Diffusivity, mobility and time-of-flight measurements: scientific fictions and 1/f-noise realization

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Influence of equilibrium thermal 1/f-type mobility fluctuations on time-of-flight measurements is considered. We show that it can explain experimental time dependencies of transient photocurrents.

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I. INTRODUCTION

It is well known that definite aspects of chaotic motion of quasi-free charge carriers in many materials can be described in terms of diffusivity, $D$, and mobility, $\mu$. According to definitions of these quantities in statistical physics, if $\Delta X(t)$ is displacement, or path, of a carrier during time interval $(0,t)$, and $t$ much exceeds characteristic memory time, $\tau_0$, of carrier’s random walk, then

\[ \frac{1}{t} \langle \Delta X^2(t) \rangle_0 = 2D, \]

\[ \frac{1}{t} \langle \Delta X(t) \rangle_f = \mu f, \]

where the angle brackets $\langle \ldots \rangle_0$ and $\langle \ldots \rangle_f$ denote averaging over thermodynamically equilibrium statistical ensemble and non-equilibrium one in presence of sufficiently weak force $f$ per carrier (to be precise, we consider projections of vectors just onto direction of this force).

Thus, $D$ and $\mu$ are averages over infinite variety of carriers. However, in practice many authors interpret relations (1–2) in the form like

\[ \Delta X(t) = \mu ft + \Delta_d X(t), \]

\[ \langle \Delta_d X^2(t) \rangle_f = 2Dt, \]

where $\Delta_d X(t)$ is “diffusive component” of the displacement. Thus, the ensemble averages $D$ and $\mu$ are assigned to a separate carrier as characteristics of its individual random trajectory!

Such the arbitrariness, or “scientific fiction”, implies illusion of complete knowledge of non-equilibrium noise which stays the same as in equilibrium. Consequently, in view of the Einstein relation, $D = T\mu$, one may think that at $\phi(t) \gg 1$, where

\[ \phi(t) = \frac{f\sqrt{Dt}}{T}, \]

the carriers’ displacement is almost non-random, and therefore the time-of-flight measurements of transient photocurrents (see e.g. works [1–6] and references therein) should give nearly ideal responses to pulse-like or step-like excitation (see Fig.1 and Fig.2).

In reality one observes [1–5] something qualitatively different, similar to what is shown in in Fig.1 and Fig.2.

Such the difference is conventionally explained as result of random variations of time of flight (TOF) because of trapping and de-trapping of excess carriers by localized states (the so-called “dispersive transport”, see e.g. [1–6] and references therein). This explanation indeed is good in many characteristic cases. But in many other cases it seems unsatisfactory. Perhaps, by this reason, for instance, in [2] the idea of “frozen” spatial variations of mobility was suggested.

Quite another explanation arises when one understand that the fantastic expression (3) should be replaced by a realistic one,

\[ \Delta X(t) = \tilde{\mu}(t)ft + \Delta_d X(t), \]

\[ \langle \tilde{\mu}(t) \rangle_f = \mu, \]

where $\tilde{\mu}(t)$ is random quantity even in absence of the trapping, merely because a separate carrier has no definite mobility (as well as a separate person does not have “mean life” and even may not know about it)! This statement is irrefutable, but its comprehension is prevented by prejudices of the naive probability-theoretical way of thinking instead of the fundamental statistical-mechanical one [7]. For the first this statement was argued in [8–11] in the course of unprejudiced statistical analysis of random walks of atomic-size particles and later in [14] (or see [15]) and in [17–20] was confirmed, by example of fluid molecules, as consequence of the first-principle equations of statistical mechanics.

Importantly, according to these investigations, a magnitude of fluctuations (uncertainty [10]) of individual mobility of charge carrier is generally on order of it itself (i.e. $\tilde{\mu} - \mu \sim \mu$). Therefore probability distributions of $\Delta X(t)$ taken at different values of the dimensionless force $\phi = \phi(t)$ (see above) differ one from another not only by their mean positions but also by their widths and shapes, as it is shown in Fig.3, so that real drift of a packet of even non-interacting carriers is accompanied by its spreading, approximately proportionally to both $t$ and $f$. Particular results of such drift are the dark-curve time dependencies in Figs.1–2.

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The purpose of the present paper is just to demonstrate that these effects of the native carrier’s mobility fluctuations resemble effects of the trapping.

II. WHY AND HOW MOBILITY FLUCTUATES BY ITSELF

Introducing related fluctuating diffusivity \( \bar{D}(t) = T \bar{\mu}(t) \), one can ask equivalently: why carrier’s diffusivity fluctuates by itself? The cause was explained in the mentioned works. It is temporal non-locality of such physical characteristics as diffusivity: the latter by its sense describes random motion of a carrier (or a particle in general) during time intervals significantly greater than the memory time \( \tau_0 \). Therefore at the end of any such interval the system already does not remember what took place at its beginning. Consequently, the system can not keep a definite value of the diffusivity.

If it is seen, then it is clear that resulting fluctuations (uncertainty) of diffusivity (and hence mobility), firstly, by their order of magnitude are comparable with its average value. Secondly, they can be arbitrary long, that is have no characteristic time scale, and thus represent a “flicker noise” whose power spectrum \( S_D(\omega) \) unboundedly grows at \( \omega \to 0 \). Thirdly, their probability distribution is close to a stable one.

Additional reasonings can be found in \[10–12, 14–24\]. To confirm them at fundamental level, we have to calculate statistical characteristics of the displacement \( \Delta X(t) \), such as its characteristic function \( \langle \exp[ik\Delta X(t)] \rangle \), merely following rigorous recipes and equations of the statistical mechanics. Or, at least, analyze admissible forms of \( \langle \exp[ik\Delta X(t)] \rangle \) at phenomenologically under minimum of assumptions.

