

Inelastic transition probabilities by the energy fluctuation model

G. Mastrocinque

Dipartimento di Scienze Fisiche dell'Università di Napoli
"Federico II" - Facoltà di Ingegneria - P.le Tecchio - 80125 Napoli

Summary

The energy fluctuation model provides a typical expression for transition probabilities in inelastic molecular collisions, based on the definition of both a collision entropy and a density of energy states encountered in these processes. By this model, advances have already been made to improve physical understanding and consistency between classical mechanics results and quantum ones. In this work, we show practically that a semi-classically-calculated probability can always be dealt with in such a way as to result in the corresponding quantum expression. To this purpose, we assume (parametrically-evaluated) prototype functions for the entropy and density of states, and show that their forms are correlated to the energy time-law occurring in a single process. An ergodic-like property of the model is enlightened, a numerical example is provided, and general physical discussion is given step by step in the paper.

PACS. 05.90 - Other topics in statistical physics and thermodynamics

1 Introduction

Amongst the various new approaches by which - still in recent years - the field of relations between classical and quantum mechanics has been addressed, the so-called "energy fluctuation model" seems to have enlightened an alternative view [1-2]. This model can be traced back to Einstein [3], Bohm and Vigier [4] and to the famous theorem on fast oscillations by Kapitza [5-7a]. One of the model's peculiarities is the increasing of the classical mechanics capability to describe energy transfers in inelastic molecular collisions. This is achieved

using improved techniques to account for detailed balance in the semi-classical transition probabilities expressions.

A semi-classical transition probability P_{sc} is generated by the time-dependent matter-wave description of a coupling between states, with interaction Hamiltonian $V_{if}(t)$ (i = initial state; f = final). If a first order perturbation technique (FOPT) is used, we generally have [8]:

$$P_{sc} = \frac{1}{\hbar^2} \left| \int_{-\infty}^{+\infty} V_{if}(t) \exp(i(E_f - E_i)/\hbar) dt \right|^2 \quad (1)$$

The energies E_i , E_f characterize the inelastic quantum collision channel.

To calculate expression (1), it is often assumed that the system vibrational motions can be “separated” from the translational one. As a typical example, let us consider the case of a (co-linear, head-on) encounter between an atom and a binary molecule. For the sake of simplicity, let no rotation be involved. Then they are only submitted to a vibro-translational (V-T) energy exchange, in a so-called uni-dimensional model. We can treat the molecule vibrational motion (assume it is harmonic with mass M , pulsation ω_{if} , internal co-ordinate r^*) by quantum mechanics (¹). The translational motion is instead treated classically. If the internal motion has small amplitude we generally get [9,10]:

$$V_{if}(t) = \langle i | r^* | f \rangle F_{if}(t) = \sqrt{\frac{\hbar}{2M\omega_{if}}} F_{if}(t) \quad (2)$$

where $|i\rangle$ and $|f\rangle$ are the involved vibrational states and $F_{if}(t)$ is the (classical-like) force time-law acting on the vibrating mass M , as determined by the collision trajectory. This last is assumed to occur with energy E . Then we have:

$$P_{sc}(E) = \left[\frac{\hbar}{2M\omega_{if}} \right] \left| \int_{-\infty}^{+\infty} F_{if}(t) \exp(i\omega_{if}t) dt \right|^2 \frac{1}{\hbar^2} \quad (3)$$

Here we see that $P_{sc}(E)$ is generally calculated by the product of two main factors. The first one is a quantum matrix element coupling the internal states of the system involved in the transition. The second one is a (squared-modulus) Fourier integral representing the effective impulse exchanged with the translational degree of freedom during the collision. The Fourier integral is, classically, a function of the collision energy E - a quantity affected by uncertainty because of the inelasticity.

As is well known, the exact quantum mechanical results are instead obtained by wavefunction superposition integrals coupling the corresponding stationary

¹For completeness, note that with the same physical assumptions taken here, the internal molecular motion can also be treated by a purely classical procedure [10,7b]. It brings to the same result (equation (3)) next quoted.

quantum states (as shown in equation (5)). The difference [9] that one finds between the expression (3) and the exact result (5) is symbolic of a remarkable part of the incongruence between classical and quantum mechanics. It still calls for many investigations and debates.

The present work is specifically addressed to show that the fluctuation model has a great capability to transform the result of the semi-classical expressions (3) into the corresponding exact quantum results obtained by (5). However, we will only do this using some practical calculation means; and mainly referring to the rather simple models available in the field of co-linear (uni-dimensional) collisions. This is indeed the case with the V-T energy transfer to which our previous equations have already been referred.

The founding relations for procedures able to impose detailed balance to the semi-classical transition probabilities were, historically, some (and somewhat celebrated) heuristic findings [11-15]. They are generally referred to as “symmetrization techniques”. For instance, Zener [11,12] used the arithmetical mean of the initial and final collision velocities into the semi-classical expression of a molecular V-T transfer probability to improve the result. Alder et al. [13-15] used the geometrical mean to symmetrize Sommerfeld factors while calculating semiclassical Coulomb cross-sections in a nuclear domain, etc.[16].

