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2008 J. Phys.: Condens. Matter 20 374103

(http://iopscience.iop.org/0953-8984/20/37/374103)

IOP PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **20** (2008) 374103 (7pp) doi:10.1088/0953-8984/20/37/374103

Simple theory of current fluctuations and noise in bridge-mediated nano-junctions

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Received 4 April 2008, in final form 26 April 2008
Published 26 August 2008
Online at stacks.iop.org/JPhysCM/20/374103

Abstract

We develop a simplified, model theory of noise caused by highly damped oscillating conformational fluctuations of a chain molecule mediating a nano-junction. Considering the most 'primitive' approximation of direct tunneling of electrons and barrier coupling with collective coordinates that describe internal conformations of the chain molecule, we derive approximate analytical formulas for the temporary current correlation function, noise power, and Fano factor. We analyze the role of different cumulative parameters of the model that affect the noise, as well as the effect of the temperature and of the number of groups in the chain. We present this analysis in expectation of experiments on this type of noise and in an attempt to trigger such experiments.

1. Introduction

Tunneling transport of electrons through nano-junctions can be strongly affected by fluctuations. This is known to influence the current dependence on temperature. Generally speaking, it is possible to gain additional information about the processes under study from the analysis of noise caused by such fluctuations. But in order to gain anything sensible from noise data, one must have a theory for such noise, and as well be sure that this noise pattern is dominating or at least distinguishable at the background of other sources of noise. But the second part of this statement is difficult to assess, before such theory is developed.

The interest in noise in tunneling junctions has a long history. Leaving aside the immense literature on conductance noise in quantum transport [1] and concentrating on the most recent studies of the effects of the molecular motions on bridge-mediated nano-junctions (for a comprehensive review with the focus on vibronic effects see e.g. [2]) we wish to outline the following main trends.

'*Ex situ*', dry wired nano-junctions, as well as '*in situ*' (in solution) are considered in the literature, but a clear cut distinction between the two cases is not always made in particular publications. The following aspects of the problem are usually considered, often separately.

There can be a 'trivial' effect of stochastic switching, related to connection or disconnection of the bridge to one of the terminals, often leading to a spectacular contribution to the noise [3]. This, however, can be, in principle, excluded by chemically anchoring the ends of the bridge molecules to the electrodes.

A set of different noise patterns are considered, related to:

- Switching between different channels for electron transport (as in Büttiker [4] or Troisi and Ratner [5]), which could manifest itself in shot-noise measurements [6].
- Mesoscopic and collective electronic effects in a nano-junction leading to not fully understood patterns of noise [7].
- Inelastic effects on shot noise due to electron–phonon interactions [8, 9], including also resonance tunneling effects and Coulomb blockade [10, 11].
- Bridge free junctions with a noise caused by the translational [12, 13] or orientational [14] motion of molecules.

In this paper, we perform a very simple, perhaps oversimplified study of the system in which the effects of the fluctuations on the current have been detected and theoretically understood, as a development of the theory of electron tunneling under the barrier formed by a chain molecule with independently fluctuating chain elements [15]. That theory, call it a semi-phenomenological one, is of entirely 'mean-field' kind; it has no electron correlation effects, no inelastic

tunneling, and no resonance tunneling, but it has successfully described experimental data of [16] on the dependence of the activation energy of the tunneling current on the length of the bridge molecule of alkanedithiol type. The same model also described other regimes of temperature dependence [15], which have not yet been experimentally studied. It has also revealed intriguing rectifying properties in the nonlinear current–voltage characteristics [17]. It seemed, therefore, reasonable to work out a basis for the study of noise patterns in this simple model.

2. The model and formulation of the problem

Before going any further, we state more precisely what our model will not contain. We will not consider effects related with the discrete nature of tunneling electrons. In what follows it is assumed that the fluctuations along the degrees of freedom coupled with electron transport are very slow. Thus, at each set of values of collective coordinates $\{q_i\}$, that describe these degrees of freedom, a large number of electrons tunnel between the electrodes, resulting in a current $i\{q_i\}$. In other words we assume that the situations where no electrons or a just a few tunnel within the characteristic time interval t'–t, corresponding to two neighboring values of $\{q_i\}$, are negligibly rare. And, as mentioned above, we will not consider multi-electron correlation effects, inelastic or resonance tunneling.