For the first such investigation was made in \[8–10\] (or see \[16\]) where thermodynamically equilibrium random walk \( \Delta X(t) \) of an electron (or other particle) in spatially uniform medium was considered basing on the only assumption that it possesses diffusive scale invariance, \( \Delta X(st) \sim \sqrt{s} \Delta X(t) \) (the tilde symbolizes statistically locally uniform medium).
Just such statistics implies the displacement distributions shown in Fig. 3 by dark curves. Its physical meaning was explained in [11, 13, 16].

One can see that characteristic functions like (4) and mean presence of “flicker”, or 1/f-noise type, fluctuations in diffusivity and mobility, with low-frequency power spectrum, namely,

$$S_D \frac{D}{D^2} = \frac{S_\mu}{\mu^2} = \frac{2\pi \alpha(\omega)}{\omega}, \quad \alpha(\omega) \approx \frac{2r_0^2}{3D\tau_0 \ln^2(\tau_0\omega)} \quad (8)$$

This theoretical estimate very well agreed with experimental data in 1983 [12] and equally well agrees with new data about semiconductors [29], carbon nano-tubes [30], graphene layers and graphene transistors [31, 32] and other electronic devices (at that revealing origin of typical values of the “Hooge constant”, $\alpha(\omega) \sim 0.002$ [12]). It should be underlined again and again that this 1/f-noise is by its nature an integral part of the atomic thermal motion and exists even in ideal crystal structure in absence any traps (see explanations in [10, 12, 16, 21, 22]!),

The fundamental microscopic approach to analogous diffusivity and mobility fluctuations so far was tried only in case of molecular random walks in fluids [14, 20], on the base of the exact Bogolyubov equations [33].

In [14] (see also [13, 16]) it was found, for atoms of a gas, that

$$\frac{S_D(\omega)}{D^2} = \frac{S_\mu(\omega)}{\mu^2} \approx \frac{\pi}{\omega} \ln \frac{1}{\tau_0\omega}, \quad (9)$$

which satisfactorily agrees with experimental data on electrolytes [12, 34] (where the Hooge constant is anomalously large).
But the underlying probability distribution of diffusivity and mobility remained unknown. It was found in [17, 20] by means of more rough but deeper penetrating approximation, and its density can be expressed as

\[ U_\beta(x) = \frac{1}{x^{\beta+2}\Gamma(\beta+1)} \exp\left(-\frac{1}{x}\right), \quad (10) \]

with \( \beta > 0 \). The spectrum (10) arose in the case when \( \beta = 1 \) [17]. The corresponding probability density \( U_1(x) \) is shown in Fig. 4 by far grey curve. Evident property of all obtained distributions is that their most probable values are significantly smaller (three times at \( \beta = 1 \)) than their mean values.

Thus, both phenomenological and microscopical approaches to the native thermal mobility fluctuations (when being correctly performed) gave qualitatively identical results.

### III. MANIFESTATION OF THE NATIVE 1/F MOBILITY FLUCTUATIONS IN TOF EXPERIMENTS

The TOF measurements of excess (injected) probe particles, e.g., photo-excited charge carriers, usually presume that \( \phi(t) \gg 1 \). According to the aforesaid, this means that \( S_\mu f^2 \gtrsim 2T\mu \), that is at corresponding time intervals contribution to particle’s path fluctuations from 1/f diffusivity/mobility fluctuations exceeds contribution from diffusion itself (i.e. from white thermal noise). In other words, TOF experiments are first of all observations of the native diffusivity/mobility 1/f-noise.

Hence, it is reasonable first to consider such imaginary (but not fantastic) situations when the above mentioned simple theory is sufficiently adequate. This would determine a background of the TOF spectra which exists even in absence of specific effects like the “dispersive transport” (transport via a large number of free electron traps) jot taken into account by the theory.

At \( \phi(t) \gg 1 \), if knowing the mobility probability distribution, one can easy find that of TOF \( \tau = L/\mu f \)
(where $L$ is distance to be overcome) and resulting time dependence of transient current (flow), and vice versa. The distributions corresponding to characteristic function \( \Phi \) have no simple analytic expression but can be approximated by simple related distributions (10). Then calculation of of transient current become so trivial that its description can be omitted.

The results for short-pulse and step-like excitations are demonstrated on Fig.6 and Fig.7 where the currents are normalized to unit start value and unit steady-state value, respectively (\( \tau_f \) there is mean TOF value).

IV. DISCUSSION AND CONCLUSION

Visual comparison of our Figs.6 and 7 with experimental data graphically resented in [1–6] (and similar works) shows rather high degree of correlation between one and another. This, gives evidence that many observations can be explained by equilibrium mobility/diffusivity 1/f-type fluctuation accompanying usual, “non-dispersive”, transport. On the other hand, we can say that many observations, when even their authors have doubts as to “dispersive transport”, do proof that the latter is not unique cause of TOF and mobility distributions.

For instance, may be, the experimental mobility distribution found in work [2] (which stimulated the present work) should be assigned not to spatial inhomogeneities but to temporal mobility fluctuations of charge carriers (otherwise, why this distribution so strongly resembles the picture in Fig.4?). Analogously, the large width and asymmetry of mobility distributions of ions in air measured in \[35\] can be manifestation of flicker fluctuations in ions’ mobilities.

At the same time, undoubtedly, our theoretical gallery does not include specific pictures of pronounced “dispersive transport”. This means merely that 1/f-noise under dispersive transport has more rich scaling properties and hence more complicated mobility statistics than what was considered; Developing of theory of such 1/f-noise from rigorous statistical mechanics, instead of probabilistic “scientific fiction”, is interesting task for the future.

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