It has been proposed [10] that a general interpretation of these findings can be conceptually obtained by considering the analogy between the mechanical transfer probabilities and the famous Einstein equation for the fluctuation probabilities P_{if} of a thermodynamical system out of equilibrium. According to the Boltzmann principle, Einstein formed his equation using an entropy concept [17]:

$$P_{if} = \exp \Delta S_{if} \tag{4}$$

ΔS_{if} is the entropy difference between the initial and the final state of the system. In the frame of the fluctuation model, the analogous interpretation has been shown to support the field of semi-classical calculations for the energy transfer probabilities. It generates improved techniques for detailed balancing [18-20], and new concepts for model developments [1-2].

In the next section, we briefly review the mentioned topics with additional important details. We shall give new developments afterwards.

2 Theoretical background

For an inelastic transfer, the quantum transition probability P_{qm} always results in a symmetric function of the energies E_i , E_f characterizing the inelastic quantum collision channel ⁽²⁾:

$$P_{qm} \equiv P_{qm}(E_i, E_f) = P_{qm}(E_f, E_i) =$$

²Following [9], in equation (5) we just give the FOPT quantum mechanical expression corresponding to the semi-classical one of our interest, shown in (3).

$$= \frac{1}{2M\hbar\omega_{if}} \left| \int_{-\infty}^{+\infty} \psi^*(E_f, x) F_{if}(x) \psi(E_i, x) dx \right|^2 \quad (5)$$

Here we named ψ the pertinent, translational wave-functions. The molecular force field $F_{if}(x)$ is actually the physical precursor of the function $F_{if}(t)$ appearing in (3); indeed this last function of time can be calculated starting from $F_{if}(x)$, whenever a proper collision time-law $x(t)$ is specified.

As seen in equation (5), the quantum expressions account for detailed balance or microreversibility by definition.

It is not the same for semi-classical-like expressions. Since they require the calculation of the collision time-law, they can generally be expressed as functions of the translation energy characterizing the direct or the reverse process:

$$P_{SC}(E_i) \neq P_{SC}(E_f) \quad (6)$$

Therefore they do not satisfy the microreversibility requirement. We have to use classical mechanics to calculate the time law and the Fourier integral involved into the expressions. But the classical calculations fail (also) in this respect, unless - as said before - we force the expression (3) by means of superimposed, "symmetrizing" corrections.

Historically many authors (e.g. Ter-Martyrosian, Zener, Sommerfeld, Heitler, Gaunt, Elwert, Bloch, Shin, Alder, Winther; see quoted references and, moreover, [21-29]) compared classical-like calculations to quantum ones in a variety of cases, introducing corrections and refinements to the former. Amongst other, one can infer from their works in a number of examples the following property. Once a (well-refined) semi-classically-calculated probability $P_{SC}(E)$ is available for a given transfer, it seems generally possible to find, in the collision energy interval, an effective value E_{eff} for which

$$P_{SC}(E_{eff}) = P_{qm}(E_i, E_f) \quad (7)$$

This finding is very interesting although unable, as such, to suggest a meaningful (classical-like) model of the quantum transition.

Our purpose in this paper is also to show that the fluctuation model is able to give a sound physical interpretation to equation (7), bringing the semi-classical calculations to the exact (quantum) results in quite general circumstances; and providing us with more information about the effective time-law of the transfer.

3 The fluctuation model brings detailed balance to the classical expressions of energy transfer probabilities

A saddle-point (SP) technique can be used to evaluate both the Fourier integral appearing in (3) and the quantum superposition integral (often with WKB

forms assumed for the wavefunctions) appearing in (5). Typical exponential forms are then obtained for both $P_{sc}(E)$ and $P_{qm}^{WKB}(E_i, E_f)$:

$$P_{sc}^{SP}(E) = A \exp[-2\omega_{if}\tau(E)] \quad (8)$$

$$P_{qm}^{WKB,SP}(E_i, E_f) = A \exp[-2B_{WKB}(E_i, E_f)] \quad (9)$$

Here $\tau(E)$ is an appropriate classical time characterizing the collision, and B_{WKB} a corresponding quantum-like exponent. The pre-exponential factor A generally turns out to be the same constant in both expressions. In a variety of practical examples shown in references [16] and [20], we could demonstrate that one always finds

$$\exp \left[\frac{1}{E_f - E_i} \int_{E_i}^{E_f} \ln [P_{sc}^{SP}(E)] dE \right] = A \exp \left[-\frac{2}{\hbar} \int_{E_i}^{E_f} \tau(E) dE \right] = P_{qm}^{WKB,SP} \quad (10)$$

This equation reads as a particularly successful symmetrization technique. It also lends itself to the quoted analogy with equation (4): if indeed a ‘‘collisional’’ entropy

$$\Delta S_{sc}(E) = \ln [P_{sc}(E)] \quad (11)$$

is introduced, then the symmetrized semi-classical probability will appear as a ‘‘fluctuation probability’’ of Einstein’s type

$$\exp \left[\frac{1}{E_f - E_i} \int_{E_i}^{E_f} \Delta S_{sc}(E) dE \right] = \exp \Delta S_{if} \equiv P_{if}(E_i, E_f) \quad (12)$$

where ΔS_{if} is the integral mean of $\Delta S_{sc}(E)$. The symmetrized $P_{sc}(E)$ is thus called a ‘‘fluctuation’’ probability $P_{if}(E_i, E_f)$.