Under these assumptions the current density at each time moment t is equal to

$$i = ev_{\mathrm{F}}\rho\Delta\varepsilon\Gamma \tag{1}$$

where ρ is the density of electron states in the metal, $\Delta\varepsilon \sim eV_{\mathrm{bias}}$ is the characteristic energy interval contributing in the current, v_{F} is the average velocity of an electron at the Fermi level, and Γ is the Gamow tunnel factor

$$\Gamma = \exp\left(-\frac{2}{\hbar}l\sum_{i=1}^{N}\sqrt{2m\left[V_i-\varepsilon_{\mathrm{F}}\right]}\right). \tag{2}$$

Here, $\hbar = h/2\pi$, h being the Planck constant, m is the mass (or an effective mass) of the electron, l is the length of each 'ith' chain element, N is the number of chain elements, and V_i is the height of the tunneling barrier across this element.

The effect of fluctuations on the barrier will be approximated by

$$V_i = V_{\min} + \gamma\left(q_i - Q\right)^2. \tag{3}$$

This form means that the barrier is minimal at a certain optimal conformation when $q_i = Q$, and it is larger at any other one; γ is a constant that couples the barrier with the fluctuations of q_i. Using a quadratic form is the simplest way to approximate this effect, which as we will see later allows for an analytical solution of the problem.

The latter, however, will not be possible without a further simplification—expanding the square root in the exponent

$$\Gamma \approx \exp\left\{-\frac{2}{\hbar}L\sqrt{2mU} - \frac{2}{\hbar}l\gamma\sqrt{\frac{m}{2U}}\sum_{i=1}^{N}\left(q_i-Q\right)^2\right\}, \tag{4}$$

where $L = lN$ is the length of the whole chain. Expansion (4) assumes that for each chain element the fluctuations are small. Using equations (4) and (1) we may write the current in the form

$$i = i_0\exp\left\{-b\sum_{i=1}^{N}\left(q_i-Q\right)^2\right\}. \tag{5}$$

Here i_0 is the current in the configuration optimal for tunneling (all $q_i = Q$),

$$i_0 = ev_{\mathrm{F}}\rho\Delta\varepsilon\exp\left\{-\frac{2}{\hbar}L\sqrt{2mU}\right\} \tag{6}$$

$$b = l\gamma\frac{1}{\hbar}\sqrt{\frac{2m}{U}}; \qquad U = V_{\min} - \varepsilon_{\mathrm{F}}. \tag{7}$$

We will assume hereafter that the ground state for all the fluctuating degrees of freedom is reached at $q_i = 0$. In other words, in order to reach optimal configuration the coordinate q_i should fluctuate to Q. In the ground state the current is smaller than the maximal current by a factor

$$\exp\left\{-b\sum_{i=1}^{N}\left(q_i-Q\right)^2\right\}\Big|_{q_i=0} = \exp\{-bQ^2N\}.$$

For a long molecule ($N \gg 1$) this could comprise orders of magnitude!

This model is rather formal and it is not easy to establish one-to-one correspondence of its parameters with the microscopic parameters of each specific molecule, but it 'semi-phenomenologically' takes into account the main physical effects (a 'chemical' justification of this model for alkanedithiols was given by Haiss *et al* [16] and analyzed in some detail in [15]). Namely, the pertinent modes of each chain element that affect the tunneling barrier may conform to reduce the barrier, and the configuration that facilitates tunneling is a higher energy one. Thus, this configuration will not be the most probable one, but most efficient for tunneling, and the tunneling electrons will have a chance to utilize this configuration. The way how this proceeds is considered in the next section.

3. Current correlation function

The goal of further treatment is the calculation of the correlation function

$$K\left(t\right) = \langle i\left(t\right)i\left(0\right)\rangle - \langle i\rangle^2 \tag{8}$$

and related quantities.

