation frequencies.

istic frequency is obtained by solving the (classical or relativistic) equations of motion that describe the behavior of the (non-linear) oscillator. The deterministic frequency is a deterministic quantity $\nu_d(E)$, and it can be calculated analytically (or numerically) as a function of the initial energy E . We prove that the two analytic expressions for statistical and deterministic frequencies, although they appear completely different, are related by a simple mathematical relationship, expressed through the Carson–Laplace transform. This relation turns out to be valid for every anharmonic oscillator and takes the same form for both classical and relativistic behavior. From the physical point of view, this result affirms that the statistical period of oscillation (at temperature T) is obtained by averaging the deterministic period (at energy E) through the density probability $\rho(E) = \frac{1}{k_B T} e^{-\frac{E}{k_B T}} \mathbf{1}(E)$ (being $\mathbf{1}(x)$ the Heaviside step function). This means that each deterministic period $1/\nu_d(E)$, associated with the initial energy E , is weighted with the Boltzmann factor $\frac{1}{k_B T} e^{-\frac{E}{k_B T}}$ in order to find the statistical period $1/\nu_s(T)$, induced by thermal fluctuations. Although this interpretation may seem obvious a priori, its mathematical demonstration allows for a deeper understanding of the frequency ν_s used in TST. This result is not only methodologically and pedagogically stimulating, but its independence from the adopted physical laws (classical or relativistic) gives it an interesting thermodynamic meaning. We discuss several examples by clarifying the physical and mathematical aspects of the subject matter.

The paper is organized as follows: In Section 2, we introduce a brief outline of the 1D TST, where we define the frequency ν_s^{AB} . In Section 3, we discuss the oscillation frequency for a classical anharmonic oscillator: We derive the statistical and deterministic frequencies ν_s and ν_d , their relationship, and some examples. Then, in Section 4, we perform the same analysis for the relativistic anharmonic oscillator, and we prove that the relationship between statistical and deterministic frequency is invariant with respect to the physical laws adopted.

2. Brief Outline of the 1D TST

The TST is a method to obtain the rates of physical–chemical processes such as chemical reactions, phase transformations, and so forth.^[1–3,5,7–9,54] It is based on some approximations, which are described in the following discussion. For the sake of simplicity, we briefly introduce here this technique for 1D geometry. Multi-dimensional extensions are straightforward and can be found in the literature. We consider a 1D potential energy $\Phi(x)$, where x is the so-called reaction coordinate. We separate the configurational space in region A with $x < x_0$, and region B with $x > x_0$. We consider the density probability $w(x, v, t)$ describing the 1D motion of a particle within the potential energy $\Phi(x)$, where x and v represent position and velocity, respectively. It means that $w(x, v, t)dx dv$ is the probability of finding the particle in the interval $(x, x + dx)$ with a velocity within $(v, v + dv)$ at time t . To develop the crossing statistics more easily, let us consider a population of N independent (non-interacting) particles described by the same density $w(x, v, t)$. This facilitates the following counting. We observe that if dN particles pass through x_0 in the time interval $(t, t + dt)$ and with velocity within $(v, v + dv)$ ($v > 0$), then they were dispersed at time t in the space interval $(x_0 - dx, x_0)$, where $dx = vdt$. It means that $dN = Nw(x_0, v, t)dx dv = Nvw(x_0, v, t)dvd t$ (if we want to reformulate this reasoning with a single particle, we need only observe that dN/N is the fraction of particle passing through x_0). If we integrate over all the positive velocities, we get the rate of particles crossing x_0 at time t from left to right

$$\left(\frac{dP_B(t)}{dt}\right)_{A \rightarrow B} = \left(\frac{1}{N} \frac{dN}{dt}\right)_{A \rightarrow B} = \int_0^{+\infty} vw(x_0^-, v, t) dv \quad (1)$$

Here, P_B is the probability to be in the region B of the real axis. Of course, we can prove a similar relation that gives the rate of particles crossing x_0 at time t from right to left

$$\left(\frac{dP_B(t)}{dt}\right)_{B \rightarrow A} = \left(\frac{1}{N} \frac{dN}{dt}\right)_{B \rightarrow A} = \int_{-\infty}^0 vw(x_0^+, v, t) dv \quad (2)$$

In Equations (1) and (2), we have indicated x_0^- (from the left) and x_0^+ (from the right) so that the formulas are exact even with any density discontinuities. Summing the two contributions, we obtain the time variation of the probability P_B

$$\frac{dP_B(t)}{dt} = \left(\frac{dP_B(t)}{dt}\right)_{B \rightarrow A} + \left(\frac{dP_B(t)}{dt}\right)_{A \rightarrow B} \quad (3)$$

We discussed here the evolution of $P_B(t)$ but we can similarly obtain the evolution of $P_A(t)$ through the relation $P_B(t) = 1 - P_A(t)$.

It is interesting to see what happens when we are at thermodynamic equilibrium. The equilibrium density probability is given by the following canonical (or Gibbs–Boltzmann) distribution

$$w_{eq}(x, v) = \frac{1}{Z_{eq}} \exp\left\{-\frac{1}{k_B T} \left[\frac{1}{2}mv^2 + \Phi(x)\right]\right\} \quad (4)$$

Here, m is the mass of the particle, T is the absolute temperature, and k_B is the Boltzmann constant. The quantity Z_{eq} represents

the partition function and can be explicitly written as follows:

$$\begin{aligned} Z_{eq} &= \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \exp\left\{-\frac{1}{k_B T} \left[\frac{1}{2}mv^2 + \Phi(x)\right]\right\} dx dv \\ &= \sqrt{\frac{2\pi k_B T}{m}} \int_{-\infty}^{+\infty} \exp\left[-\frac{\Phi(x)}{k_B T}\right] dx \end{aligned} \quad (5)$$

Then, at equilibrium, from Equations (1) and (2), we have the results

$$\begin{aligned} \left(\frac{dP_B(t)}{dt}\right)_{A \rightarrow B}^{eq} &= \int_0^{+\infty} vw_{eq}(x_0, v) dv \\ &= \frac{k_B T \exp\left[-\frac{\Phi(x_0)}{k_B T}\right]}{mZ_{eq}} \\ &= \sqrt{\frac{k_B T}{2\pi m}} \frac{\exp\left[-\frac{\Phi(x_0)}{k_B T}\right]}{\int_{-\infty}^{+\infty} \exp\left[-\frac{\Phi(x)}{k_B T}\right] dx} \end{aligned} \quad (6)$$

and

$$\begin{aligned} \left(\frac{dP_B(t)}{dt}\right)_{B \rightarrow A}^{eq} &= \int_{-\infty}^0 vw_{eq}(x_0, v) dv \\ &= -\frac{k_B T \exp\left[-\frac{\Phi(x_0)}{k_B T}\right]}{mZ_{eq}} \\ &= -\sqrt{\frac{k_B T}{2\pi m}} \frac{\exp\left[-\frac{\Phi(x_0)}{k_B T}\right]}{\int_{-\infty}^{+\infty} \exp\left[-\frac{\Phi(x)}{k_B T}\right] dx} \end{aligned} \quad (7)$$

Hence, we obtain, $dP_B(t)/dt = 0$, which means that P_A and P_B are constant at equilibrium and assume indeed the values

$$P_{A,eq} = \frac{\int_{-\infty}^0 \exp\left[-\frac{\Phi(x)}{k_B T}\right] dx}{\int_{-\infty}^{+\infty} \exp\left[-\frac{\Phi(x)}{k_B T}\right] dx} \quad (8)$$

$$P_{B,eq} = \frac{\int_0^{+\infty} \exp\left[-\frac{\Phi(x)}{k_B T}\right] dx}{\int_{-\infty}^{+\infty} \exp\left[-\frac{\Phi(x)}{k_B T}\right] dx} \quad (9)$$

Moreover, we observe from Equations (6) and (7) that

$$\left(\frac{dP_B(t)}{dt}\right)_{A \rightarrow B}^{eq} = -\left(\frac{dP_B(t)}{dt}\right)_{B \rightarrow A}^{eq} = v_s^{AB} \quad (10)$$

where v_s^{AB} is defined as the thermally induced (or statistical) oscillation frequency between the two states A and B at equilibrium. It represents the number of times per second a single particle passes through x_0 from left to right. The result is valid for any shape of the energetic landscape $\Phi(x)$. Although the motion is not periodic because it is generated by thermal fluctuations, we still name this value frequency (or statistical frequency). This

frequency v_s^{AB} will be further studied in the following. All results obtained up to this point are free of approximations.

