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Microscopic explanation of non-Debye relaxation for heat transfer

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Abstract

We give a microscopic explanation of both Debye and non-Debye thermalization processes that have been recently reported by Gall and Kutner [Physica A 352 (2005) 347]. Due to reduction of the problem to first passage phenomena we argue that relaxation functions $f(t)$ introduced by the authors directly correspond to survival probabilities $S(t)$ of particles in the considered systems. We show that in the case of broken ergodicity (i.e., in the case of mirror collisions) the survival probability decays as a power law $S(t) = \tau/t$.
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1. Introduction: motivation and aims

Relaxation of a typical macroscopic observable $\mathscr{A}$ towards its equilibrium value is usually described by exponential function

$$f(t) = \frac{\Delta \mathscr{A}(t)}{\Delta \mathscr{A}(0)} = e^{-t/\tau_0}, \tag{1}$$

where t represents time, and $\Delta \mathscr{A}(t) = \mathscr{A}(t) - \mathscr{A}(\infty)$. On that score, probably the best-known example is the Newton's law of cooling where the relaxation function $f(t)$ refers to thermalization process (i.e., $\mathscr{A} = T$). Apart from ordinary exponential relaxation, there also exist phenomena which obey slower relaxation. For example, a large class of systems is characterized by power-law decay (e.g., Refs. [1–5])

$$f(t) = \left(\frac{t}{\tau}\right)^{-d}. \tag{2}$$

In particular, Weron et al. [6–8] have analysed the probabilistic approach to non-Debye relaxation. The authors have shown that fat-tailed relaxation functions may result from a superposition of exponential

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processes with different relaxation times. In Ref. [8], they have studied model of dielectric materials where the regression to equilibrium of polarization fluctuations is a random variable that depends for each relaxing dipole on two other random variables: the waiting time, and the dissipation rate drawn from some given distributions.

It was also noticed that non-Debye relaxation is usually observed in systems which violate the ergodicity condition. In such systems, the lack of ergodicity results from long-range interactions, microscopic memory effects or from (multi)fractal structure of phase space. It was argued that such systems are well described by the so-called non-extensive statistics introduced by Tsallis [9,10]. The *conjectured* relaxation function for such systems [11,12] is given by the *q*-exponential decay[1]

$$f(t) = e_q^{-t/\tau_q} = \left[1 + (q-1)\frac{t}{\tau_q}\right]^{1/(1-q)} \tag{3}$$

which is equivalent to formula (1) for $q \simeq 1$, whereas for $q > 1$ it coincides with (2).

In the context of the ongoing discussion on possible relations between non-ergodicity and non-extensivity, the phenomenon of non-Debye relaxation that has been recently reported by Gall and Kutner [15] seems to be particularly interesting (see also Ref. [16]). The authors have numerically studied a simple molecular model as a basis of irreversible heat transfer through a diathermic partition. The partition has separated two parts of box containing ideal point particles (i.e., ideal gases) that have communicated only through this partition (see Fig. 1a). The energy transfer between the left and right-hand side gas samples has consisted in equipartition of kinetic energy of all outgoing particles colliding with the partition during a given time period. The authors have analysed and compared two essentially different cases of the system's dynamics:

 (i) the first case, where the border walls of the box and the diathermic partition have randomized the direction of the motion of rebounding particles, and
(ii) the case, where mirror collisions of particles with the border walls and the partition have been considered.

They have found that although the mechanism of heat transfer has been analogous in both cases the long-time behaviour of both thermalization processes has been completely different. In the first case (i) ordinary Debye relaxation of the system towards its equilibrium state has been observed

$$\Delta T(t) \sim e^{-t/\tau_0}, \tag{4}$$

where $\Delta T(t) = T_1(t) - T_2(t)$ is the temperature difference between both gas samples, while in the second case (ii) the power-law decay has been noticed

$$\Delta T(t) \sim \frac{\tau}{t}. \tag{5}$$

In order to describe the phenomenon of the non-Debye relaxation Gall and Kutner [15] have derived an extended version of the thermodynamic Fourier–Onsager theory [17,18] where heat conductivity was assumed to be time-dependent quantity. The authors have argued that from the microscopic point of view the non-Debye relaxation results from the fact that the gas particles always move along fixed orbits in the case (ii). They have also argued that this regular motion may be considered as non-ergodic, violating the molecular chaos hypothesis (Boltzmann, 1872).

In this paper we propose a more rigorous microscopic explanation of both Debye and non-Debye thermalization processes reported by Gall and Kutner. We also stress that our explanation is restricted to the phenomenon observed in Ref. [15] and does not extend to non-Debye relaxation in general.