Assuming that all q_i are independent, we write

$$\langle i\left(t\right)i\left(0\right)\rangle = i_0^2\mathrm{e}^{-2bNQ^2}\left[s\left(t\right)\right] \tag{9}$$

where

$$s\left(t\right) = \langle \mathrm{e}^{-bq^2(t)-bq_0^2+2bQ\left[q(t)+q_0\right]}\rangle^N \tag{10}$$

and $q_0 = q\left(0\right)$. Technically, the average sign here means

$$\langle\cdots\rangle = \int \mathrm{d}q\,\mathrm{d}q_0 P\left(q_0\right)\mathrm{P}\left(q|t;\,q_0\right)\cdots \tag{11}$$

where $P(q_0)$ is the equilibrium distribution function of an oscillator

$$P\,(q_0) = (2\pi k_{\rm B}T/\hbar\omega)^{-1/2} \exp\left(-\frac{\hbar\omega q_0^2}{2k_{\rm B}T}\right) \tag{12}$$

whereas $P(q|t; q_0)$ is the probability of having a value q at time t provided it was q_0 at time $t = 0$. To proceed further we need to adopt a model of the random process that generates fluctuations of q. This model will specify $P(q|t; q_0)$.

4. Analytical expression for the current correlation function in the model of overdamped modes

The model for $P(q|t; q_0)$ will be based on a strong assumption, but which is physically plausible for *in situ* junctions. We will assume that oscillations of q_i are *overdamped*, and thus [18]

$$\mathrm{P}\,(q|t; q_0) = \left[2\pi\frac{k_{\rm B}T}{\hbar\omega}\left(1-\mathrm{e}^{-2t/\tau}\right)\right]^{-1/2} \times \exp\left\{-\frac{\hbar\omega\left(q-q_0\mathrm{e}^{-t/\tau}\right)^2}{2k_{\rm B}T\left(q-q_0\mathrm{e}^{-2t/\tau}\right)}\right\}. \tag{13}$$

One may expect that this may be true when the fluctuating fragments of the molecule are large, whatever it means. For instance, if the bridge molecule consists of a chain of aromatic rings, their rotation will meet even stronger resistance than the rotation of water molecules, which are known to be strongly damped. The friction against rotation of such rings caused by the resistance of the surrounding solvent will be the stronger, the larger the rings (especially if the rings have long substituents). But even for the chain of alkanedithiols the rotation of each chain element around the main axis of the chain in water is not friction-free, and the friction should be of the same order of magnitude as for rotation of water molecules themselves. Somehow, one must not forget about the assumption underpinning equation (13): for a bridged-system for which the oscillator modes are not overdamped the expressions derived below will not be valid.

To keep notations compact we will use below dimensionless variables

$$x_0 = q_0\sqrt{\hbar\omega/2k_{\rm B}T}; \qquad x = q\sqrt{\hbar\omega/2k_{\rm B}T}. \tag{14a}$$

and parameters

$$Y = Q\sqrt{\hbar\omega/2k_{\rm B}T}; \qquad B = b2k_{\rm B}T/\hbar\omega; \qquad \beta = B/(1+B). \tag{14b}$$

With these notations equation (10) takes the form

$$s\,(t) = \left\{\frac{1}{\pi}\frac{1}{\sqrt{1-u^2}}\int \mathrm{d}x_0\,\mathrm{d}x\,\exp\left(-H\,(x, x_0)\right)\right\}^N, \tag{15}$$

where

$$H\,(x, x_0) = \left\{x_0^2 + \frac{(x-x_0u)^2}{1-u^2} + B\left(x^2 - 2Yx\right) + B\left(x_0^2 - 2Yx_0\right)\right\} \tag{16}$$

and

$$u = \mathrm{e}^{-t/\tau}. \tag{17}$$

For the calculation of the integral in equation (15) u is just a 'parameter'. The integral is Gaussian and thus can be calculated exactly. It is equal to

$$\left(2\pi/\sqrt{D}\right)\exp\left[-H\left(x^*, x_0^*\right)\right] \tag{18}$$

where D is the determinant of second derivatives of H

$$D = \frac{4}{1-u^2}\left[1+2B+B^2\left(1-u^2\right)\right] \tag{19}$$

and (x^*, x_0^*) is the point of minimum of $H\,(x, x_0)$

$$x^* = x_0^* = \frac{BY\left(1-u^2\right)}{1+B\left(1-u^2\right)-u} = \frac{BY\,(1+u)}{1+B\,(1+u)}. \tag{20}$$

As a result we obtain an exact expression for $s\,(t)$

$$s\,(t) = \left(\sqrt{\frac{1}{1+2B+B^2\left(1-u^2\right)}}\right)^N \times \exp\left\{\frac{2NB^2Y^2\,(1+u)}{1+B\,(1+u)}\right\} \tag{21}$$

where the t-dependence is involved only in u.