Within the TST, the system is considered out-of-equilibrium and its evolution is studied under the following approximation. The probability density is not the one we have already seen at equilibrium but rather the following

$$w_{TST}(x, v, t) = \frac{P_B(t)}{P_{B,eq}} w_{eq}(x, v), \quad x > x_0 \quad (11)$$

$$w_{TST}(x, v, t) = \frac{P_A(t)}{P_{A,eq}} w_{eq}(x, v), \quad x < x_0 \quad (12)$$

which represents a sort of local equilibrium distribution, proportional to the equilibrium distribution $w_{eq}(x, v)$ by means of weights representing the normalized probabilities of being in the two states (it shows a discontinuity for $x = x_0$).^[54] It is not difficult to prove that this function fulfills the correct normalization $\int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} w_{TST}(x, v, t) dx dv = P_A(t) + P_B(t) = 1$. The choice made in Equations (11) and (12) evidently represents an approximation to introduce a simple, out of equilibrium behavior of the system described by compact expressions written in closed form.^[54] We reiterate that these are not the exact solutions of the problem but only a particular working assumption, useful for the following developments of the TST. It is easy to realize that this approximation is more true when the two energy wells corresponding to states A and B are strongly populated and thus the two wells can be imagined as unlimited reservoirs of particles. Of course, this may be true at the beginning of the process but turns out to be a strong approximation when one of the two wells tends to empty due to the dynamics of the system. Anyway, by using this approximation in Equations (1) and (2), we obtain

$$\left(\frac{dP_B(t)}{dt} \right)_{A \rightarrow B}^{TST} = \int_0^{+\infty} v \frac{P_A(t)}{P_{A,eq}} w_{eq}(x_0, v) dv = \frac{P_A(t)}{P_{A,eq}} v_s^{AB} \quad (13)$$

and

$$\left(\frac{dP_B(t)}{dt} \right)_{B \rightarrow A}^{TST} = \int_{-\infty}^0 v \frac{P_B(t)}{P_{B,eq}} w_{eq}(x_0, v) dv = -\frac{P_B(t)}{P_{B,eq}} v_s^{AB} \quad (14)$$

where v_s^{AB} is the equilibrium frequency between the two states A and B, as defined previously. We see here that the value of this frequency is crucial to define the main elements of the TST. Intuitively, this frequency is important in this context because it measures the probability of moving from one state to another, and thus overcoming the energy barrier, due to thermal fluctuations alone. By summing the two last expressions, we get the rate equations

$$\frac{d}{dt} P_A(t) = K_{AB} P_B(t) - K_{BA} P_A(t) \quad (15)$$

$$\frac{d}{dt} P_B(t) = K_{BA} P_A(t) - K_{AB} P_B(t) \quad (16)$$

where $K_{BA} = v_s^{AB}/P_{A,eq}$ and $K_{AB} = v_s^{AB}/P_{B,eq}$ are the so-called rate constants (see, e.g., Equation (19) in ref. [12], or Equa-

tion (4.16) in ref. [54]). More explicitly, we can write these rate constants as

$$K_{BA} = \sqrt{\frac{k_B T}{2\pi m}} \frac{\exp\left[-\frac{\Phi(x_0)}{k_B T}\right]}{\int_{-\infty}^0 \exp\left[-\frac{\Phi(x)}{k_B T}\right] dx} \quad (17)$$

$$K_{AB} = \sqrt{\frac{k_B T}{2\pi m}} \frac{\exp\left[-\frac{\Phi(x_0)}{k_B T}\right]}{\int_0^{+\infty} \exp\left[-\frac{\Phi(x)}{k_B T}\right] dx} \quad (18)$$

The rate equations stated in Equations (15) and (16) with rate constants given in Equations (17) and (18) are strongly approximated since they are based on the assumption of the local equilibrium within the two regions A and B, introduced through the transition state density in Equations (11) and (12). However, they are largely used to study the dynamics of complex systems and sometimes give reasonable results (see, e.g., ref. [55]).

A classical example concerns a bistable potential energy, as shown in Figure 1. We can see a barrier at the point $(x_0, \Phi_0 = \Phi(x_0))$, which separates the two potential wells with minima at $(x_A, \Phi_A = \Phi(x_A))$ and $(x_B, \Phi_B = \Phi(x_B))$. We can approximate the shape of the potential energy with a quadratic function near the two minima. It means that $\Phi(x) \simeq \Phi_p + (1/2)h_p(x - x_p)^2$ with $p = A, B$. The integrals in the denominators of Equations (17) and (18) can be approximated by extending the integral to the whole real axis and we get

$$K_{BA} = \frac{1}{2\pi} \sqrt{\frac{h_A}{m}} \exp\left[-\frac{\Phi_0 - \Phi_A}{k_B T}\right] \quad (19)$$

$$K_{AB} = \frac{1}{2\pi} \sqrt{\frac{h_B}{m}} \exp\left[-\frac{\Phi_0 - \Phi_B}{k_B T}\right] \quad (20)$$

Interestingly, we observe in the rate constants the familiar Arrhenius activation energies $\Phi_0 - \Phi_A$ and $\Phi_0 - \Phi_B$,^[56] and the frequency prefactors $\frac{1}{2\pi} \sqrt{\frac{h_A}{m}}$ and $\frac{1}{2\pi} \sqrt{\frac{h_B}{m}}$. In general, these prefactors are approximated and are correct only if each region can be considered as an unlimited reservoir of particles at equilibrium. More refined forms for the prefactors can be obtained through the Kramers' theory or more advanced approaches,^[4,6,57] which are outside the scope of this work. Although the TST is used in systems characterized by at least one energy barrier separating two regions, the characteristic frequency v_s^{AB} defined above remains valid for an arbitrary form of potential energy. In particular, if the potential energy is arbitrary but convex, the statistical frequency describe the behavior of an anharmonic oscillator at temperature T , as discussed in the next section. Studying more thoroughly the problem with a single energy well is indeed certainly easier and can provide a broader understanding of the relationship between deterministic and stochastic phenomena in statistical mechanics. To be precise, we used the symbol v_s^{AB} to denote the statistical frequency describing the transitions at equilibrium between the A and B states of a bistable potential, as in Figure 1, and we will use the symbol v_s to indicate the statistical frequency induced by thermal fluctuations in a convex potential energy, as in Figure 2.

3. Oscillation Frequency of a Classical Anharmonic Oscillator

We compare here the statistical frequency ν_s of an anharmonic oscillator, as introduced in the previous section through the TST, with the deterministic frequency ν_d of the same oscillator without thermal fluctuations. We determine a universal relationship between these two quantities which is based on purely thermodynamic grounds.

3.1. Statistical Oscillation Frequency

Let us try to give a deeper interpretation to the expression which gives the characteristic frequency ν_s of the TST. To fix ideas, we now consider a system at thermodynamic equilibrium composed of a single particle. It is described by an energy potential well $\Phi(x)$ as shown in Figure 2, with $\Phi(0) = 0$. If we fix $x_0 = 0$, then we can calculate the frequency of oscillation as

$$\nu_s = \int_0^{+\infty} \nu w_{eq}(0, \nu) d\nu \quad (21)$$

where the equilibrium density probability is given by the canonical (or Gibbs) distribution (see Equation (4)). The quantity ν_s can be interpreted as an oscillation frequency as it measures the rate (times per second) of the particle crossing (from left to right) through the point $x = 0$, which corresponds to the minimum of the potential energy (see Figure 2). In Equation (4), the quantity Z_{eq} represents the partition function, explicitly given in Equation (5). By substituting Equations (4) and (5) into Equation (21), we obtain the final result

$$\nu_s(T) = \sqrt{\frac{k_B T}{2\pi m}} \frac{1}{\int_{-\infty}^{+\infty} \exp\left[-\frac{\Phi(x)}{k_B T}\right] dx} \quad (22)$$

representing the statistical frequency of oscillation for a particle embedded in an arbitrary potential well $\Phi(x)$ at a given temperature T . It corresponds to Equation (6) or to Equation (7) when $x_0 = 0$.

3.2. Deterministic Oscillation Frequency

We consider now the same potential energy $\Phi(x)$ introduced in the previous section, and we approach the problem from a purely mechanical point of view. It means that we neglect here the thermal fluctuations and therefore we take into account the energy conservation

$$\frac{1}{2} m \left(\frac{dx}{dt} \right)^2 + \Phi(x) = E \quad (23)$$

where E is the total energy of the system, imposed through suitable initial conditions. As usual, this integral of motion yields a first-order differential equation for the dynamics of the system

$$\frac{dx}{dt} = \pm \sqrt{\frac{2}{m} [E - \Phi(x)]} \quad (24)$$

If we integrate this equation over a period, we simply obtain a direct expression for the deterministic frequency of oscillation

$$\nu_d(E) = \sqrt{\frac{1}{2m}} \frac{1}{\int_{x_m}^{x_M} \frac{dx}{\sqrt{E - \Phi(x)}}} \quad (25)$$

where $\Phi(x_m) = \Phi(x_M) = E$, with $x_m < 0$ and $x_M > 0$ (see Figure 2).