Equation (10) also shows us that the continuous spectrum of energy values included in the inelastic interval (E_i, E_f) must be taken into account to approach the quantum mechanical expressions when starting from the semi-classical ones. Actually, it shows that performing the simple integral mean of $\ln [P_{sc}(E)]$ is quite effective when dealing with SP-approximated expressions. But unfortunately, the same rule will not work as well when the SP approximation is dropped off, and exact calculations of the integrals are performed. In order to understand how to get a more general rule, we now consider the following.

In the time-dependent wave-equation formalism for the coupling of quantum states, a mixed state is formed, with time-dependent probability amplitude coefficients affecting both the initial and final states. During the time evolution therefore, the energy of the system sweeps continuously across the interval from E_i to E_f . So in the corresponding statistical ensemble of states, a density of

states $P(E)$ (number of energy states between E and $E+dE$) available to the system should enter equation (12). Indeed, the function $P(E)$ can be identified in the same equation just as the constant function $1/(E_f-E_i)$.

In the present paper we want to evolve towards a more general case; then for improved calculations, the general rule given by the fluctuation model to apply detailed balancing will be to calculate the symmetrized quantity

$$P_{if}(E_i, E_f) = \exp[\langle \Delta S_{sc}(E) \rangle] = \exp \int_{E_i}^{E_f} \ln [P_{sc}(E)] P(E) dE \quad (13)$$

where a more suitable, general expression of $P(E)$ must now be applied.

Indeed, we are going to introduce a very typical expression for this function, showing that it is able in practice to make expression (13) always equal to the corresponding quantum-mechanical one. In other words, under very practical but rather general assumptions, for each given transfer process we are able to find a function $P(E)$ such that

$$P_{if}(E_i, E_f) = \exp \int_{E_i}^{E_f} \ln [P_{sc}(E)] P(E) dE \simeq P_{qm}(E_i, E_f) \quad (14)$$

The achievement of this result is in principle made possible by the very equation (7), which must be considered a fundamental assumption in this paper. Yet we want to stress that finding the appropriate density expression $P(E)$ is not a trivial matter at all, because it must not only be submitted to condition (14) in a mathematical sense; but it also has to behave consistently with the real transfer physics. Indeed, the mathematical structure of equation (13) provides us with some very peculiar information about the transfer time-law (see next section), so that $P(E)$ must be able to account for it. Complying with the mentioned conditions will bring us, at least conceptually ⁽³⁾, to a complete classical modelling of the quantum transfer in the present work.

Since it is not possible to perform general calculations of equation (13) for any arbitrary function $P_{sc}(E)$, we have to find help in a favorable, and possibly general, position. For computational purposes therefore, we assume a parabolic interpolation for $\ln P_{sc}(E)$ in the (E_i, E_f) interval. This is mathematically acceptable for a great number of cases, unless the function $\ln P_{sc}(E)$ has a very fast variation in the interval. We write

$$\ln P_{sc}(E) \simeq p + qE + rE^2 \quad (15)$$

$$E_i \leq E \leq E_f \quad (16)$$

The interpolation coefficients p , q , r are such that

$$\ln P_{sc}(E_i) = p + qE_i + rE_i^2 \quad (17)$$

³From a technical point of view, it is clear that corrections or refinements are always admissible to our proposed expressions (20) to (23); to the distorted potentials in (36) and (37), and to the $\Delta S_{sc}(E)$ expression itself for improved description.

$$\ln P_{SC}(E_f) = p + q E_f + r E_f^2 \quad (18)$$

$$\ln P_{SC}(E_{eff}) = p + q E_{eff} + r E_{eff}^2 = \ln P_{qm}(E_i, E_f) \quad (19)$$

In this way, the mathematical expression of $\ln P_{SC}(E)$ is simplified but its essential behavior in the reference interval is preserved.

Now consider the (normalized to 1, singular in E_{eff}) density:

$$P(E) = c_i \frac{(E - E_i)}{\sqrt{E_{eff} - E}} \quad E_i \leq E < E_{eff} \quad (20)$$

$$c_i = \frac{3(E_f - E_{eff})(7q + (3E_f + 11E_{eff})r)}{4(E_{eff} - E_i)^{3/2}(E_f - E_i)(7q + (3E_f + 8E_{eff} + 3E_i)r)} \quad (21)$$

$$P(E) = c_f \frac{(E_f - E)}{\sqrt{E - E_{eff}}} \quad E_f \geq E > E_{eff} \quad (22)$$

$$c_f = \frac{3(E_{eff} - E_i)(7q + (3E_i + 11E_{eff})r)}{4(E_f - E_{eff})^{3/2}(E_f - E_i)(7q + (3E_f + 8E_{eff} + 3E_i)r)} \quad (23)$$

This proposed function is quite a peculiar microcanonical-like energy distribution for the statistical ensemble. In this field, one generally finds more common functions as Dirac deltas, rectangular, exponential etc., which are suitable for simpler models in a general statistical physics domain. With equations (20)-(23) we have given instead a more specific function, able to meet with all physical and mathematical requirements of the present model; none of the quoted simpler forms can be brought to the same performances as we are going to expound in this paper.