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[1]As a matter of fact, the only satisfactory proof of the property (3) exists for such systems in which non-extensivity arises from intrinsic fluctuations of some parameters describing the system's dynamics [13,14].
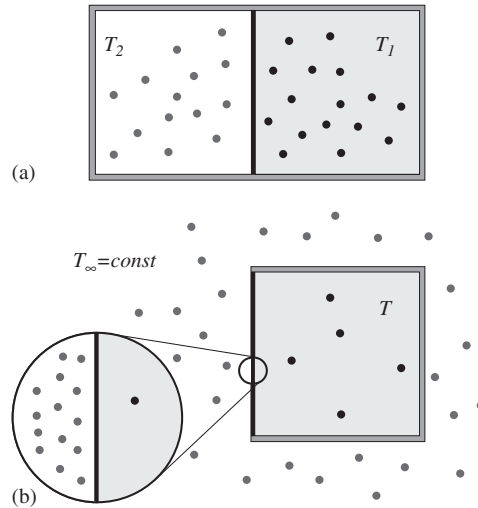
Fig. 1. (a) *Original experimental system* [15]. Two gas samples exchanging heat through a diathermic partition. (b) *Reduced model system.* Gas sample in thermal contact with a huge heat reservoir at constant temperature T_∞ (detailed description is given in the text).

2. Microscopic model for non-Debye heat transfer

In the paper [15], the authors have analysed two-dimensional systems consisting of two gas samples of comparable size (see Fig. 1a). Here, due to analytical simplicity we assume that one gas sample is significantly larger and denser than the second one i.e., the larger sample may be referred to as a heat reservoir with constant temperature $T_\infty = const$ (see Fig. 1b). We also assume that the smaller sample is confined in a square box of linear size l, and its initial temperature equals T_0. We have numerically checked that such a simplification of the original system does not affect general properties of the observed relaxation processes. It is natural to expect that in the course of time thanks to the existence of the diathermic partition the temperature of the smaller sample will tend to the reservoir temperature $T(t) \to T_\infty$.

At the moment, before we analytically justify the relaxation functions (4) and (5) let us recall crucial assumptions of the numerical experiment performed by Gall and Kutner [15]. First, the authors have defined the temperature of the given gas sample $T(t)$ as proportional to the average kinetic energy of all particles in the sample

$$kT(t) = \frac{1}{N} \sum_{i=1}^{N} \varepsilon_i(t). \tag{6}$$

Second, they have assumed a monoenergetic energy distribution function $P(\varepsilon) = \delta(\varepsilon - kT_i)$ as the initial condition for each gas sample $i = 1, 2$ (see Fig. 1a). In fact, since the applied thermalization mechanism evens out kinetic energies of all particles colliding with the diathermic partition at a given time not only initial but also final (i.e., equilibrium) energy distributions are monoenergetic.

Now, having in mind the above assumptions, one can simply conclude that during the heat transfer occurring in the system presented at Fig. 1b particles of the smaller and thinner gas sample get the final energy immediately after *the first collision* with the diathermic partition[2] i.e., $\varepsilon_0 \to \varepsilon_\infty$, where $\varepsilon_0 = kT_0$ and $\varepsilon_\infty = kT_\infty$ (6). It is possible due to existence of the huge and dense heat reservoir which causes that the number of particles with energy ε_∞ colliding with the diathermic partition at a given time is overwhelmingly larger than

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[2]Gall and Kutner have proved that the systems presented at Fig. 1a possess a similar feature for asymptotic times (cf. Eq. (45) in Ref. [15]).

the number of particles with the energy ε_0 which at the same time collide with the partition from the other site (see the inset in Fig. 1b).

The above considerations allow us to write the temperature difference between both gas samples in the following way:

$$\Delta T(t) = T(t) - T_\infty = \frac{N(t)}{N}(T_0 - T_\infty), \tag{7}$$

where $N(t)$ is the number of particles of the smaller sample which have not hit the diathermic partition by time t. Now, one can see that the relaxation function $f(t)$ of the considered systems is equivalent to the particle survival probability[3] $S(t) = N(t)/N$

$$f(t) = \frac{T(t) - T_\infty}{T_0 - T_\infty} \equiv S(t). \tag{8}$$

The last formula makes possible to reduce the phenomena of Debye and non-Debye relaxations to the first passage processes [19–21]. In this sense, the case (i) of rough border walls directly corresponds to the problem of diffusing particles in a finite domain with an absorbing boundary. The survival probability $S(t)$ typically decays exponentially with time for such systems [19]. That is the reason why the thermalization process characterizing the case (i) is equivalent to Debye relaxation (see Eq. (4)). In the remainder of the section we show that the case (ii), where mirror bouncing walls and absorbing diathermic partition are taken into account, is indeed characterized by the power-law decay of the survival probability $S(t)$ (see Eq. (5)).