3.3. Classical Relation between ν_s and ν_d

The aim of this section is to elucidate the conceptual relation between Equations (22) and (25). Both expressions give a frequency oscillation of the system for an arbitrary potential energy $\Phi(x)$, but they show a completely different mathematical form. We prove, however, a simple and direct relationship between them. While we describe here such a relation for the classical mechanics (Newton theory), we postpone the relativistic analysis to the following section. To begin, we calculate the ensemble average of the deterministic period $1/\nu_d$ (corresponding to the energy E) by means of the Boltzmann weight $e^{-\frac{E}{k_B T}}$. The use of Equation (25) immediately leads to the double integral

$$\int_0^{+\infty} \frac{1}{\nu_d(E)} e^{-\frac{E}{k_B T}} dE = \sqrt{2m} \int_0^{+\infty} \int_{x_m}^{x_M} \frac{e^{-\frac{E}{k_B T}} dx dE}{\sqrt{E - \Phi(x)}} \quad (26)$$

It can be easily handled by observing that $\int_0^{+\infty} \int_{x_m}^{x_M} f(x, E) dx dE = \int_{-\infty}^{+\infty} \int_{\Phi(x)}^{+\infty} f(x, E) dE dx$ is true for any function $f(x, E)$, and therefore, we get

$$\int_0^{+\infty} \frac{1}{\nu_d(E)} e^{-\frac{E}{k_B T}} dE = \sqrt{2m} \int_{-\infty}^{+\infty} \int_{\Phi(x)}^{+\infty} \frac{e^{-\frac{E}{k_B T}} dE dx}{\sqrt{E - \Phi(x)}} \quad (27)$$

This expression can now be simplified by considering the integral

$$\int_a^{+\infty} \frac{e^{-bz} dz}{\sqrt{z-a}} = \sqrt{\frac{\pi}{b}} e^{-ab}, \quad b > 0 \quad (28)$$

which can be directly proved by applying the change of variable $y = \sqrt{z-a}$. Hence, the double integral in Equation (27) simplifies eventually delivering

$$\int_0^{+\infty} \frac{1}{\nu_d(E)} e^{-\frac{E}{k_B T}} dE = \sqrt{2\pi k_B T m} \int_{-\infty}^{+\infty} e^{-\frac{\Phi(x)}{k_B T}} dx \quad (29)$$

and, by using Equation (22), this can be finally written as

$$\frac{1}{k_B T} \int_0^{+\infty} \frac{1}{\nu_d(E)} e^{-\frac{E}{k_B T}} dE = \frac{1}{\nu_s(T)} \quad (30)$$

This is an important result introducing a conceptual relationship between Equations (22) and (25). It means that the statistical period of oscillation (at temperature T) is obtained by averaging the deterministic period (at energy E) through the density probability $\rho(E) = \frac{1}{k_B T} e^{-\frac{E}{k_B T}} \mathbf{1}(E)$ (which is correctly normalized). Here,

$\mathbf{1}(x)$ represents the Heaviside step function defined as $\mathbf{1}(x) = 1$ if $x \geq 0$, and $\mathbf{1}(x) = 0$ if $x < 0$. In other words, each deterministic period, associated with the initial energy E , is weighted with the Boltzmann factor $\frac{1}{k_B T} e^{-\frac{E}{k_B T}}$ in order to find the statistical period induced by thermal fluctuations. It is interesting to observe that if we define $s = 1/k_B T$, we obtain a Laplace–Carson transform between $1/\nu_d$ and $1/\nu_s$, that is,

$$s \int_0^{+\infty} \frac{1}{\nu_d(E)} e^{-sE} dE = \frac{1}{\nu_s(T)} \quad (31)$$

In general, the Laplace–Carson transform $\mathcal{L}_c\{f\}$ of a function $f(E)$ is defined as follows: $\mathcal{L}_c\{f\}(s) = s \int_0^{+\infty} f(E) e^{-sE} dE$.^[58] It corresponds to the classical Laplace transform $\mathcal{L}\{f\}(s) = \int_0^{+\infty} f(E) e^{-sE} dE$ multiplied by the variable s of the transformed domain: $\mathcal{L}_c\{f\}(s) = s\mathcal{L}\{f\}(s)$.^[59] To conclude, we can say that from the mathematical point of view, the statistical period of oscillation at a given temperature is given by the Laplace–Carson transform of the purely mechanical period of oscillation (integrated with respect to the energy of the system).

Let us add an important remark to avoid ambiguity. When we consider a physical observable $f(q, p)$ in statistical mechanics, we define its average value as $\langle f \rangle = \iint f(q, p) \exp[-H(q, p)/K_B T] dq dp / Z$, where $Z = \iint \exp[-H(q, p)/K_B T] dq dp$ is the classical partition function and $H(q, p)$ is the Hamiltonian of the system. Now, if the function $f(q, p)$ depends on (p, q) only through the Hamiltonian, we can write $f(q, p) = f(H(q, p))$, and its average value can be eventually calculated by

$$\langle f \rangle = \frac{\int_0^{+\infty} f(E) \Omega(E) \exp[-E/K_B T] dE}{\int_0^{+\infty} \Omega(E) \exp[-E/K_B T] dE} \quad (32)$$

where we introduced the density of states $\Omega(E) = \frac{d\Theta(E)}{dE} = \int \delta(E - H(q, p)) dq dp$ through the auxiliary function $\Theta(E) = \int_{H(q, p) < E} dq dp$. All this to say that Equations (30) and (31) do not represent canonical average values in phase space as the density of states that can be seen in Equation (32) is absent (moreover, $\Omega(E)$ cannot be constant with an arbitrary potential $\Phi(x)$). Therefore, Equations (30) and (31) must be interpreted as the average of the deterministic period (at energy E) through the density probability $\rho(E) = \frac{1}{k_B T} e^{-\frac{E}{k_B T}} \mathbf{1}(E)$, which is a correct averaging process but not coinciding with the canonical averaging in the phase space.

3.4. Frequency Calculation Examples

The simpler example concerns the harmonic oscillator with potential energy $\Phi(x) = \frac{1}{2} k_s x^2$, where k_s is the spring constant. The direct calculation of the statistical frequency leads to $\nu_s = \omega_0 / (2\pi)$, where $\omega_0 = \sqrt{k_s/m}$. This value clearly coincides with the deterministic frequency ν_d . In this simple case, both frequencies assume the same constant value. Hence, the relationship in Equation (31) is satisfied since the Laplace–Carson transform of 1 is 1 (or, equivalently, the Laplace transform of 1 is $1/s$).

A second example concerns the particle in a box or, equivalently, in an infinite square well having a width a . By means of

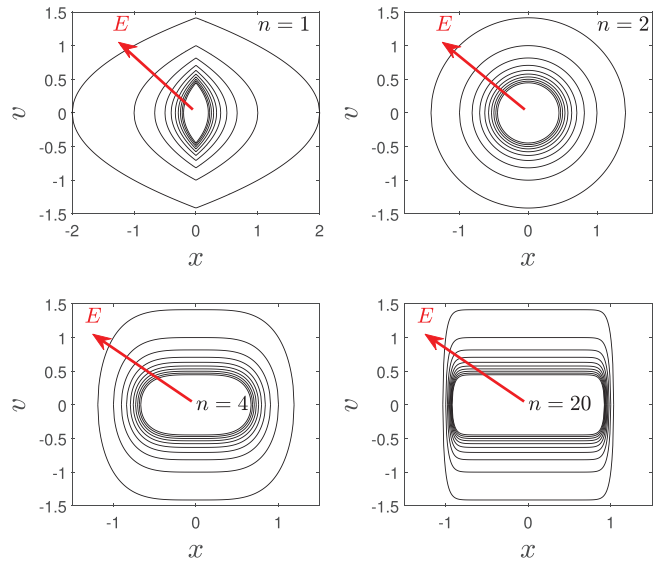


Figure 3. Example of phase space trajectories for the anharmonic oscillator with different values of the exponent $n = 1, 2, 4$, and 20 and the energy $E = 1/k$ ($k = 1, \dots, 10$). We adopted the parameters $k_0 = 1/2$ and $m = 1$ in arbitrary units.