If the quadratic interpolation (15) is also used in (13), one can easily show that with the density (20)-(23) we obtain

$$P_{if}(E_i, E_f) = \exp[p + q E_{eff} + r E_{eff}^2] = P_{qm}(E_i, E_f) \quad (24)$$

Therefore, a conceptual consistency of the classical-to-quantum probability expressions can be considered already insured by assumption (7), also appearing in (19); but here, we not only have good modelling from a mathematical point of view, but also a sound physical model, able to describe the effective time-law of the transfer (in the next section).

4 A “quasi-ergodic postulate” brings from $P(E)$ to the effective time-law

The structure of equation (13) reveals a bridge between the ensemble statistics and the time evolution of a single process. It is a multiple joint probability to

step continuously from one energy state to the following, all across the interval from E_i to E_f (here $E_i \equiv E_1$, $E_f \equiv E_m$):

$$\begin{aligned} P_{if}(E_i, E_f) &= \exp dS_1 \exp dS_2 \dots \exp dS_m = \\ &= P_{SC}(E_1)^{P(E_1)dE_1} \dots P_{SC}(E_m)^{P(E_m)dE_m} \end{aligned} \quad (25)$$

This suggests that when a single transfer occurs, a path is followed across the interval from E_i to E_f , and the ensemble probability of each state E can be linked to its effective time life dt by (what we call) a quasi-ergodic postulate:

$$P(E)dE = \eta(t) \frac{dt}{\tau} \quad (26)$$

Here τ is the mean collision time. We called this postulate quasi-ergodic because, if the function $\eta(t)$ could (for now hypothetically) be set equal to 1, then the statistical average of every function g would be equal to its corresponding time-average⁽⁴⁾:

$$\int_{E_i}^{E_f} g(E)P(E)dE = \frac{1}{\tau} \int_{-\tau/2}^{\tau/2} g(t)dt \quad (27)$$

However, this is not the case for the model which is being expounded here. We therefore must explain the physical meaning of the function $\eta(t)$, and we will do it later in the paper. But once this point has been made clear, at last, we will also see that a simple re-definition of our main quantities will bring us straight to an ergodic model, with equation (27) always satisfied. The enlightening of this final step is reserved to the section “ergodic model” at the end of the paper.

Equation (26) gives us a solution $E(t)$ for the energy time-law followed by a single transfer, whenever a function $\eta(t)$ is specified. This also means that when we know the effective time-law for the energy in a transfer process (classically modelled), for each of them we can solve the classical trajectory equation characterizing the collision (remember our model is uni-dimensional in the x-co-ordinate space-domain):

$$\frac{1}{2}\mu v^2 + U(x) = E(t) \quad E_i \leq E \leq E_f \quad (28)$$

Therefore we will determine, in the next section, a suitable $\eta(t)$ for good modelling. But this will be just done by the reverse method, i.e. finding the $\eta(t)$ function consequent to a few very simple, but rational assumptions we can take on the collision time-law in the space-time domain. We will obviously check the plausibility of the result afterwards.

⁴If we set $\eta(t) = 1$ indeed, equation (26) actually reduces to the known “ergodic hypothesis”. Please note that we used the attribute “quasi-ergodic” not just in the technical sense of the known theorems, but simply as an ordinary language statement able to excite easy physical understanding about the proposed model.

5 Distorted potentials technique

If we assume that the time variable t is given as a function of x via the inverse time-law, we can define the distorted potential

$$U_{eff}(x) = U(x) - E[t(x)] + E_{eff} \quad (29)$$

and equation (28) will read

$$\frac{1}{2}\mu v^2 + U_{eff}(x) = E_{eff} \quad (30)$$

In order to deal with these equations we can proceed as follows. First we note that the time-derivative of the function $E(t)$ must be 0 in E_{eff} (consider that in equation (26) $P(E_{eff}) \rightarrow \infty$). Then, if x_0 is the maximum approach distance characterizing the trajectory, we have:

$$t(x_0) = 0 \quad (31)$$

$$v(x_0) = 0 \quad (32)$$

$$U_{eff}(x_0) = U(x_0) = E_{eff} \quad (33)$$

Now the simplest but physically meaningful expression for $E[t(x)]$ is

$$E[t(x)] = E_i + \left(1 - \frac{E_i}{E_{eff}}\right) U(x) \quad (-\infty < t \leq 0) \quad (34)$$

$$E[t(x)] = E_f + \left(1 - \frac{E_f}{E_{eff}}\right) U(x) \quad (0 \leq t < \infty) \quad (35)$$

These equations are indeed compliant with condition (33); and with $E_i \leq E \leq E_f$, if $\lim_{|x| \rightarrow \infty} U(x) = 0$ - as is generally the case.

