Problem of Thermally Driven Diffusion in Terms of Occupation Numbers

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Abstract

In the new approach to the diffusion problem conventional statistical derivation is reconsidered deterministically using the partition function for thermal velocities. The resulting relation for time evolution of particle distribution is an integro-differential equation. Its first approximation provides the conventional partial differential equation - the second Fick's law with the diffusion transport coefficient proportional to the temperature.

The diffusion in the present context is understood as an evolution of any spatial distribution, usually a concentration or a density of arbitrary quantity. The time-dependent distribution function for the evolution of diffusion type is subject to the partial differential equation of second order in space coordinates and of first order in time.

The classical derivation of the governing PDE in case of the *linear diffusion* in a usual way is based on the *first Fick's law* for diffusion flow, which is postulated empirically (the flow is supposed to be proportional to the gradient of concentration).

Then, the *second Fick's law* - the actual 'diffusion equation' follows from the first one combined with the continuation equation, which connects the divergence of the flow with the time rate of the concentration change [2]. In the framework of statistical physics [1, 3] the conventional approach is the probabilistic formulation in terms of Einstein's probability density entering

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the 'master equation' The change of the concentration is related to the 'jump' probability distribution. Under special requirements (e.g. a Botzmannian distribution of energy) it provides the local relation having a form of the second Fick's law (e.g.[3] for details).

In the present note a reformulation of the Einstein's problem of randomly-jumping objects is performed in terms of site-occupation numbers for the state of a system consisting of spatial sites, occupied by countable units (particles) changing in time. The probabilistic postulation for the transition probability distribution is formulated deterministically as the given partition function for transition velocities. It has been shown, that this formulation leads immediately to the first-order dynamical system for infinitely-dimensional state vector. In a continuum limit it provides an integro-differential dynamical equation. The diffusion equation results as its local approximation.

The main difference from the classical approach is the formulation in terms of occupation numbers instead of number of moving individual units in elementary space volume (in a three-dimensional case). In this approach the formulation is also well-appropriate for quantum statistical systems. In particular, the problem outlined below relates to the case of bosonic system. The buildup of this formalism is the main idea of the present note.

Starting with the discrete formulation for the state of a statistical system as a set of sites with integer occupation numbers, this approach leads to the dynamical (first order in time) system of ODE's with the standard exact solution in a matrix exponential form.

A generalization of this system in the continuum limit provides the integro-differential equation for the time - dependent space distribution. The subsequent local approximation of this equation reveals the desired construction of the second Fick's law. The coefficient appearing in this pattern as the diffusion constant is clearly interpreted as the first power of temperature.

Formulation of the Problem in terms of occupation numbers

We start initially with the one-dimensional formulation. A subsequent generalization for three dimensions is straightforward.

Suppose, a one-dimensional configuration space consists of discrete sites, enumerated by $..., i-1, \ ... \ \ i, \ i+1, \ i+2, \ ...$ and occupied by numbers $..., \ n_{i-1} \ n_i, \ n_{i+1}, \ n_{i+2}, \ ....$

The 'motion' of objects of any nature in this representation is defined as a change of its position i, and should result therefore in a change of occupation numbers of the site i. It is appropriate to consider the problem in an infinite space, so that the site number i runs as $-\infty < i < \infty$.

The *velocity* of a single unit is understood conventionally as the shift m in its position per single time-tick $d\tau$. In a microscopically discrete representation, the minimal change $d\tau$ of a quantum time-reference state ('clock') is $d\tau = 1$. From the physical point of view, an observer cannot follow the position i of each unit in each time point during a measurement of $n(i)$. Moreover, in the sense of quantum mechanics this approach is not consistent, since all units in all sites are not distinguished. For this situation we could still consider a total ensemble of units with different velocities which are distributed statistically by means of the corresponding partition function. The *partition of velocities* v_k represents the *fraction* $n_i v_k$ of the units n_i (occupation number of the site i) which is shifted per $d\tau$ by k positions along the scale $..., i-1, \ ... \ \ i, \ i+1, \ i+2, \ ...$
In other words it means, that $v_k n_i$ units shift from the site i to the site $i+k$ per time tick $d\tau$