Equation (22), we obtain the statistical frequency as

$$\nu_s(T) = \frac{1}{a} \sqrt{\frac{k_B T}{2\pi m}} \quad (33)$$

As regards the deterministic frequency, if we consider a constant velocity v_0 , we have a period of oscillation given by $1/\nu_d = 2a/v_0$. Moreover, since $E = \frac{1}{2} m v_0^2$, we have that $v_0 = \sqrt{2E/m}$. This is true since, in this case, the total energy coincides with the kinetic energy. We then obtain the deterministic frequency as

$$\nu_d(E) = \frac{1}{a} \sqrt{\frac{E}{2m}} \quad (34)$$

Now, Equation (31), relating statistical and deterministic frequencies, is confirmed by the Laplace–Carson transform of $1/\sqrt{E}$, which is $2\sqrt{\pi s}$ (or, equivalently, by the Laplace transform of $1/\sqrt{E}$, which is $2\sqrt{\pi/s}$).

As a more complicated example, we take into consideration the anharmonic potential well described by $\Phi(x) = k_0|x|^n$, where k_0 and n are parameters. The phase space trajectories are characterized by $mv^2/2 + k_0|x|^n = E$, as shown in **Figure 3** for different values of the parameters. We see that the circular trajectories, observed for $n = 2$, correspond to a linear oscillator while the other values of n generate a strongly nonlinear behavior. The expression for the statistical frequency yields

$$\nu_s(T) = \sqrt{\frac{k_B T}{2\pi m}} \left[2 \int_0^{+\infty} \exp\left(-\frac{k_0 x^n}{k_B T}\right) dx \right]^{-1} \quad (35)$$

where the integral can be calculated through the result

$$\int_0^{+\infty} \exp(-Ax^n) dx = \frac{1}{nA^{1/n}} \Gamma\left(\frac{1}{n}\right), \quad A > 0 \quad (36)$$

This property can be easily proved by using the change of variable $y = x^n$ and by introducing the Euler gamma function^[60–62]

$$\Gamma(z) = \int_0^{+\infty} t^{z-1} e^{-t} dt \quad (37)$$

The statistical frequency is eventually given by

$$\nu_s(T) = \frac{n}{2} \sqrt{\frac{k_B T}{2\pi m}} \left(\frac{k_0}{k_B T}\right)^{1/n} \frac{1}{\Gamma\left(\frac{1}{n}\right)} \quad (38)$$

On the other hand, the deterministic frequency is given by

$$\nu_d(E) = \sqrt{\frac{1}{2m}} \left[2 \int_0^{x_M} \frac{dx}{\sqrt{E - k_0 x^n}} \right]^{-1} \quad (39)$$

where $x_M = (E/k_0)^{1/n}$. The change of variable $y^n = (k_0/E)x^n$ delivers

$$\nu_d(E) = \frac{1}{2} \sqrt{\frac{E}{2m}} \left(\frac{k_0}{E}\right)^{1/n} \left[\int_0^1 \frac{dy}{\sqrt{1-y^n}} \right]^{-1} \quad (40)$$

The integral in the brackets can be solved by the change of variable $u = y^n$, by reminding that $\Gamma(1/2) = \sqrt{\pi}$, and by using the Euler beta function^[60–62]

$$B(\alpha, \beta) = \int_0^1 t^{\alpha-1} (1-t)^{\beta-1} dt = \frac{\Gamma(\alpha)\Gamma(\beta)}{\Gamma(\alpha+\beta)} \quad (41)$$

The result, after straightforward calculation, reads as

$$\int_0^1 \frac{dy}{\sqrt{1-y^n}} = \frac{\sqrt{\pi}}{n} \frac{\Gamma\left(\frac{1}{n}\right)}{\Gamma\left(\frac{1}{n} + \frac{1}{2}\right)} \quad (42)$$

Summing up, the deterministic frequency is obtained in the form

$$\nu_d(E) = \frac{n}{2} \sqrt{\frac{E}{2\pi m}} \left(\frac{k_0}{E}\right)^{1/n} \frac{\Gamma\left(\frac{1}{n} + \frac{1}{2}\right)}{\Gamma\left(\frac{1}{n}\right)} \quad (43)$$

It is interesting to observe that ν_s is proportional to $(k_B T)^{1/2-1/n}$ while ν_d is proportional to $E^{1/2-1/n}$. It means that both frequencies are independent of the energy contribution (thermal or elastic) for $n = 2$, that is, for the harmonic oscillator, as expected (see Figures 4 and 5). Moreover, the frequency increases with increasing energy when $n > 2$ and decreases if $n < 2$, as one can deduce from Figures 4 and 5. As before, the Laplace–Carson transform between $1/\nu_d$ and $1/\nu_s$ is confirmed as one can directly verify by applying Equation (31), and by using the definition of gamma function given in Equation (37).

4. Oscillation Frequency of a Relativistic Anharmonic Oscillator

Given the theoretical importance and the wide range of applications of the relativistic oscillator,^[63–68] we investigate here the relationship between the statistical and deterministic frequencies

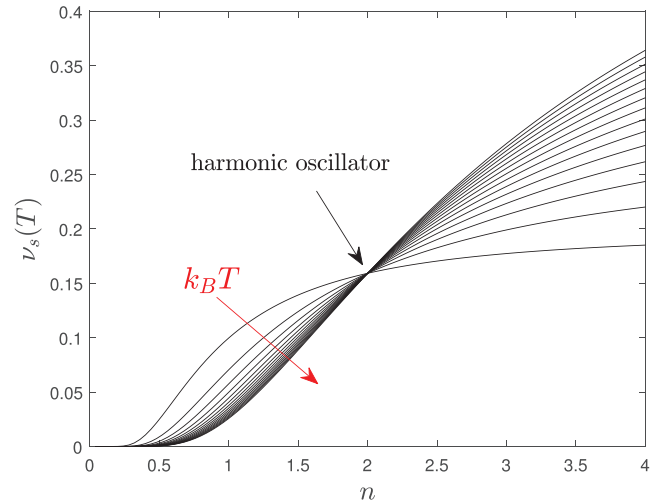


Figure 4. Statistical frequency $\nu_s(T)$ of the anharmonic oscillator as function of n and the thermal energy $k_B T = 1, \dots, 15$. We adopted the parameters $k_0 = 1/2$ and $m = 1$ in arbitrary units.

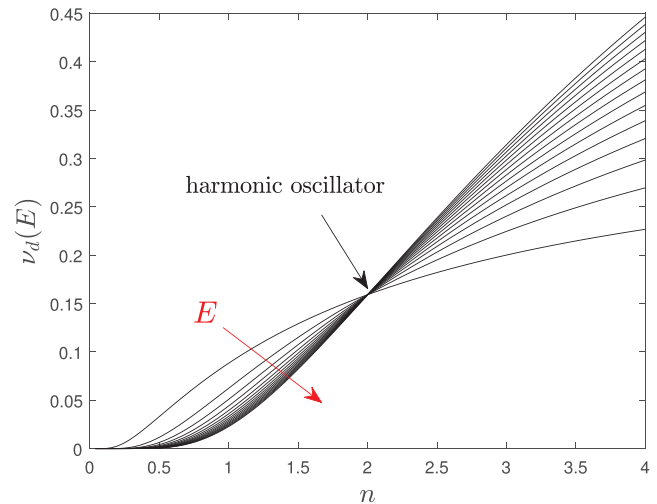


Figure 5. Deterministic frequency $\nu_d(E)$ of the anharmonic oscillator as function of n and the initial energy $E = 1, \dots, 15$. We adopted the parameters $k_0 = 1/2$ and $m = 1$ in arbitrary units.

for this system. The results are also useful in the context of relativistic quantum mechanics.^[69,70] We are able to show that this relationship is exactly as in the classical case, thus proving its thermodynamic ground, independent of the physical theory considered.