In a similar way we obtain the expression for $\langle i\rangle^2$

$$\langle i\rangle^2 = i_0^2\frac{1}{(1+B)^N}\exp\left\{-\frac{2BNY^2}{1+B}\right\} \tag{22}$$

where it is taken into account that $bQ^2 = BY^2$.

Combining equations (9), (21), and (22) we obtain for $K\,(t)$ in equation (8) an exact expression

$$K\,(t) = i_0^2\frac{1}{(1+B)^N}\exp\left\{-\frac{2NBY^2}{1+B}\right\} \times \left\{\left(\sqrt{\frac{(1+B)^2}{1+2B+B^2\left(1-u^2\right)}}\right)^N \times \exp\left\{\frac{2NB^2Y^2u}{(1+B)\,(1+B+Bu)}\right\} - 1\right\}. \tag{23}$$

Using the notation for β introduced in equation (14) we may rewrite it in a slightly more compact form,

$$K\,(t) = i_0^2\,(1-\beta)^N\exp\left\{-2N\beta Y^2\right\} \times \left\{\left(\sqrt{\frac{1}{1-\beta^2u^2}}\right)^N \exp\left\{\frac{2N\beta^2Y^2u}{(1+\beta u)}\right\} - 1\right\}. \tag{24}$$

5. Noise power

Aiming to calculate below the so-called *noise power*

$$S\,(\omega = 0) = \int_0^\infty \mathrm{d}t\;K\,(t) \tag{25}$$

and keeping in mind that the main contribution to this integral comes from the K-values at small t, we introduce a new function which is small at small t

$$v\,(t) = 1 - u\,(t) = 1 - \exp\left(-t/\tau\right). \tag{26}$$

In terms of this new variable the noise power takes the form

$$S(\omega = 0) = \tau \int_0^1 \mathrm{d}v\, K(v)/(1 - v) \tag{27}$$

where the correlation function in terms of $v(t)$ reads

$$K(t) = i_0^2 (1-\beta)^N \mathrm{e}^{-2N\beta Y^2} \left\{ \left(\sqrt{\frac{1}{1-\beta^2(1-v)^2}} \right)^N \times \exp\left\{ \frac{2N\beta^2 Y^2 (1-v)}{1+\beta(1-v)} \right\} - 1 \right\}. \tag{28}$$

The integral in equation (27) with expression (28) for the v dependence of K can be easily calculated numerically. We, however, may obtain an approximate result for the noise power, if we approximate expression $K(t)$ by its expansion near $v = 0$, i.e.

$$K(t) \approx i_0^2 \left(\frac{1-\beta}{1+\beta} \right)^{N/2} \exp\left\{ -\frac{2N\beta Y^2}{1+\beta} \right\} \times \exp\left\{ -N\beta^2 \left[\frac{2Y^2}{(1+\beta)^2} + \frac{1}{1-\beta^2} \right] v \right\}. \tag{29}$$

Insertion of equation (27) into equation (28) and replacement of $1 - v$ by 1 in the denominator of the integrand gives an approximate expression for the noise power

$$S(\omega = 0) \approx \tau i_0^2 \left(\frac{1-\beta}{1+\beta} \right)^{N/2} \frac{\exp\left(-\frac{2N\beta Y^2}{1+\beta} \right)}{N\beta^2 \left[\frac{2Y^2}{(1+\beta)^2} + \frac{1}{1-\beta^2} \right]}. \tag{30}$$

6. The Fano factor

It is common to represent the noise power in the form

$$S(\omega = 0) = 2e \langle i \rangle F \tag{31}$$

where the coefficient F (which has a dimension of inverse area) is known under the name of the *Fano factor*. Equation (22) for the average current in the same notation has the form

$$\langle i \rangle = i_0 (1-\beta)^{N/2} \exp\left(-N\beta Y^2 \right). \tag{32}$$

We hope that the definition of the Fano factor in equation (31) in terms of the current *density* (rather than in terms of the current commonly used) will not provoke any confusion since the conversion to the common definition is trivial. Moreover, the Fano factor defined by equation (31) involves the factor $i_0\tau/e$ which depends on the bias voltage and relaxation time and therefore through these parameters it depends on the specific experimental conditions. Therefore, let us discuss below a *reduced Fano factor*, a dimensionless quantity defined as

$$F^{\mathrm{r}} = eF/i_0\tau. \tag{33}$$

It is not that this quantity is a directly measurable one. We simply focus the analysis on the part that does not include i_0 and τ, as we may not know these values.