In order to get a consistent formulation in terms n_i, we should change from the representation of motion as the position change v_k of each individual unit to the representation in terms of occupation numbers $..., \ n_{i-1} \ n_i, \ n_{i+1}, \ n_{i+2}, \ ...$

To this end we observe the change dn_i of occupation number n_i corresponding to the change $d\tau$ of time-reference. Thus, per *time-tick* $d\tau$ the quantity

$$dn_i^{\rightarrow} = n_i(... + v_{-2} + v_{-1} + v_0 + v_1 + v_2 + ...)$$

leaves the site i, while the quantity

$$dn_i^{\leftarrow} = ... \ + n_{i-2}v_2 + n_{i-1}v_1 - n_i \sum_{m=-\infty}^{\infty} v_m + n_{i+1}v_{-1} + n_{i+2}v_{-2} + ...$$

arrives from the entire environment $-\infty, ..., i-1, i+1, ..., \infty$, per definition of the fraction v_k. For the entire ensemble n_i depicted as a column vector it

looks as

$$\begin{bmatrix} . \\ . \\ . \\ dn_{i-1} \\ dn_i \\ dn_{i+1} \\ . \\ . \\ . \end{bmatrix} = \begin{bmatrix} . & . & . & . & . & . \\ . & . & . & . & . & . \\ . & . & . & . & . & . \\ ... + n_{i-2}v_1 & - n_{i-1}\sum_{m=-\infty}^{\infty} v_m & + n_i v_{-1} & + n_{i+1}v_{-2} & + n_{i+2}v_{-3} & + ... \\ ... + n_{i-2}v_2 & + n_{i-1}v_1 & - n_i \sum_{m=-\infty}^{\infty} v_m & + n_{i+1}v_{-1} & + n_{i+2}v_{-2} & + ... \\ ... + n_{i-2}v_3 & + n_{i-1}v_2 & + n_i v_1 & - n_{i+1}\sum_{m=-\infty}^{\infty} v_m & + n_{i+2}v_{-1} & + ... \\ . & . & . & . & . & . \\ . & . & . & . & . & . \\ . & . & . & . & . & . \end{bmatrix} \quad (3)$$

Thus, the resulting first order equation in the vector form reads

$$\frac{dn_i}{d\tau} := \dot{n}_i =: \dot{\mathbf{n}} = M(v_m)\mathbf{n} := [m(v_m)]_{ik}\, n_k \quad (1)$$

with the vector n_i and the matrix M

$$\mathbf{n} = \begin{bmatrix} . \\ . \\ n_{i-1} \\ n_i \\ n_{i+1} \\ . \\ . \end{bmatrix}; \quad M = \begin{bmatrix} . & . & . & . & . & . \\ . & . & . & . & . & . \\ ...v_1 & 0 & v_{-1} & v_{-2} & v_{-3} & ... \\ ... \ v_2 & v_1 & 0 & v_{-1} & v_{-2} & ... \\ ... \ v_3 & v_2 & v_1 & -0 & v_{-1} & ... \\ . & . & . & . & . & . \\ . & . & . & . & . & . \end{bmatrix} - \mathcal{I} \sum_{m=-\infty}^{\infty} v_m, \ \mathcal{I}- \text{ identity matrix}$$

Here the obvious fact for remaining fraction

$$v_0 = 0$$

is used, since only the velocity fraction of shifting, but not remaining elements is encountered in dn_i. For a given partition of velocities v_k the solution of the linear infinite-dimensional dynamical system (1) is obtained as

$$\mathbf{n}(\tau) = e^{M\tau}\mathbf{n}(0), \quad (2)$$

in terms of the matrix exponent of $M\tau$.

Suppose, we have a simplest *isothermal* case, such that the thermal of velocity partition does not depend on time τ and position i. Then, in the *continualization limit* $-\infty < i, k < \infty$ the vectors n_i, v_k are functions of continuous arguments n(i), v(k) and the the summations in (1) become

$$... + n_{i-2}v_2 + n_{i-1}v_1 + n_i v_0 + n_{i+1}v_{-1} + n_{i+2}v_{-2} + ... \to \int_{-\infty}^{\infty} n(i-k)v(k)$$

$$-n_i \sum_{m=-\infty}^{\infty} v_m ... \to \int_{-\infty}^{\infty} v(m)dm.$$

Thus the system of linear equations (1) becomes to the integro-differential equation

$$\dot{n}(i) = \int_{-\infty}^{\infty} n(i-k)v(k) - n(i) \int_{-\infty}^{\infty} v(m)dm, \tag{3}$$

where:

$n(i)$ the occupation distribution;

$v(m)$ the partition of velocities.