4.1. Statistical Oscillation Frequency

This section deals with the relativistic analysis of a particle embedded in a potential energy $\Phi(x)$ and in contact with a thermal bath at temperature T . The 1D relativistic equation of motion can be written as $\frac{dp}{dt} = -\frac{d\Phi}{dx}$ where $p = \frac{mv}{\sqrt{1-v^2/c^2}}$ is the momentum of the particle and c is the speed of light. The particle velocity v can be written in terms of the momentum as $v = \frac{pc}{\sqrt{p^2+m^2c^2}}$. This allows us to introduce the relativistic Hamilton motion equations in the

form

$$\frac{dp}{dt} = -\frac{d\Phi}{dx} = -\frac{\partial H}{\partial x} \quad (44)$$

$$\frac{dx}{dt} = \frac{pc}{\sqrt{p^2 + m^2c^2}} = \frac{\partial H}{\partial p} \quad (45)$$

where the Hamiltonian of the system is given by

$$H(x, p) = c\sqrt{p^2 + m^2c^2} - mc^2 + \Phi(x) \quad (46)$$

In order to consider the thermal fluctuations in this system, we can introduce the so-called Maxwell–Jüttner density probability,^[71–74] which is the starting point of the relativistic thermodynamics and, in particular, of the relativistic gas theory.^[75–77] For instance, it is useful to describe several high-energy and astrophysical effects. For a 1D system, it can be written as

$$W(x, p) = \frac{\exp\left[-\frac{H(x, p)}{k_B T}\right]}{\mathcal{Z}} = W_X(x) W_P(p) \quad (47)$$

where

$$W_X(x) = \frac{e^{-\frac{\Phi(x)}{k_B T}}}{\mathcal{Z}_X}, \quad \text{with } \mathcal{Z}_X = \int_{-\infty}^{+\infty} e^{-\frac{\Phi(x)}{k_B T}} dx \quad (48)$$

and

$$W_P(p) = \frac{e^{-\frac{c\sqrt{p^2 + m^2c^2}}{k_B T}}}{\mathcal{Z}_P}, \quad \text{with } \mathcal{Z}_P = \int_{-\infty}^{+\infty} e^{-\frac{c\sqrt{p^2 + m^2c^2}}{k_B T}} dp \quad (49)$$

represent the marginal probability densities of position and momentum, respectively, together with the corresponding partition functions. In particular, the momentum partition function \mathcal{Z}_P can be evaluated as follows. We adopt the change of variable $\gamma = \frac{c}{k_B T} \sqrt{p^2 + m^2c^2}$ in Equation (49) and we easily get

$$\begin{aligned} \mathcal{Z}_P &= 2 \int_0^{+\infty} e^{-\frac{c\sqrt{p^2 + m^2c^2}}{k_B T}} dp \\ &= \frac{2k_B T}{c} \int_{\frac{mc^2}{k_B T}}^{+\infty} \frac{\gamma e^{-\gamma}}{\sqrt{\gamma^2 - \left(\frac{mc^2}{k_B T}\right)^2}} d\gamma \end{aligned} \quad (50)$$

The last integral can be evaluated by means of the following result (see Equation (3.365.2) in ref. [60])

$$\int_u^{+\infty} \frac{\gamma e^{-\alpha\gamma}}{\sqrt{\gamma^2 - u^2}} d\gamma = u K_1(\alpha u) \quad (\alpha > 0) \quad (51)$$

where $K_n(z)$ represents the modified Bessel function of the second kind and order n . The simplified expression for \mathcal{Z}_P assumes the form

$$\mathcal{Z}_P = 2mcK_1\left(\frac{mc^2}{k_B T}\right) \quad (52)$$

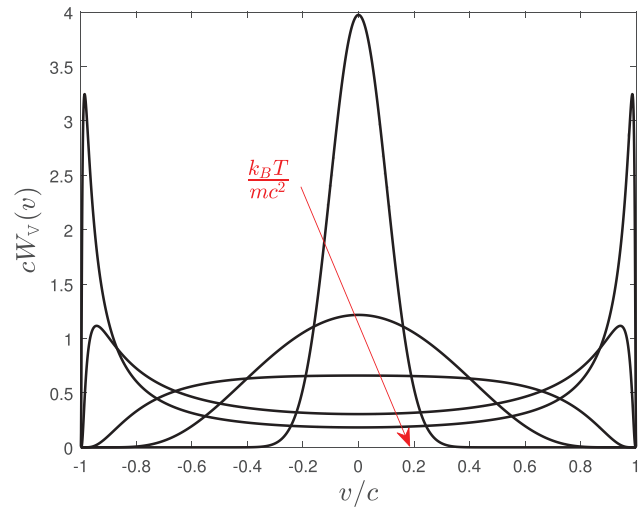


Figure 6. Relativistic velocity probability density $W_V(v)$ versus the velocity v (we used the dimensionless quantities $cW_V(v)$ and v/c) as a function of the inverse relativistic coldness $\frac{k_B T}{mc^2} = 0.01, 0.1, 0.3, 1, \text{ and } 2$.

where the argument $\frac{mc^2}{k_B T}$ is the so-called relativistic coldness.^[71–75] When it is much larger than 1, we have a non-relativistic system, and when it is much smaller than 1, we have an ultra-relativistic system.^[71–75]

In order to define the statistical oscillation frequency of the system, we need to know the probability density $W_V(v)$ of the particle velocity. As usual, it can be obtained by differentiating the probability distribution $F_V(v)$, which is simply calculated by properly integrating the probability density $W_P(p)$ of the particle momentum. Summing up, after straightforward calculations, we get $W_V(v)$ as follows

$$\begin{aligned} W_V(v) &= \frac{d}{dv} F_V(v) = \frac{d}{dv} \Pr\{V \leq v\} \\ &= \frac{d}{dv} \Pr\left\{P \leq \frac{mv}{\sqrt{1 - v^2/c^2}}\right\} \\ &= \frac{d}{dv} \int_{-\infty}^{\frac{mv}{\sqrt{1 - v^2/c^2}}} W_P(p) dp \\ &= \frac{1}{2cK_1\left(\frac{mc^2}{k_B T}\right)\left(1 - \frac{v^2}{c^2}\right)^{3/2}} e^{-\frac{mc^2}{k_B T} \frac{1}{\sqrt{1 - v^2/c^2}}} \end{aligned} \quad (53)$$

which is defined for $|v| < c$. The shape of this velocity probability density can be found in **Figure 6** as a function of $\frac{k_B T}{mc^2}$, that is, the inverse of the relativistic coldness. We can see that for small values of $\frac{k_B T}{mc^2}$, we have densities similar to the classical Maxwell distribution (non-relativistic system), while for larger values we observe the emergence of two peaks near $v = \pm c$ (ultra-relativistic system). Now, through the velocity probability density, the statistical oscillation frequency can be defined as

$$\nu_s(T) = \int_0^c v W_X(0) W_V(v) dv \quad (54)$$

similarly to Equation (21), holding for the classical case. Here, of course, we integrate over the positive particle velocities up to the speed of light c . This integral over v can be calculated by means of the change of variable $y = \frac{mc^2}{k_B T} (1 - v^2/c^2)^{-1/2}$, eventually obtaining the final expression

$$v_s(T) = \frac{k_B T}{2mc} \frac{1}{e^{\frac{mc^2}{k_B T}} K_1\left(\frac{mc^2}{k_B T}\right)} \frac{1}{\int_{-\infty}^{+\infty} \exp\left[-\frac{\Phi(x)}{k_B T}\right] dx} \quad (55)$$

giving the statistical oscillation frequency of a relativistic particle subjected to an energy potential $\Phi(x)$ and in contact with a thermal bath at temperature T . This result represents the relativistic counterpart of Equation (22).

4.2. Deterministic Oscillation Frequency

Following the same reasoning previously applied to the classical case, the problem can be now approached by neglecting the effect of thermal fluctuations. In this case, the relativistic energy conservation can be stated as

$$\frac{mc^2}{\sqrt{1 - \frac{v^2}{c^2}}} + \Phi(x) = mc^2 + E \quad (56)$$

where E represents the energy of the system (it is the total energy without the rest energy mc^2). In Equation (56), we can replace v with $\frac{dx}{dt}$, and therefore, we obtain a first-order differential equation describing the relativistic motion of the particle

$$\frac{dx}{dt} = \pm c \sqrt{1 - \left[\frac{mc^2}{E + mc^2 - \Phi(x)} \right]^2} \quad (57)$$

By integrating the latter over one period of oscillation, we get the result

$$v_d(E) = \frac{c}{2 \int_{x_m}^{x_M} \frac{dx}{\sqrt{1 - \left[\frac{mc^2}{E + mc^2 - \Phi(x)} \right]^2}}} \quad (58)$$

representing the deterministic frequency of oscillation for an arbitrary relativistic anharmonic oscillator. As before, an arbitrary shape of $\Phi(x)$ together with the definition of x_m , x_M , and E can be found in Figure 2.