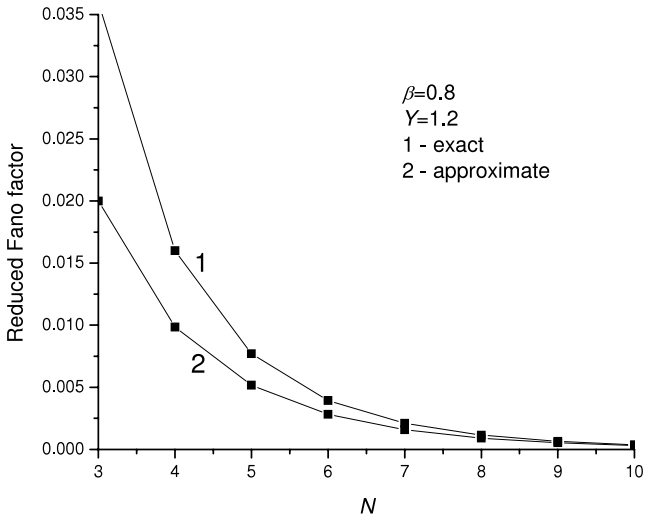

Figure 1. Example of the reduced Fano-factor dependence on the number of the chain elements in the bridge molecule, calculated using equations (33) and (34) {exact formulas}, as compared with the one given by (33) and (35) {approximate formulas}. The reduced Fano factor decreases with the increase of N, as should be expected. Its absolute values calculated according to approximate formulas differ significantly from the exact ones.

The exact expression for the reduced Fano factor reads

$$F^{\mathrm{r}} = (1-\beta)^{N/2} \mathrm{e}^{-N\beta Y^2} \frac{1}{2} \int_0^1 \frac{\mathrm{d}v}{1-v} \left\{ \left[\frac{1}{1-\beta^2(1-v)^2} \right]^{N/2} \times \exp\left\{ \frac{2N\beta^2 Y^2 (1-v)}{1+\beta(1-v)} \right\} - 1 \right\}. \tag{34}$$

This integral can be easily calculated numerically for given parameters; an approximate form gives us an analytical expression

$$F^{\mathrm{r}}_{\mathrm{approx}} \approx \frac{1}{2} \frac{1}{(1+\beta)^{N/2}} \frac{\exp\left[-\frac{N\beta(1-\beta)Y^2}{1+\beta} \right]}{N\beta^2 \left[\frac{2Y^2}{(1+\beta)^2} + \frac{1}{1-\beta^2} \right]}. \tag{35}$$

Figure 1 shows the reduced Fano factor as a function of the number N of the elements of the chain molecule and figure 2 presents its normalized value (with respect to its value at $N = 3$). Figures 3–5 show similar dependences on the strength of coupling with vibrations, represented by the quantity β, and figures 6 and 7 on the value of the coordinate corresponding to the optimum potential barrier, Y (i.e. Q), characterizing how far from the ground state it lies.

7. Noise dependence on the characteristics of the bridge and temperature

The most interesting dependences which could be sought in experimental studies are the length and temperature dependences of the noise. Figures 1 and 2 show the dependence of the Fano factor on the length of the molecule. It decreases with the increase of N, which agrees with the general result on the relative decrease of fluctuations with the increase of the number of independently fluctuating