Now equation (28) will read

$$\frac{1}{2}\mu v^2 + \frac{E_i}{E_{eff}} U(x) = E_i \quad (-\infty < t \leq 0) \quad (36)$$

$$\frac{1}{2}\mu v^2 + \frac{E_f}{E_{eff}} U(x) = E_f \quad (0 \leq t < \infty) \quad (37)$$

We can also write

$$\frac{1}{2}\mu \frac{E_{eff}}{E_i} v^2 + U(x) = E_{eff} \quad (-\infty < t \leq 0) \quad (38)$$

$$\frac{1}{2}\mu\frac{E_{eff}}{E_f}v^2 + U(x) = E_{eff} \quad (0 \leq t < \infty) \quad (39)$$

These equations are essentially the ordinary energy theorem in which the effective masses $\mu E_{eff}/E_i$ and $\mu E_{eff}/E_f$, in the two respectively quoted domains of time, now appear. In the assumptions we have taken, the time-laws for classical trajectories subtending the inelastic transfer can therefore be obtained by all the known results for standard potentials, whenever the effective masses are inserted into their expressions.

Using equations (26), (38) (39) (34) (35) we can also write

$$P(E)dE = \eta(t)\frac{dt}{\tau} \equiv \eta(t(x))\frac{dx}{v_x(x)\tau} \equiv \eta(x)\frac{|dx|}{v(x)\tau} = \quad (40)$$

$$= \eta(x)\sqrt{\frac{\mu}{2E_i}\frac{E_{eff}-E_i}{E_{eff}-E(x)}}\frac{|dx|}{\tau} \quad (-\infty < t < 0) \quad (41)$$

$$= \eta(x)\sqrt{\frac{\mu}{2E_f}\frac{E_f-E_{eff}}{E(x)-E_{eff}}}\frac{|dx|}{\tau} \quad (0 < t < \infty) \quad (42)$$

and by comparison with equations (20) to (23) we find the η function (now of x):

$$\eta(x) = \beta_i \left| \frac{dU}{dx} \right| U(x) \quad E_i \leq E < E_{eff} \quad (43)$$

$$\beta_i = \frac{3\tau\sqrt{E_i}(E_f-E_{eff})(7q+3E_f r+11E_{eff} r)}{\sqrt{8\mu}E_{eff}(E_f-E_i)[7q+(3E_f+8E_{eff}+3E_i) r]} \quad (44)$$

$$\eta(x) = \beta_f \left| \frac{dU}{dx} \right| U(x) \quad E_f \geq E > E_{eff} \quad (45)$$

$$\beta_f = \frac{3\tau\sqrt{E_f}(E_{eff}-E_i)(7q+3E_i r+11E_{eff} r)}{\sqrt{8\mu}E_{eff}(E_f-E_i)[7q+(3E_f+8E_{eff}+3E_i) r]} \quad (46)$$

6 Discussion and remarks

During an effective transfer, the system starts with a collision energy E_i (the collision partners are still at far distance from each other), reaches a “maximum

approach distance” where the energy is evaluated as E_{eff} in our model, and goes again back to far relative distances where the final energy is E_f . So the energy values E_i and E_f (and their next neighbors) play their proper role of translational energies only at far distances, where the transfer effectiveness is much lower than it is at the closest ones. Then a (relatively) smaller rate of change of the energy should be taken into account at far distances, because in our calculations the probability $P_{sc}(E)$ is evaluated at “unperturbed energy”, by a FOPT procedure. With no weight η , the real lifetime dt of energy values at far distances would be underestimated in equation (26); or alternatively, we could also say that the entropy $\ln P_{sc}(E)$ in the integrand of (14) would turn out overestimated when $E \rightarrow E_i$ or $E \rightarrow E_f$. The physical meaning of the function η is therefore to smooth out the effect of the FOPT approximation, weighting differently far and close distances. This should be done in agreement with a proper space dependence of the interaction Hamiltonian. We therefore see that our expressions (43) to (46) for η reveal an implicit assumption of our model on the interaction: to the effect of calculating η , it appears as the gradient of the (squared) diffusion potential. Conceptually, this may be considered a very admissible function, if limited to the present simple and general description. Indeed for small-amplitude molecular oscillations, the interaction Hamiltonian is known to have (in principle) a general dependence on the first derivative of the intermolecular potential (the function $F_{if}(x)$). But from a practical point of view, when some extent of negative interference between the coupled internal states is considered, a stronger power should be taken to represent non-resonant transfers in the present context. Then we conclude that the expression of η , given in equations (43) to (46), is appropriate to the present simple framework; and has a great potential to evolve into more refined expressions when more accurate distorted potentials than we have chosen in equations (36), (37) will be used in future work.

7 Numerical example

Let us consider here the case of a (V-T) energy transfer between molecules. Let it be governed by an exponential-repulsive intermolecular potential

$$U(x) = D \exp[-\alpha x] \quad (47)$$

with intensity D and characteristic rate α , as investigated already by Zener [11,12]. This author expressed the semi-classical FOPT transition probability (co-linear head-on encounters, small velocities) as

$$P_{sc}(E) = \frac{8\pi^2\mu^2\omega}{\alpha^2\hbar M} \frac{1}{4} \frac{1}{\sinh^2[\pi\omega/(\alpha\sqrt{\frac{2}{\mu}E})]} \quad (48)$$