4.3. Relativistic Relation between v_s and v_d

At this time, we are interested in understanding the relationship between Equations (55) and (58), yielding the statistical $v_s(T)$ and the deterministic $v_d(E)$ oscillation frequencies of a relativistic oscillator, respectively. To approach the problem, we follow the same procedure applied for the classical case, and we integrate the period $1/v_d(E)$, multiplied by the Boltzmann factor $e^{-\frac{E}{k_B T}}$, over

the whole range of energy. We obtain

$$\begin{aligned} & \int_0^{+\infty} \frac{1}{v_d(E)} e^{-\frac{E}{k_B T}} dE \\ &= \frac{2}{c} \int_0^{+\infty} \int_{x_m}^{x_M} \frac{e^{-\frac{E}{k_B T}} dx dE}{\sqrt{1 - \left[\frac{mc^2}{E + mc^2 - \Phi(x)} \right]^2}} \\ &= \frac{2}{c} \int_{-\infty}^{+\infty} \int_{\Phi(x)}^{+\infty} \frac{e^{-\frac{E}{k_B T}} dE dx}{\sqrt{1 - \left[\frac{mc^2}{E + mc^2 - \Phi(x)} \right]^2}} \end{aligned} \quad (59)$$

where we used the property of inversion of integrals $\int_0^{+\infty} \int_{x_m}^{x_M} f(x, E) dx dE = \int_{-\infty}^{+\infty} \int_{\Phi(x)}^{+\infty} f(x, E) dE dx$, holding for an arbitrary function $f(x, E)$. Now, the integral over the energy E can be directly calculated by means of the result

$$\int_u^{+\infty} \frac{e^{-\alpha y}}{\sqrt{1 - \left(\frac{\beta}{\gamma + \beta - u} \right)^2}} dy = \beta e^{\alpha\beta} e^{-\alpha u} K_1(\alpha\beta) \quad (60)$$

that is valid for $\alpha > 0$, and which can be proved through the substitution $z = \gamma + \beta - u$, and with the help of Equation (51). So, we get from Equation (59)

$$\begin{aligned} & \int_0^{+\infty} \frac{1}{v_d(E)} e^{-\frac{E}{k_B T}} dE \\ &= 2mc e^{\frac{mc^2}{k_B T}} K_1\left(\frac{mc^2}{k_B T}\right) \int_{-\infty}^{+\infty} \exp\left[-\frac{\Phi(x)}{k_B T}\right] dx \end{aligned} \quad (61)$$

Hence, by using Equation (55), we can confirm that the following relationship

$$\frac{1}{k_B T} \int_0^{+\infty} \frac{1}{v_d(E)} e^{-\frac{E}{k_B T}} dE = \frac{1}{v_s(T)} \quad (62)$$

is valid also for the relativistic case. The independence of this result from the nature of the physical laws used gives it a special importance that derives directly from the thermodynamic foundations.

As before, we remember that Equation (62) does not represent a canonical average value in phase space since the density of states is absent (see Equation (32)). Therefore, Equation (62) must be simply interpreted as the average of the relativistic deterministic period (at energy E) through the density probability $\rho(E) = \frac{1}{k_B T} e^{-\frac{E}{k_B T}} \mathbf{1}(E)$.

4.4. Example: The Relativistic Hookean Oscillator

We consider here a relativistic 1D system with a potential energy $\Phi(x) = \frac{1}{2} h x^2$. The trajectories of the oscillating point in the phase

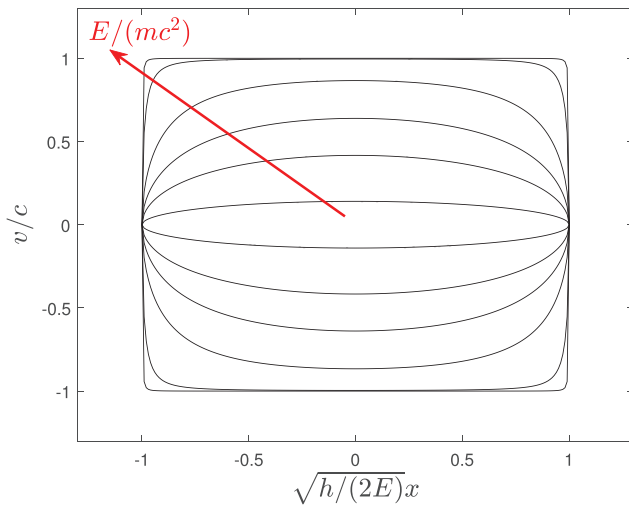


Figure 7. Relativistic trajectories in the phase space of the Hooke oscillator with $\Phi(x) = \frac{1}{2}hx^2$, represented through the dimensionless quantities $\sqrt{h/(2E)}x$ and v/c , and parametrized by $E/(mc^2)$.

space can be obtained through the implicit equation

$$\frac{h}{2E}x^2 = \frac{mc^2}{E} \left[1 + \frac{E}{mc^2} - \frac{1}{\sqrt{1 - \frac{v^2}{c^2}}} \right] \quad (63)$$

and can be represented through the dimensionless quantities $\sqrt{h/(2E)}x$ and v/c , as shown in **Figure 7**. We observe that the system dynamics exhibits a classical behavior when the energy value E is small with respect to mc^2 (elliptic trajectories in the phase space). However, the system becomes heavily nonlinear for larger values of $E/(mc^2)$ (nearly rectangular trajectories). We also remark that, E being the total energy of the system, we can write the end-points of the explored interval as $x_M = -x_m = \sqrt{2E/h}$. Hence, if we apply Equation (58), the deterministic period of oscillation can be written as

$$\frac{1}{v_d(E)} = \frac{4}{c} \int_0^{\sqrt{\frac{2E}{h}}} \frac{\left(E + mc^2 - \frac{1}{2}hx^2\right) dx}{\sqrt{\left(E + mc^2 - \frac{1}{2}hx^2\right)^2 - (mc^2)^2}} \quad (64)$$

Then, we use the change of variable $y = E + mc^2 - \frac{1}{2}hx^2$ and we get

$$\frac{1}{v_d(E)} = \frac{1}{c} \sqrt{\frac{8}{h}} \int_{mc^2}^{E+mc^2} \frac{y dy}{\sqrt{y^2 - (mc^2)^2} \sqrt{E + mc^2 - y}} \quad (65)$$

This integral can be calculated through the result (see Equation (3.132.5) in ref. [60])

$$\int_a^b \frac{y dy}{\sqrt{y^2 - a^2} \sqrt{b - y}} = 2\sqrt{a+b}E(r) - \frac{2a}{\sqrt{a+b}}K(r) \quad (66)$$

where $r = \sqrt{\frac{b-a}{b+a}}$ ($b > a$) and the functions $E(r)$ and $K(r)$ are the complete elliptic integrals of the first and second kinds, respectively.^[60–62] They are defined as follows

$$E(r) = \int_0^1 \sqrt{\frac{1-r^2x^2}{1-x^2}} dx \quad (67)$$

$$K(r) = \int_0^1 \sqrt{\frac{1}{(1-r^2x^2)(1-x^2)}} dx \quad (68)$$

with $0 < r < 1$. Finally, by considering $a = mc^2$ and $b = E + mc^2$, we obtain the deterministic period as

$$\frac{1}{v_d(E)} = 4\sqrt{\frac{m}{h}} \left[\frac{2}{\sqrt{1-r^2}}E(r) - \sqrt{1-r^2}K(r) \right] \quad (69)$$

where $r = \sqrt{\frac{E}{E+2mc^2}}$. This result shows that, contrarily to the classical case, the frequency of oscillation of a relativistic Hooke oscillator depends on the initial conditions, that is, on the energy E of the system. By further considering the first order expansions $E(r) = \pi/2(1 - r^2/4 + \dots)$, and $K(r) = \pi/2(1 + r^2/4 + \dots)$, holding for $r \rightarrow 0$,^[62] we also obtain the relativistic perturbation of the classical period in the form

$$\frac{1}{v_d(E)} = 2\pi\sqrt{\frac{m}{h}} \left(1 + \frac{3}{8} \frac{E}{mc^2} + \dots \right) \quad (70)$$

which is valid when $mc^2 \gg E$.