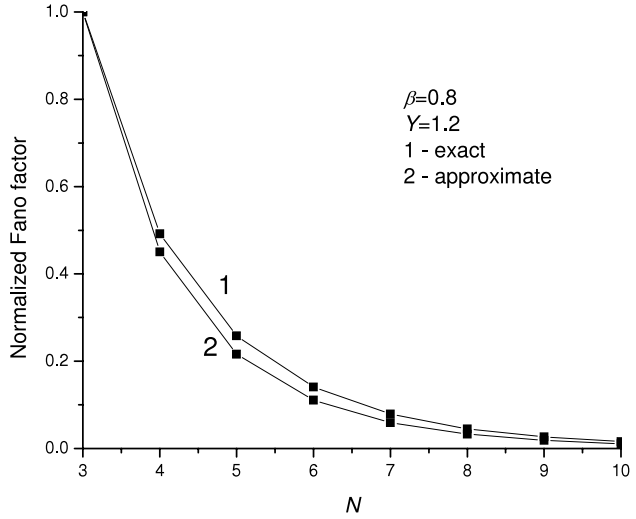

Figure 2. The same as in figure 1, but for the Fano factor normalized to its value at $N = 3$. The approximate formula describes well the relative behavior of the Fano factor.

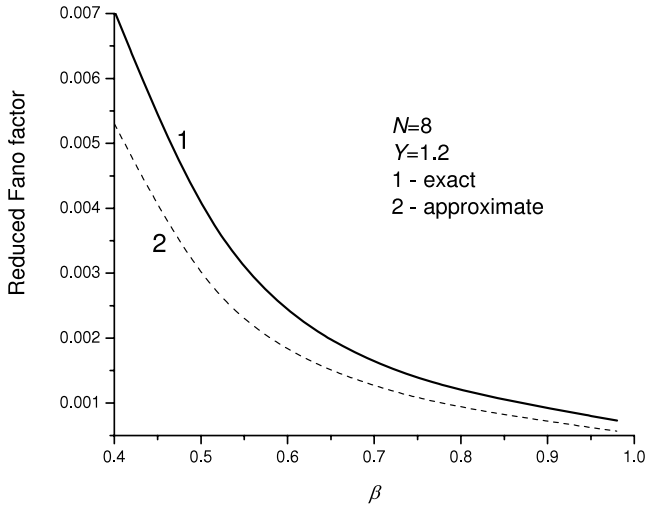

Figure 4. The same as in figure 3 but at moderate and large β-values where approximate formula can be used.

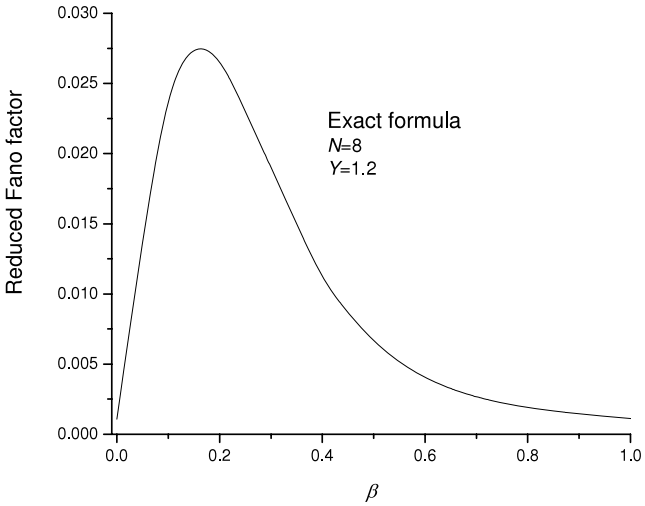

Figure 3. The same as in figure 1 but as a function of the strength of coupling with vibrational modes. The β-dependence shows a maximum that is understood from the behavior of the correlation function at small and large β (see the text).

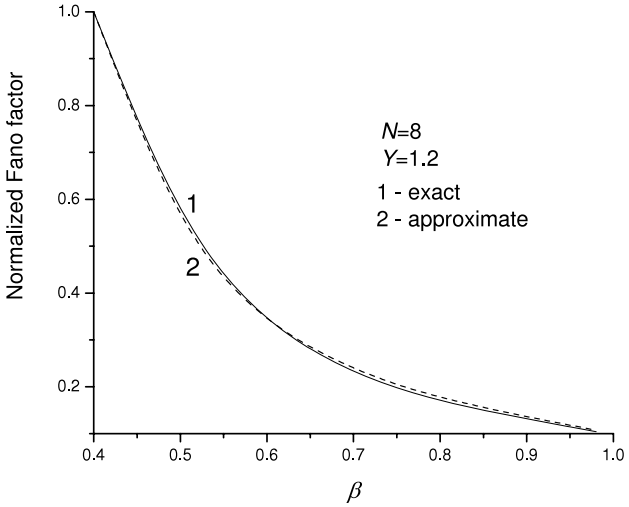

Figure 5. The same as in figure 4 but for the Fano factor normalized to its value at $\beta = 0.4$. This figure demonstrates that the approximate formula provides a good relative behavior of the Fano factor also as a function of the coupling strength (cf to figure 2).