Here μ is the reduced mass of the collisional system. M is the internal vibrating mass, ω the pulsation of the internal (harmonic) motion, and \hbar is the Planck's constant. For the same transfer, and actually with the same physical assumptions taken by Zener already, Jackson and Mott [30] provided the quantum mechanical result corresponding to equation (48):

$$P_{qm}(E_i, E_f) = \frac{8\pi^2\mu^2\omega}{\alpha^2\hbar M} \frac{\sinh[2\pi\mu\sqrt{\frac{2}{\mu}E_i}/(\hbar\alpha)] \sinh[2\pi\mu\sqrt{\frac{2}{\mu}E_f}/(\hbar\alpha)]}{(\cosh[2\pi\mu\sqrt{\frac{2}{\mu}E_i}/(\hbar\alpha)] - \cosh[2\pi\mu\sqrt{\frac{2}{\mu}E_f}/(\hbar\alpha)])^2} \quad (49)$$

For this case, we have solved numerically the equations (7) (17) (18) (19) in p , q , r , E_{eff} (given a predefined set of values for E_i, E_f) and show the results in numerical tables (in Appendix; the energies are indicated with an additional index n because they all have been normalized to the value $\hbar^2\alpha^2/(8\pi^2\mu)$). Amongst other, the tables show that E_{eff} , consistently, always lies between the values E_i, E_f . This gives sense to the coefficients p , q , r and to our model comprehensively. Numerical values for the coefficients c_i , c_f appearing in equations (21) and (23) for the probability density are also given. They all come out positive numbers as they must, for a consistent density definition. At last, we solved the equations (38) and (39) for the case at hand and show here the resulting distorted time-laws. As is clear by simple inspection, they give space vs time relations for a couple of colliders starting in $x_i = \infty$ at a time $t = -\infty$ with energy E_i ; joining the maximum approach distance $x_0 = -(1/\alpha) \ln[E_{eff}/D]$ when $t = 0$ with an energy E_{eff} ; and going back to far distances $x_f = \infty$ at a time $t = \infty$ with final energy now changed into E_f :

$$x_i(t) = \sqrt{\frac{2E_i}{\mu}}t - \frac{1}{\alpha} \ln[4\frac{E_{eff}}{D}] + \frac{2}{\alpha} \ln[1 + \exp[-\sqrt{\frac{2E_i}{\mu}}\alpha t]] \quad (50)$$

$$(-\infty < t \leq 0)$$

$$x_f(t) = -\sqrt{\frac{2E_f}{\mu}}t - \frac{1}{\alpha} \ln[4\frac{E_{eff}}{D}] + \frac{2}{\alpha} \ln[1 + \exp[\sqrt{\frac{2E_f}{\mu}}\alpha t]] \quad (51)$$

$$(0 \leq t < \infty)$$

From equations (34), (35) we finally have the energy time-law

$$E(t) = E_i + 4\frac{E_{eff} - E_i}{[1 + \exp[-\alpha\sqrt{\frac{2E_i}{\mu}}t]]^2} \exp[-\alpha\sqrt{\frac{2E_i}{\mu}}t] \quad (52)$$

$$(-\infty < t \leq 0)$$

$$E(t) = E_f + 4 \frac{E_{eff} - E_f}{[1 + \exp[\alpha \sqrt{\frac{2E_f}{\mu}} t]^2]} \exp[\alpha \sqrt{\frac{2E_f}{\mu}} t] \quad (53)$$

$$(0 \leq t < \infty)$$

To the purposes of the next section, we also add here the expression of the factor η for the case at hand here :

$$\eta(E) = \beta_i \alpha E_{eff}^2 \frac{(E - E_i)^2}{(E_{eff} - E_i)^2} \quad E_i \leq E < E_{eff} \quad (54)$$

$$\eta(E) = \beta_f \alpha E_{eff}^2 \frac{(E - E_f)^2}{(E_{eff} - E_f)^2} \quad E_f \geq E > E_{eff} \quad (55)$$

8 Ergodic model

By the remarks in previous sections, we now come to the following view. Assuming - as we have said to be generally our case - that the semi-classically calculated probability $P_{sc}(E)$ evaluates at “unperturbed energy”, we have found that a weight factor $\eta(t)$ is necessary in equation (26) for good modelling. If improved definitions (or more accurate calculations as well) for $P(E)$, $\Delta S_{sc}(E)$ and for the transfer time-law $E(t)$ could be used, we would expect this factor to be gradually reduced to unity, so that the ergodic equation (27) is satisfied. Such an outcome is expected because a quantum-mechanical probability is known to apply even to a single collision. But a straight (although somewhat artificial) way to achieve the result is simply as follows. We re-normalize our quantities including the factor η both in the $\Delta S_{sc}(E)$ and $P(E)$ expressions (by the energy time-law $E(t)$, consider now η as a function of E):

$$\Delta S_{sc}(E) = \ln P_{sc}(E) \rightarrow \Delta S'_{sc}(E) = \eta(E) \ln P_{sc}(E) \quad (56)$$

$$P(E) \rightarrow P'(E) = \frac{P(E)}{\eta(E)} \quad (57)$$

Then equations (13) and (26) write

$$P_{if}(E_i, E_f) = \exp \int_{E_i}^{E_f} \Delta S_{sc}(E) P(E) dE = \exp \int_{E_i}^{E_f} \Delta S'_{sc}(E) P'(E) dE \quad (58)$$

$$P'(E)dE = \frac{dt}{\tau} \quad (59)$$

and the general equation (27) is satisfied by $P'(E)$. This situation clearly features what we have called the ergodic model.