In order to achieve the claimed scale-free decay of the survival probability $S(t)$ one has to find the first passage (life-time) probability density function $F(t)$, which describes probability that a particle of the considered gas sample hits the diathermic partition for the first time at time t

$$S(t) = 1 - \int_0^t F(t')\,dt'. \tag{9}$$

In the case of mirror bouncing walls, due to asymmetry of the initial conditions (i.e., due to the fact that particles can either move towards the diathermic partition—in the direction described by an angle α, or towards mirror reflection of the partition—in the direction characterized by an angle β, c.f. Fig. 2b) the integral in Eq. (9) must be replaced by two integrals

$$S(t) = 1 - \frac{1}{2}\int_{t_\alpha}^t F_\alpha(t')\,dt' - \frac{1}{2}\int_{t_\beta}^t F_\beta(t')\,dt', \tag{10}$$

where $t_\alpha = x/v_0$ and $t_\beta = (2l - x)/v_0$ represent the shortest time periods after which the collision of particles with the partition or its mirror reflection may occur.

At the moment, let us remind that before the collision with the diathermic partition each particle has the same velocity v_0, thus $F_\phi(t)$ (where $\phi \in \{\alpha, \beta\}$) is simply related to the particle path length probability density function $\widetilde{F}_\phi(r)$

$$F_\phi(t) = \left|\frac{dr}{dt}\right|\widetilde{F}_\phi(r) = v_0\widetilde{F}_\phi(r). \tag{11}$$

Let us also note, that due to the symmetry of the considered problem (i.e., due to equivalence of paths $0 \to A \to B \to C \to D$ and $0 \to A \to b \to c \to d$, see Fig. 2a) one may further simplify the last expression

$$F_\phi(t) = v_0 P(\phi)\left|\frac{d\phi}{dr}\right| = v_0\frac{2}{\pi}\left|\frac{d\phi}{dr}\right|, \tag{12}$$

where in accordance with the original experiment [15] we have assumed uniform angle distributions $P(\phi) = P(\alpha) = P(\beta) = 2/\pi$.

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[3]Note that the system's survival probability is an appropriate function of this ratio.
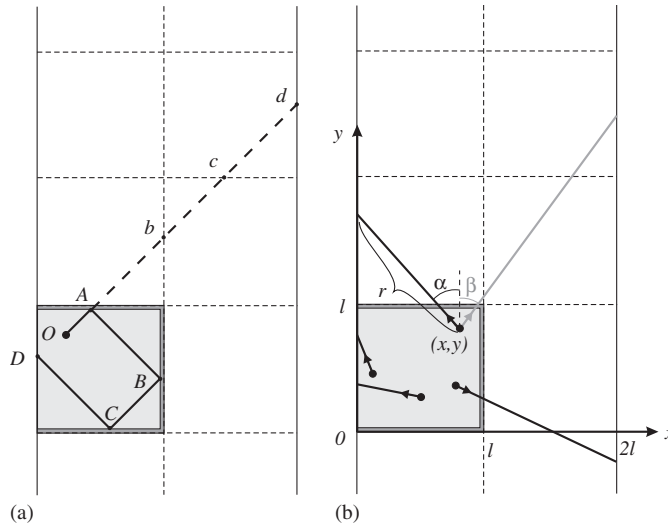
Fig. 2. Ideal point particles in the box with mirror border walls (detailed description is given in the text).

Finally, inserting the below relations

$$\left|\frac{\mathrm{d}\alpha}{\mathrm{d}r}\right| = \left|\frac{\mathrm{d}\,\arcsin(x/r)}{\mathrm{d}r}\right|, \tag{13}$$

and

$$\left|\frac{\mathrm{d}\beta}{\mathrm{d}r}\right| = \left|\frac{\mathrm{d}\,\arcsin((2l-x)/r)}{\mathrm{d}r}\right| \tag{14}$$

to Eq. (12), and then substituting the equation into (10) one obtains the desired formula for the survival probability $S(t)$

$$S(t) = \frac{1}{\pi}\arcsin\left(\frac{t_\alpha}{t}\right) + \frac{1}{\pi}\arcsin\left(\frac{t_\beta}{t}\right), \tag{15}$$

which justifies the non-Debye thermalization process for $t \gg t_\alpha, t_\beta$[4]

$$S(t) \simeq \frac{\tau}{t}, \quad \text{where} \quad \tau = \frac{2l}{\pi v_0}. \tag{16}$$

We have numerically verified the last relation for a few different values of both the initial velocity v_0 and the box size l. In all the considered cases we have obtained very good agreement of recorded survival probabilities with the formula (16) (see Fig. 3).