elements. Figures 3–7 show the dependence of the Fano factor on cumulative, dimensionless parameters β and Y that characterize different effects through combined quantities. β characterizes the value of the coupling constant b relative to the characteristics of the thermal fluctuations $\hbar\omega/2k_BT$. Similarly, Y characterizes the value of the dimensionless normal coordinate corresponding to the maximum decrease of the potential barrier relative to $(\hbar\omega/2k_BT)^{-1/2}$.

Therefore the dependence of the Fano factor shown in figures 3–5, when being considered at fixed temperature, is in fact its dependence on the coupling constant b. As seen from figure 3 the dependence of the Fano factor on β reveals a maximum and tends to zero at small and large values of β. This behavior can be understood keeping in mind that in the limit $\beta \to 0$ (i.e. $b \to 0$) the fluctuations do not alter the height of the potential barrier, i.e. there is simply no noise. At large values of β the main contribution to the current comes from the region near $q = Q$ the width of the region decreasing with the increase of β.

In the region of β-values after the maximum point the approximate expression for the Fano factor may be also used (see figures 4 and 5). As seen from figure 4 the accuracy of the approximate formula in the absolute values of the Fano factor is rather poor. However, it reproduces rather well its 'relative' behavior (figure 5).

The dependence of the Fano factor on Y being considered at constant temperature is in fact its dependence on Q (figures 6 and 7). The reason for its decrease with the increase of Y is the same as in the case of its dependence on β.

In order to calculate the temperature dependence, one should take into account that both β and Y depend on the temperature. The result is shown in figure 8. In general

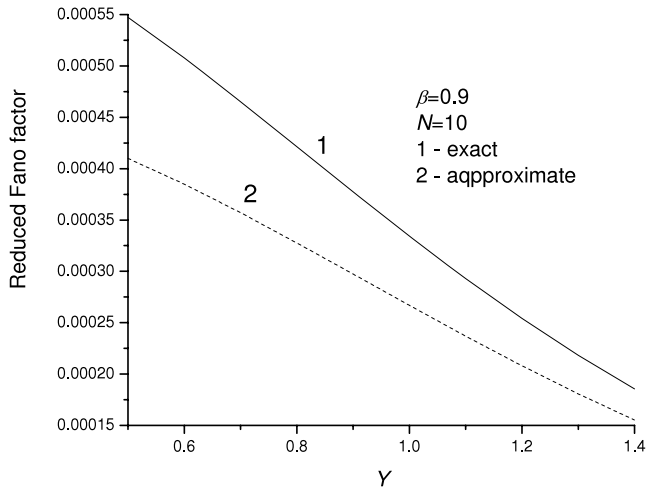

Figure 6. The same as in figure 1, but as a function of the coordinate of the optimal potential barrier. The demand for larger fluctuations needed to reach an optimum value of the height of the potential barrier results in narrowing of the region giving contribution to the current and therefore to a decrease of the Fano factor.

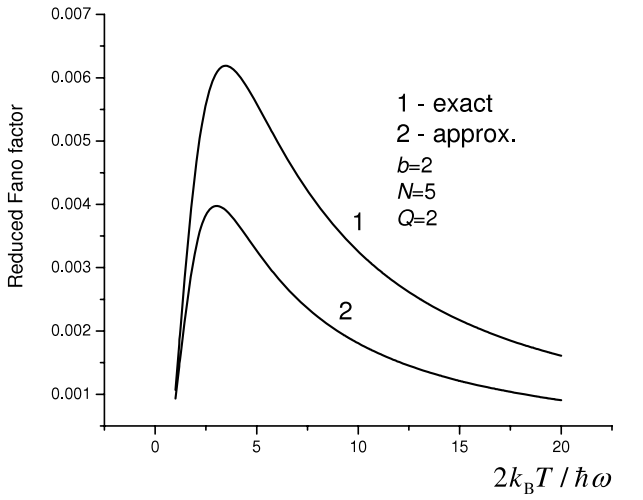

Figure 8. Dependence of the reduced Fano factor (equation (33)) on reduced temperature. The qualitative shape of the curve is similar to that for the β-dependence, showing that the temperature dependence involved in Y is not quite significant at moderate Q-values.