Now consider the typical case of a many-particle physical system in a disordered thermal motion. For a case, that the displacement k, (e.g. per elementary quantum clock unit, e.g. $d\tau = 1$ in a discrete formulation) is small compared to the site occupation number $n(i)$, it can be referred to the 'slow thermal drift'.

In this case

- distribution of velocities is isotropic, since the thermal motion is stochastic; for a one-dimensional problem the isotropy condition reduces to the symmetry condition $v(k) = v(-k)$;
- the main contribution in $v(k)$ comes from relatively slight velocities (small k), the fraction v decreases rapidly for big ones.

Then a local approximation for $k \to \infty$ is justified. The function $n(i-k)$ in (3) can be replaced by its power series at small k

$$n(i-k) = n(i) - n'(i)k + n''(i)\frac{k^2}{2} - ... ,$$

that provides

$$\dot{n}(i) = n(i) \int_{-\infty}^{\infty} v(k)dk - n'(i) \int_{-\infty}^{\infty} kv(k)dk + n''(i) \int_{-\infty}^{\infty} \frac{k^2}{2} v(k)dk - n(i) \int_{-\infty}^{\infty} v(m)dm - ... \tag{4}$$

The fourth term cancels with the first one, the second term vanishes identically as an integral of an antisymmetric function over the symmetric interval (likewise, all integrals with odd powers of k disappear as well), and the remaining approximation reproduces in the leading order the conventional diffusion equation -*second Fick's law*.

Since the k has the meaning of velocity, we recover form (4) that the *diffusion constant* - the coefficient D_2 at $n''(i)$

$$D_2 = \int_{-\infty}^{\infty} \frac{k^2}{2} v(k)dk$$

is proportional to the *expectation value of kinetic energy*, namely the *temperature* Θ and defines the *normal linear diffusion*. The next non-vanishing term in (4) is

$$D_4 = \frac{n''''(i)}{6} \int_{-\infty}^{\infty} \left[\frac{k^2}{2} v(k)dk \right]^2 \sim \Theta^2,$$

and further terms with even derivatives of n contribute to the *nonlinear diffusion*.

Considering three cartesian components instead and replacing one-dimensional coordinate i by cartesian coordinates x, y, z as

$$\frac{d}{d\tau} \to \frac{\partial}{\partial \tau}; \quad \frac{d}{di} \to \frac{\partial}{\partial i}; k \to k_i, \quad i = \{x, y, z\}$$

we obtain the three-dimensional generalization, which follows by summation over i straightforwardly.

Discussion and conclusions

As it has been shown in the note, the diffusion law can be obtained directly for a system of drifting units, which are not distinguished from each

other, each site (state) can be occupied arbitrary many times - the case of bosonic quantum statistics.

Instead of the probability distribution in a classical probabilistic approach [**?**], the derivation is represented in terms the deterministic velocity distribution for thermal motion. The resulting diffusion can be called for this reason 'thermally driven', in opposite to the 'statistically driven', which is treated as a nonequilibrium phenomen and issues from the construction of entropy. It can be obtained therefore by applying the local entropy maximization [4], and has been recently performed in [5].

Although the philosophy of this formalism is similar to the Einstein's approach, for instance integro-differential evolution equation resembles the 'master-equation' and is also global in the space of states, the approach outlined above works more frugal and requires a minimal supply of conditions and formulations, thus avoiding several unnecessary definitions and assumptions, which are mandatory for the conventional statistical approach [2, 1, **?**]. Especially, no pre-assumptions for ergodicity, Boltzmannian energy distribution, special properties of entropy function or interaction/transition potential between different particles in different positions.

Since the existence of the velocity distribution $v(k)$ is assured, a straightforward counting of occupation numbers subjected to the thermal motion $v(k)$ leads to the first order linear dynamical system in a discrete representation, which corresponds to integro-differential equation in a continuum.

A local approximation for a typical thermal velocity distribution provides in the Fick's diffusion law in the leading order, higher orders contribute to the nonlinear diffusion.

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