Concerning the statistical oscillation frequency, from Equation (55), we immediately obtain

$$\frac{1}{v_s(T)} = 2\pi\sqrt{\frac{m}{h}} \sqrt{\frac{2}{\pi}} \sqrt{\frac{mc^2}{k_B T}} e^{\frac{mc^2}{k_B T}} K_1\left(\frac{mc^2}{k_B T}\right) \quad (71)$$

In **Figure 8**, one can find the ratio $\frac{1}{2\pi v_s} \sqrt{\frac{h}{m}}$ between the statistical relativistic period $\frac{1}{v_s}$ and the classical period $2\pi\sqrt{\frac{m}{h}}$ versus $\frac{k_B T}{mc^2}$ (red curve), and the ratio $\frac{1}{2\pi v_d} \sqrt{\frac{h}{m}}$ between the deterministic relativistic period $\frac{1}{v_d}$ and the classical period $2\pi\sqrt{\frac{m}{h}}$ versus $\frac{E}{mc^2}$ (blue curve). We see that both curves converge to 1 when $\frac{E}{mc^2} \rightarrow 0$ or $\frac{k_B T}{mc^2} \rightarrow 0$ (i.e., in the non-relativistic limit). When $E \gg mc^2$ or $k_B T \gg mc^2$, we observe that the two periods are sensibly different from the classical case and they are also different from each other. Again, we can elaborate on the first order approximation of Equation (71), valid for $mc^2 \gg k_B T$ (classical limit). To this aim, we take advantage of the asymptotic expression $K_1(z) = \sqrt{\frac{\pi}{2z}} e^{-z} \left(1 + \frac{3}{8z} + \dots\right)$, for $z \rightarrow \infty$, of the modified Bessel functions (see Equation (9.7.2) in ref. [61]). Then, Equation (71) becomes

$$\frac{1}{v_s(T)} = 2\pi\sqrt{\frac{m}{h}} \left(1 + \frac{3}{8} \frac{k_B T}{mc^2} + \dots \right) \quad (72)$$

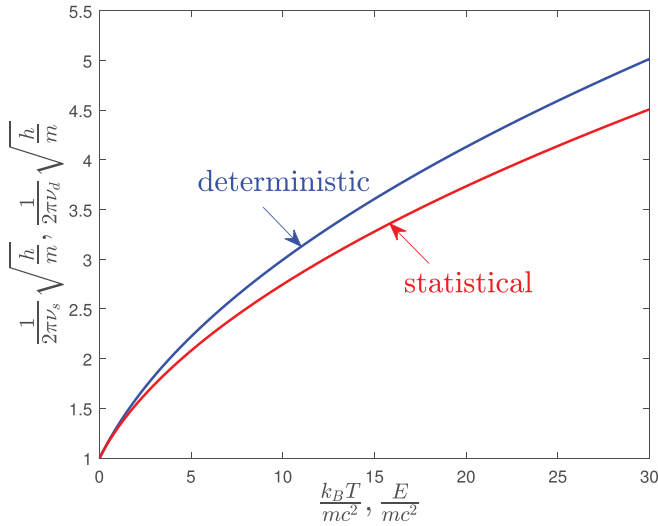


Figure 8. Ratio $\frac{1}{2\pi v_s} \sqrt{\frac{\hbar}{m}}$ between the statistical relativistic period $\frac{1}{v_s}$ and the classical period $2\pi \sqrt{\frac{m}{h}}$ versus $\frac{k_B T}{m c^2}$ (red curve), and ratio $\frac{1}{2\pi v_d} \sqrt{\frac{\hbar}{m}}$ between the deterministic relativistic period $\frac{1}{v_d}$ and the classical period $2\pi \sqrt{\frac{m}{h}}$ versus $\frac{E}{m c^2}$ (blue curve). Both curves converge to 1 when $\frac{E}{m c^2} \rightarrow 0$ or $\frac{k_B T}{m c^2} \rightarrow 0$ (non-relativistic limit).

for $m c^2 \gg k_B T$. The slope of the two curves in Figure 8, when $\frac{E}{m c^2} \rightarrow 0$ or $\frac{k_B T}{m c^2} \rightarrow 0$, is $3/8$, as one can deduce from Equations (70) and (72). A rather complicated calculation, omitted here for the sake of brevity, proves that Equations (69) and (71) are related through the Laplace–Carson transform, as stated in Equation (62). It is easier to verify that this relation is true for the approximated expressions stated in Equations (70) and (72). To do this, we can write

$$\begin{aligned} \frac{1}{k_B T} \int_0^{+\infty} \frac{1}{v_d(E)} e^{-\frac{E}{k_B T}} dE & \\ &= \frac{2\pi}{k_B T} \sqrt{\frac{m}{h}} \int_0^{+\infty} \left(1 + \frac{3}{8} \frac{E}{m c^2} + \dots\right) e^{-\frac{E}{k_B T}} dE \quad (73) \\ &= 2\pi \sqrt{\frac{m}{h}} \left(1 + \frac{3}{8} \frac{k_B T}{m c^2} + \dots\right) = \frac{1}{v_s(T)} \end{aligned}$$

where we used the property $\int_0^{+\infty} E^n e^{-\frac{E}{k_B T}} dE = n! (k_B T)^{n+1}$ for $n = 0$ and $n = 1$. This approach can be generalized in order to consider an arbitrary number of terms in the series of Equations (70) and (72). More precisely, one can obtain

$$\frac{1}{v_d(E)} = 2\pi \sqrt{\frac{m}{h}} \left(1 + \frac{3}{8} \xi - \frac{15}{256} \xi^2 + \frac{35}{2048} \xi^3 - \frac{1575}{262144} \xi^4 \dots\right) \quad (74)$$

$$\frac{1}{v_s(T)} = 2\pi \sqrt{\frac{m}{h}} \left(1 + \frac{3}{8} \eta - \frac{15}{128} \eta^2 + \frac{105}{1024} \eta^3 - \frac{4725}{32768} \eta^4 \dots\right) \quad (75)$$

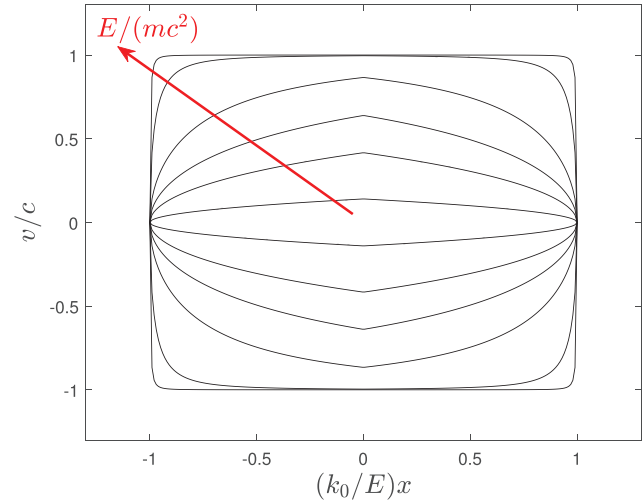


Figure 9. Relativistic trajectories in the phase space of the anharmonic oscillator with $\Phi(x) = k_0|x|$, represented through the dimensionless quantities $(k_0/E)x$ and v/c , and parametrized by $E/(m c^2)$.

where $\xi = \frac{E}{m c^2}$ and $\eta = \frac{k_B T}{m c^2}$. Then, the Laplace–Carson transform is proved by using again the relation $\int_0^{+\infty} E^n e^{-\frac{E}{k_B T}} dE = n! (k_B T)^{n+1}$ for increasing values of n .

4.5. Example: A Relativistic Non-Hookean Oscillator

Let us consider now one last example concerning a relativistic anharmonic oscillator characterized by a potential energy $\Phi(x) = k_0|x|$ (corresponding to the classical case with $n = 1$ studied in Section 3.4). The phase space trajectories can be found in Figure 9. First of all, we can determine the statistical period of oscillation by means of Equation (55). We easily get

$$\frac{1}{v_s(T)} = \frac{4mc}{k_0} e^{\frac{m c^2}{k_B T}} K_1\left(\frac{m c^2}{k_B T}\right) \quad (76)$$

Concerning the deterministic period of oscillation, we use Equation (58), and we can write

$$\frac{1}{v_d(E)} = \frac{4}{c} \int_0^{E/k_0} \sqrt{\frac{(E + m c^2 - k_0 x)^2}{(E + m c^2 - k_0 x)^2 - (m c^2)^2}} dx \quad (77)$$

Then, by using the change of variable $\gamma = E + m c^2 - k_0 x$, we obtain

$$\frac{1}{v_d(E)} = \frac{4}{k_0 c} \int_{m c^2}^{E+m c^2} \frac{\gamma}{\sqrt{\gamma^2 - (m c^2)^2}} d\gamma \quad (78)$$

where the integral can be solved by elementary functions, yielding the result

$$\frac{1}{v_d(E)} = \frac{4}{k_0 c} \sqrt{E(E + 2m c^2)} \quad (79)$$

It is interesting to develop the classical limit of Equations (76) and (79), by obtaining