3. Summary and concluding remarks

In this paper we have given a microscopic explanation of Debye and non-Debye thermalization processes that have been recently reported by Gall and Kutner [15]. The authors have studied a simple molecular mechanism of heat transfer between two comparable gas samples. Owing to analytical simplicity we have reduced the problem to one gas sample being in thermal contact with the huge and dense heat reservoir at constant temperature. For the case we have shown that the thermalization mechanism described by Gall and

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[4]The Maclaurin series for the inverse sine with $-1 \leqslant x \leqslant 1$ is given by $\arcsin x = x + \frac{1}{6}x^3 + \frac{3}{40}x^5 + O(x^7)$ [22].
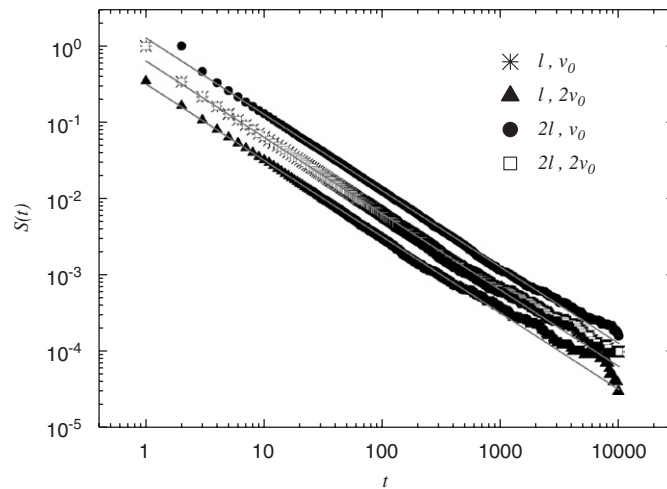
Fig. 3. Survival probability $S(t)$ against time t in systems presented at Fig. 2. Points correspond to results of numerical simulations whereas solid lines represent theoretical prediction of the formula (16). Each simulation was performed for $N = 10^5$ particles. Deviations from the strait line result from finite size effects.

Kutner can be reduced to first passage phenomena. Taking advantage of the idea we have found an analytical justification for both exponential (4) and non-exponential (5) relaxation functions observed in Ref. [15].

References

 [1] T.V. Ramakrishnan, M. Ray Lakshmi, Non-Debye Relaxation in Condensed Matter, World Scientific, Singapore, 1987.
 [2] W. Bauer, G.F. Bertsch, Phys. Rev. Lett. 65 (1990) 2213.
 [3] V.B. Kokshenev, M.C. Nemes, Physica A 275 (2000) 70.
 [4] E. Vicentini, V.B. Kokshenev, Physica A 295 (2001) 391.
 [5] Y.S. Weinstein, S. Lloyd, C. Tsallis, Phys. Rev. Lett. 89 214101 (2002).
 [6] P. Hetman, B. Szabat, K. Weron, D. Wodziński, Acta Phys. Pol. B 34 (2003) 3717.
 [7] P. Hetman, B. Szabat, K. Weron, D. Wodziński, J. Non-Cryst. Solids 330 (2003) 66.
 [8] K. Weron, J. Phys. Condens. Matter 3 (1991) 9151.
 [9] C. Tsallis, J. Stat. Phys. 52 (1988) 479.
[10] M. Gell-Mann, C. Tsallis (Eds.), Nonextensive Entropy—Interdisciplinary Applications, Oxford University Press, New York, 2004.
[11] C. Tsallis, Physica D 193 (2004) 3.
[12] F. Brouers, O. Sotolongo-Costa, K. Weron, Physica A 344 (2004) 409.
[13] G. Wilk, Z. Włodarczyk, Phys. Rev. Lett. 84 (2000) 2770.
[14] G. Wilk, Z. Włodarczyk, Phys. Lett. A 290 (2001) 55.
[15] M. Gall, R. Kutner, Physica A 352 (2005) 347.
[16] J. Hurkała, M. Gall, R. Kutner, M. Maciejczyk, Eur. J. Phys. 26 (2005) 673.
[17] R. Kubo, M. Toda, N. Hashitsume, Statistical Physics II. Nonequilibrium Statistical Mechanics, Springer, Berlin, 1985.
[18] R.L. Stratonovich, Nonlinear Nonequilibrium Thermodynamics I, Springer, Berlin, 1992.
[19] S. Redner, A guide to First-Passage Processes, Cambridge University Press, Cambridge, 2001.
[20] H. Risken, The Fokker–Planck Equation: Methods of Solution and Applications, Springer, New York, 1988.
[21] C.W. Gardiner, Handbook of Stochastic Methods, Springer, New York, 1985.
[22] E.W. Weisstein, Inverse Sine from Math World—A Wolfram Web Resource, ⟨ http://mathworld.wolfram.com/InverseSine.html⟩.