In this way, it is better expounded now that a proper definition of the collisional entropy must take into account the weight factor (so we can call η a “local entropy factor”). This is necessary in order to cut off the assumed FOPT expression $\ln P_{SC}(E)$ at far distances; then we also understand that the $\eta(E)$ definition is strictly correlated to the accuracy we can have in calculating the function $P_{SC}(E)$.

Amongst other, we see that equations (56) to (59) preserve the time-laws (50) to (53) we have found in the previous section for the given example ⁽⁵⁾.

At last, therefore, we propose here that the entropy definition (56), including factor η , be introduced from now on into the semi-classical-like transfer calculations; and that the function $P'(E)$ be correspondingly used. In such a way the popular semi-classical-like, “unperturbed energy” approximations are improved; and further refinements of our model simply have to point to greater accuracy in the evaluation of $\Delta S'_{SC}(E)$ and $P'(E)$ with correlated distorted potentials and time-laws forms.

9 Conclusion

In this paper, we have taken a very practical point of view for our demonstrations. They have been based on the “parametric” assumptions expressed by equations (7) and (15) to (19); but from a conceptual point of view, we believe having shown a great potentiality of the energy fluctuation model to obtain the exact quantum mechanical results in the domain at hand. Certainly, refinements or corrections must be applied in future developments of the model; as a matter of fact, many other specific examples should be analyzed in order to insure that it will still be suitable in some more extreme cases than here discussed (for instance, when a parabolic approximation for $P_{SC}(E)$ cannot be accepted). Yet the framework given here seems to us a rather general one, and useful to enlighten a subtended physical interpretation at a classical mechanics level. Then it may hopefully provide a further reference to the many attempts which still nowadays are diffusely carried out for a deeper understanding of the relations between classical and quantum physics.

⁵These time-laws do not depend on the value of τ , introduced in (26): yet equation (59) shows that normalizing to unity the density $P'(E)$ for the assumed example requires $\tau \rightarrow \infty$ (this may look improper at a first glance but is not a model failure. It is instead a mathematical paradox generated by the fact that the potential (47) is analytically defined in the space domain $(-\infty < x < \infty)$ of infinite extension). Simple approximations cutting off the exponential tails in the energy time-law can easily eliminate this computational edge.

10 References

- [1] MASTROCINQUE G., Annales de la Fondation Louis de Broglie, 27, 113 (2002); 27, 661 (2002)
- [2] MASTROCINQUE G., Annales de la Fondation Louis de Broglie, 27, 9 (2002); 28, 119 (2003)
- [3] EINSTEIN A., Phys. Z. 10, 185 (1909)
- [4] BOHM D. and VIGIER J. P., Phys. Rev. 96, 208 (1954)
- [5] KAPITZA P. L., Usp. Fiz. Nauk 44, 7 (1951)
- [6] KAPITZA P. L., Zh. Eksp. Teor. Fiz. 21, 588 (1951)

- [7] LANDAU L. D. and LIFSHITZ E. M., Mécanique (a, § 30; b, (§22)), Mir, Moscou (1969)
- [8] LANDAU L. D. and LIFSHITZ E. M., Meccanica Quantistica (§ 41), Boringhieri, Torino (1969)
- [9] SHIN H. K., Chem. Phys. Lett. 18, 359 (1973)
- [10] MASTROCINQUE G., Nuovo Cimento B 91, 179 (1986)
- [11] ZENER C., Phys. Rev. 38, 277 (1931)
- [12] ZENER C., Proc. Cambridge Philos. Soc. 29, 136 (1933)
- [13] ALDER K. and WINTHER A., Phys. Rev. 96, 237 (1954)
- [14] ALDER K., BOHR A., HUUS T., MOTTELSON B. and WINTHER A., Rev. Mod. Phys. 28, 432 (1956); 30, 353 (1958)
- [15] BIEDENHARN L. C. and THALER R. M., Phys. Rev. 104, 1643 (1956)
- [16] MASTROCINQUE G. and QUARTIERI J., Lett. a Nuovo Cimento 33, 227 (1982)
- [17] LANDAU L. D. and LIFSHITZ E. M., Statistical Physics (§ 110), Pergamon Press, London (1969)
- [18] MASTROCINQUE G. and FORESTI M., Lett. Nuovo Cimento 44, 678 (1985)
- [19] MASTROCINQUE G., Nuovo Cimento B 105, 1315 (1990)
- [20] MASTROCINQUE G., Nuovo Cimento B 111, 1 (1996); 111, 19 (1996)
- [21] BOHR N., Kgl. Dansk. Vid. Selsk. 18, No 8 (1948)
- [22] TREANOR C. E., J. Chem. Phys. 43, 532 (1965)
- [23] GENTRY W. R. and GIESE C. F., J. Chem. Phys. 63, 3144 (1975)

- [24] BLOCH F., Ann. Phys. (Leipzig) 16, 285 (1933)
- [25] LIVINGSTON M. S. and BETHE H. A., Rev. Mod. Phys. 9, 245 (1937)