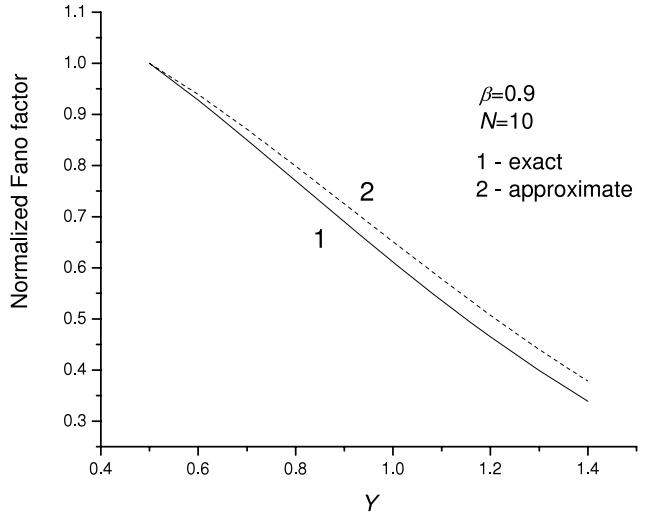

Figure 7. The same as in figure 6, but for the Fano factor normalized to its value at $Y = 0.4$. Again the relative behavior provided by the approximate formula is better than the absolute values.

the temperature dependence is qualitatively similar to the β-dependence. The role of the parameter Y is not of great importance at moderate Q-values.

Note that the temperature enters in combination $k_BT/\hbar\omega$, thus showing this combined variable in the range of 1–50, although, of course, we do not mean to vary temperature in that range! This plot instructs us that we may expect both growth or decrease of the Fano factor with temperature, depending on which side of the maximum we are.

The length dependence of the reduced Fano factor follows the expected trend, the Fano factor decreasing with increase of the length. Its dependence on coupling constant and temperature at moderate Q-values is governed mainly by one parameter β. Still, how to rationalize in simple terms the non-monotonous character of the temperature dependence of the Fano factor, which has a maximum at intermediate temperatures? The physics of this effect is as follows.

At low temperatures the increase of the Fano factor with the temperature is quite trivial; it means that thermal fluctuations in this region are largely suppressed, and the increase of the temperature results in the increase of deviations from the equilibrium configuration. These deviations may be further from the optimal configuration or closer to it, but at low temperature it is still a problem to reach the optimal configuration—its average population is low. Somehow, those fluctuations that bring the system closer to the optimal tunneling configuration amplify the current more strongly than those fluctuations that move the system away from it decrease the current. In the end, thermal activation of such fluctuations reduces the barrier [14]. This increases the average current as well as the Fano factor.

When we further increase the temperature, reaching the optimal configuration for tunneling becomes no longer an issue. But the number of states around it is then visited so often and the width of the region becomes so large that it 'dilutes' the population of the optimal state and reduces the average current, as well as the Fano factor. This effect is certainly much less trivial. In between there must be a maximum! If detected experimentally, its existence would be a strong argument in favor of the considered model.

8. Conclusion

We have laid the basis for a description of noise in a tunneling current across the bridge molecule in a pure under-barrier tunneling mechanism of electron transport through it. Any further speculations would be hardly constructive prior to experiments, which are not available so far. We would be happy if this theory stimulated such experiments, but there are major challenges facing them, as there are a number of much more trivial, apparatus-related sources of noise (for discussion

see e.g. [19]), which must be subtracted from the overall signal. In comparing the results with experimental data one should also carefully compare the data against the prediction of other models, see e.g. [8, 9]. Note that in the considered model the reduced Fano factor is voltage independent, whereas the voltage dependence of the Fano factor scales with the voltage dependence of the average current. The theories based on inelastic tunneling predict more sophisticated behavior [8, 10].

Acknowledgments

The authors are thankful to the The Leverhulme Trust for a Visiting Professorship to AMK and to the Royal Society of London for the Wolfson Research Merit Award to AAK that supported this work.

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