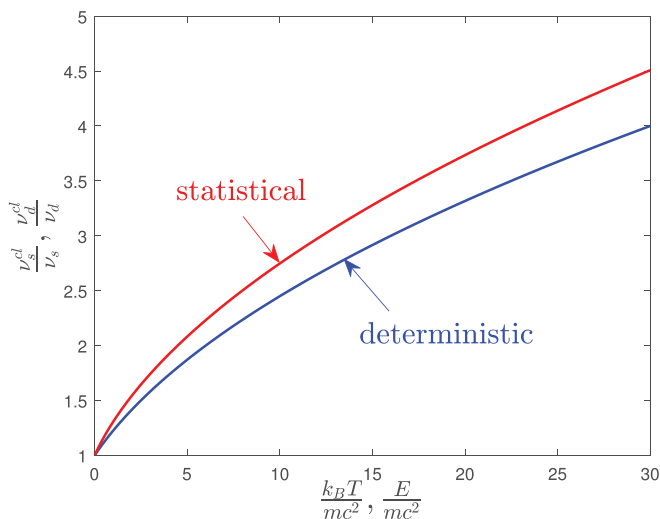


Figure 10. Effect of the energy on the relativistic anharmonic oscillator. Ratio $\frac{v_s^{cl}}{v_s}$ between the relativistic and the classical statistical periods versus $\frac{k_B T}{m c^2}$ (red curve), and ratio $\frac{v_d^{cl}}{v_d}$ between the relativistic and the classical deterministic periods versus $\frac{E}{m c^2}$ (blue curve).

$$\frac{1}{v_s^{cl}(T)} = \lim_{c \rightarrow \infty} \frac{1}{v_s(T)} = \frac{4}{k_0} \sqrt{\frac{\pi m k_B T}{2}} \quad (80)$$

$$\frac{1}{v_d^{cl}(E)} = \lim_{c \rightarrow \infty} \frac{1}{v_d(E)} = \frac{4}{k_0} \sqrt{2 m E} \quad (81)$$

These relations exactly correspond to the classical results obtained in Equations (38) and (43), for $n = 1$, in Section 3.4. In **Figure 10**, one can find the effect of the thermal or initial energy on the relativistic anharmonic oscillator. The ratio $\frac{v_s^{cl}}{v_s}$ is plotted versus $\frac{k_B T}{m c^2}$ (red curve), while the ratio $\frac{v_d^{cl}}{v_d}$ is plotted versus $\frac{E}{m c^2}$ (blue curve). These curves show that by increasing the energies we progressively deviate from the classical behavior. We can finally verify Equation (62), linking statistical and deterministic periods, as follows. We consider the integral

$$\begin{aligned} \frac{1}{k_B T} \int_0^{+\infty} \frac{1}{v_d(E)} e^{-\frac{E}{k_B T}} dE &= \frac{4}{k_0 c k_B T} \int_0^{+\infty} \sqrt{E(E + 2 m c^2)} e^{-\frac{E}{k_B T}} dE \\ &= \frac{4 m^2 c^3}{k_0 k_B T} \int_0^{+\infty} \sqrt{\xi(\xi + 2)} e^{-\frac{m c^2}{k_B T} \xi} d\xi \end{aligned} \quad (82)$$

and we use the property given in Equation (3.372) of ref. [60], stating that

$$\int_0^{+\infty} \sqrt{\xi(\xi + 2)} e^{-p\xi} d\xi = \frac{e^p}{p} K_1(p) \quad (83)$$

So doing, Equation (82) assumes exactly the form of Equation (76), by proving that the relationship given in Equation (62) is verified, as expected.

5. Conclusions

In this paper, we studied the relation between the oscillation frequency of an arbitrary 1D anharmonic oscillator, induced by thermal fluctuations, and its deterministic counterpart, obtained through a purely mechanical approach. At the beginning, we introduced the concept of statistical oscillation frequency by means of the 1D TST, where this frequency value intervenes in defining the characteristic rate constants (although in a rather approximated form). These constants are used in the so-called rate equations and describe the non-equilibrium transitions between two energy wells separated by a given energy barrier, with application to chemical reactions and other physicochemical transformations, as detailed in Section 1. Interestingly, the statistical frequency can be also defined for a convex potential energy, and it represents an exact result at thermodynamic equilibrium. We obtained this statistical frequency for a classical and a relativistic arbitrary anharmonic oscillator, and we compared these results with their deterministic counterparts, based on classical and relativistic mechanics. We then obtained a simple relationship between these two different, statistical and deterministic, kinds of frequencies. Interestingly, this expression is exactly the same for the classical and relativistic approaches. This means that the proved relationship follows directly from the first principles of thermodynamics and not from the class of physical laws used.

If we look at the original definition of statistical frequency, we can say that it is related to the flux at thermodynamic equilibrium in a given direction and at a given point (see Equation (21)). By means of the demonstrated relationship, this definition can also be reformulated by stating that the statistical frequency $v_s(T)$ can be obtained from the deterministic frequency $v_d(E)$ by averaging its values through probability density $\rho(E) = \frac{1}{k_B T} e^{-\frac{E}{k_B T}} \mathbf{1}(E)$, which represents the normalized Boltzmann exponential. We have also emphasized the fact that this average does not correspond to the canonical average in phase space, but simply represents the average of a random variable according to a given probability density. The new point of view on the statistical frequencies can be useful from a theoretical and pedagogical standpoint to give further meaning to the mathematical expressions of rate constants of the TST. In order to clarify the meaning of the found relationship, we showed various examples of calculation of statistical and deterministic frequencies both in the classical and relativistic cases. From a mathematical point of view, the mapping between the statistical and the deterministic frequencies can be summarized through a Laplace–Carson transform, as we explicitly showed in the examples considered. Obviously, the relationship obtained is exact and therefore true for every form of the potential energy $\Phi(x)$. Nevertheless, the development of calculations for particular energy profiles helps to better understand its physical and mathematical significance.

Although this work presents an interesting relationship concerning the oscillation frequencies of an arbitrary energy well, it has limitations that are briefly described below.

First of all, our analysis has been performed for a 1D geometry, which represents a limitation from the application point of view. It is important to remark that the rate constants, within the TST, can be calculated for a multidimensional system. In fact, the problem is somehow brought back to a 1D case by defining a reaction coordinate, which is the function of all degrees of freedom. It is, for example, negative for products and positive for reactants, thus rendering the problem mathematically solvable.^[78–81] Several developments in this direction can be found in ref. [6]. However, the time evolution of a Hamiltonian system is not, in general, periodic, and therefore, it is difficult, if not impossible, to search for relationships between statistical and deterministic oscillation frequencies for multidimensional systems. Of course, there are criteria for the existence of periodic orbits in Hamiltonian systems,^[82,83] but their application to our context is beyond the scope of our work and requires further research. The aim of our relationship between statistical and deterministic frequencies is to give a simple and pedagogical interpretation to the statistical frequency (and therefore to the rate constants), even if limited to the 1D case.

Second, in previous analyses, we never considered possible quantum effects on the oscillation frequencies of the studied systems. The consideration of these possible effects is a very complicated problem and we add here only some comments useful for further investigations. We can say that all previous results concerning statistical oscillation frequencies are influenced by quantum perturbations, and in particular, the relationship between statistical and deterministic oscillation frequencies no longer holds in the quantum domain. From a historical point of view, it is worth mentioning that the search for quantum perturbation to the phase space canonical probability density of statistical mechanics largely interested the first half of the twentieth century. In this context, we can cite the works of Wigner,^[84] Uhlenbeck and Gropper,^[85] and Kirkwood.^[86] The idea of these approaches is to write the quantum partition function and the quantum canonical distribution $w_Q(q, p)$ of a system (in the complete phase space) as a perturbation of the same classical quantities (typically up to the second order in the Planck constant \hbar). For instance, more details can be found in Section 33 of Landau's classic textbook.^[87] Although approximate, these results make it possible to determine the statistical oscillation frequency given by Equation (21). A better solution takes into account a quasiprobability distribution in the phase space without the approximation induced by considering only the second order perturbation in \hbar . A quasiprobability distribution in quantum mechanics is defined in the phase space and allows the calculation of the average value of observables, but in general, it is not everywhere positive as the standard probability densities.^[84,88–90] The quasiprobability density can be directly calculated at thermodynamic equilibrium,^[91,92] facilitating the implementation of Equation (21). This approach has been efficiently used to develop different quantum TSTs.^[93,94] More general techniques can be found in the literature (see, for instance, refs. [95, 96]). To conclude, the quantum effects are important in evaluating the statistical frequencies of oscillators and then are relevant for studying rate constants of the TST.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

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

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anharmonic oscillator, relativistic dynamics, transition state theory

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