- [26] SOMMERFELD A., Ann. Phys. (Leipzig) 11, 257 (1931)
- [27] ELWERT G., Ann. Phys. (Leipzig) 34, 178 (1939)
- [28] HEITLER W., The Quantum Theory of Radiation, 2nd and 3rd edition, Clarendon Press, Oxford (1949,1954)
- [29] JACKSON J. D., Classical Electrodynamics (Ch.13), J. Wiley & Sons, N. Y. (1962)

[30] JACKSON J. D. and MOTT N. F., Proc. of Royal Soc London, Ser. A, 13, 703 (1932)

11 Appendix

Energies are normalized to the value of $\hbar^2\alpha^2/(8\pi^2\mu)$:

$$E_n = E \frac{8\pi^2\mu}{(\hbar\alpha)^2} = E \xi \quad (60)$$

Initial energies E_{ni} values set : 0.01, 0.1, 1, 10; final energies E_{nf} values set : 1.1 E_{ni} , 2 E_{ni} , 5 E_{ni} , 10 E_{ni} , 100 E_{ni} .

The effective values of the coefficients p , q , r , c_i , c_f in the text can be obtained as

$$p = p^* + \ln\left[\frac{\mu}{M}\right] \quad (61)$$

$$q = q^*\xi \quad (62)$$

$$r = r^*\xi^2 \quad (63)$$

$$c_i = c_i^*\xi^{3/2} \quad (64)$$

$$c_f = c_f^*\xi^{3/2} \quad (65)$$

In normalized energies, equation (19) reads

$$\begin{aligned} & \ln \frac{(E_{nf} - E_{ni})}{4 \sinh^2[(E_{nf} - E_{ni})/(4\sqrt{E_{neff}})]} = \\ & = p^* + q^* E_{neff} + r^* E_{neff}^2 = \ln \frac{(E_{nf} - E_{ni}) \sinh[\sqrt{E_{ni}}] \sinh[\sqrt{E_{nf}}]}{(\cosh[\sqrt{E_{ni}}] - \cosh[\sqrt{E_{nf}}])^2} \quad (66) \end{aligned}$$

Numerical results in matrix form :

p^* -matrix

$E_{ni} \backslash E_{nf}$	1.1 E_{ni}	2 E_{ni}	5 E_{ni}	10 E_{ni}	100 E_{ni}
.01	2.23596	0.202606	-0.857248	-1.49367	-5.36067
.1	2.23591	0.198892	-0.902454	-1.69066	-14.1228
1	2.23542	0.160998	-1.34215	-3.37732	-46.7355
10	2.23018	-0.229697	-4.82182	-12.8193	-155.296

q^* -matrix

$E_{ni} \setminus E_{nf}$	$1.1E_{ni}$	$2E_{ni}$	$5E_{ni}$	$10E_{ni}$	$100E_{ni}$
.01	190.729	142.859	94.4094	70.6733	41.8346
.1	19.0733	14.3089	9.61277	7.5787	7.6821
1	1.90775	1.45499	1.12982	1.16651	1.84438
10	0.191263	0.172065	0.244696	0.328942	0.57032

r^* -matrix

$E_{ni} \setminus E_{nf}$	$1.1E_{ni}$	$2E_{ni}$	$5E_{ni}$	$10E_{ni}$	$100E_{ni}$
.01	-4543.75	-2451.14	-901.781	-408.369	-35.098
.1	-45.4386	-24.5566	-9.20462	-4.41324	-0.61502
1	-0.454505	-0.250487	-0.11055	-0.069621	-0.013804
10	-0.0045602	-0.0030882	-0.0025723	-0.0020053	-0.00042378

E_{neff} -matrix

$E_{ni} \setminus E_{nf}$	$1.1E_{ni}$	$2E_{ni}$	$5E_{ni}$	$10E_{ni}$	$100E_{ni}$
.01	0.0104881	0.0141442	0.0223938	0.0317899	0.118086
.1	0.104883	0.141624	0.226769	0.33162	2.01687
1	1.04898	1.43014	2.44604	3.98171	29.2961
10	10.4937	14.5588	26.1582	43.2888	302.462

c_i^* -matrix

$E_{ni} \setminus E_{nf}$	$1.1E_{ni}$	$2E_{ni}$	$5E_{ni}$	$10E_{ni}$	$100E_{ni}$
.01	35246.3	1546.28	337.819	158.298	17.4064
.1	1113.55	48.4099	10.1826	4.42445	0.195919
1	34.9472	1.41835	0.240221	0.0807895	0.00279939
10	1.08381	0.0388011	0.00567654	0.00193994	0.0000823099

c_f^* -matrix

$E_{ni} \setminus E_{nf}$	$1.1E_{ni}$	$2E_{ni}$	$5E_{ni}$	$10E_{ni}$	$100E_{ni}$
.01	31939.5	753.116	61.892	13.519	0.158741
.1	1010.93	24.0281	2.03332	0.469957	0.0101988
1	32.2082	0.813318	0.0814118	0.0226249	0.000552783
10	1.03824	0.0293344	0.00327535	0.000883702	0.0000183646

Last scientific revision : 11.01.07