Heat conduction in a fermionic crystal

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Abstract. Linear diffusion in a system of non-interacting Fermion oscillators is constructed using the methods of statistical dynamics. The temperature distribution is shown to obey the heat equation $C_v(T)\partial T/\partial t = \lambda \operatorname{div}(C_v(T)\operatorname{grad}T)/2$ where $C_v = \partial\langle E\rangle/\partial T$ is the heat capacity/molecule. An example shows that the system violates the 'principle of minimal entropy production' at a stationary state. The model confirms the similar conclusion drawn by M J Klein in 1956.

1. Introduction and summary

The Fermion analogue of the Einstein crystal [1] consists of non- interacting atoms, one at each vertex of a cubic lattice Λ with two energy levels, 0 and $\hbar\omega$. Let $(1 - s_j, s_j)$ denote the probability distribution of site $j \in \Lambda$. This defines the temperature T_j at j by

$$s_j = e^{-\beta_j \hbar\omega}/(1 + e^{-\beta_j \hbar\omega}) \qquad k_B T_j = 1/\beta_j. \tag{1.1}$$

The average energy $\langle E\rangle$ of site j is $\hbar\omega s_j$, and the specific heat/atom is $C_V = \partial\langle E\rangle/\partial T = \hbar\omega\partial s/\partial T$.

We shall describe the dynamics of heat conduction through the crystal by a stochastic model, which leads to the heat equation

$$\frac{ds(x,t)}{dt} = \frac{\lambda}{2} \operatorname{div}\operatorname{grad} s(x,t). \tag{1.2}$$

Since s is a function of $T(x,t)$, we get $ds/dt = ds/dT\,dT/dt$ etc, leading to an equation for $T(x,t)$:

$$C_v\frac{\partial T}{\partial t} = \frac{\lambda}{2}\operatorname{div}(C_V\operatorname{grad}T(x,t)). \tag{1.3}$$

At the boundary of the crystal, the inward heat flow is at the rate $\lambda/2\,\partial E(x,t)/\partial n$ where n is the outward normal, and so the flow of entropy (created by the system) at a stationary distribution is:

$$\dot{S} = \frac{\lambda}{2}\oint_{\partial\Lambda}\frac{\hbar\omega}{T(x,t)}\frac{\partial s(x,t)}{\partial n}\cdot dS. \tag{1.4}$$

Prigogine *et al* [2], using 'non-equilibrium thermodynamics', have suggested that the rate of entropy production decreases along the orbit, and reaches a minimum at the stationary distribution, at least, if we start in a neighbourhood of the stationary point. If true for the heat equation, this would indeed be a remarkable variational principle. However, we show from a simple discrete model that, while $\frac{dS}{dt}$ is indeed zero at the stationary solution, it is not a minimum. This was shown to be the general situation for chemical reactions at a fixed temperature by Denbigh [3], who correctly pointed out the approximate nature of Prigogine's argument. A detailed stochastic model, suggested by Klein, shows the same result [4]. Our model turns out to be equivalent to Klein's in a mathematical sense; this helps to clarify the argument in Kittel' book [4].

2. The stochastic model

This is an example of the construction described in [5]. Let $\Omega_j = \{0,1\}$ for all $j \in \Lambda$ be the sample space at each point, and $\Omega = \prod_{j \in \Lambda} \Omega_j$ be the total sample space. The state of the system is described by a probability p on Ω; the state space of Ω will be denoted $\Sigma(\Omega)$. If $\underline{s}_j \in \Sigma(\Omega_j)$, then $\underline{s}_j = (1 - s_j, s_j), 0 \leqslant s_j \leqslant 1$. The points of the lattice are independent in the state $\underline{p} \in \Sigma(\Omega)$ if and only if $\underline{p}$ is a product: $\underline{p} = \otimes_{j \in \Lambda} \underline{s}_j$. Each $\underline{p} \in \Sigma(\Omega)$ defines its marginal distributions $\underline{p}_j \in \Sigma(\Omega_j)$, obtained by summing over all configurations except the component in Ω_j:

$$p_j(\sigma_j) = \sum_{\omega = \prod_k \omega_k \,:\, \omega_j = \sigma_j} \underline{p}(\omega) \qquad \sigma_j \in \Omega_j . \tag{2.1}$$

Then $\otimes_j \underline{p}_j$ is the product state with the same marginal distributions as $\underline{p}$ itself. We call $\otimes_{j \in \Lambda} \underline{p}_j = Q\underline{p}$ the *Stosszahlansatz*. It coincides with the diagonal quasifree map of [6] when Ω is identified with a fermion system. It is known that Q is entropy non-decreasing.

Diffusion will be represented by a bistochastic map $T : \Sigma(\Omega) \to \Sigma(\Omega)$, followed by the map Q

$$\underline{s}_j \longmapsto \otimes_{j \in \Lambda} \underline{s}_j \longmapsto T(\otimes_j \underline{s}_j) \longmapsto QT(\otimes_j \underline{s}_j) = \otimes_{j \in \Lambda} \underline{s}_j'. \tag{2.2}$$

This gives one time-step in the evolution of the state, which can be described by the occupation numbers $\underline{s}_j(t)$, $t = 0, 1, 2 \ldots$, where $\underline{s}_j(t + 1) = \underline{s}_j'(t)$.

We choose T as follows. To each pair j, k of neighbours in Λ, consider $\Sigma(\Omega_j x \Omega_k)$, on which we define

$$T_{jk} = \begin{array}{c|cccc} & 00 & 01 & 10 & 11 \\ \hline 00 & 1 & & & \\ 01 & & 1-\lambda & \lambda & \\ 10 & & \lambda & 1-\lambda & \\ 11 & & & & 1 \end{array} \qquad 0 < \lambda < 1. \tag{2.3}$$

The product state $\otimes \underline{s}_j$ in this basis restricted to $\Sigma(\Omega_j \times \Omega_k)$, is the 4-vector $\underline{s}_j \otimes \underline{s}_k = ((1 - s_j)(1 - s_k), (1 - s_j)s_k, s_j(1 - s_k), s_j s_k)^t$. The mapping T_{jk} leaves $\underline{s}_i (i \neq j, k)$ unchanged, and changes $\underline{s}_j \otimes \underline{s}_k$ into $T_{jk}(\underline{s}_j \otimes \underline{s}_k)$, namely

$((1-s_j)(1-s_k), (1-\lambda)(1-s_j)s_k + \lambda s_j(1-s_k), \lambda(1-s_j)s_k + (1-\lambda)s_j(1-s_k), s_j s_k) = (p'_{00}, p'_{01}, p'_{10}, p'_{11})$ say. The marginal distributions, called $\underline{s}'_j, \underline{s}'_k$, are determined by the occupation numbers $s'_j = p'_{10} + p'_{11} = s_j + \lambda(s_k - s_j)$, the quadratic terms cancelling. We see that the net rate of increase of s_j is proportional to the number–particle gradient $s_k - s_j$ (k and j neighbours), with rate λ.

The full map T is the convex sum of all T_{jk} (with equal weights). For example, if j, k are neighbours on the line i.e. $k = j+1$, or $k = j-1$, give rise to the convex sum $\frac{1}{2}(T_{j-1,j} + T_{j,j,+1})$ and the time evolution from this is

$$s'_j = s_j + \tfrac{1}{2}\lambda(s_{j+1} - 2s_j + s_{j-1}) \quad \text{if} \quad j-1, j, j+1 \in \Lambda. \tag{2.4}$$

In the continuum limit we get the heat equation for $s(x, t)$, and in 3 dimensions we get similarly equation (1.2), leading to (1.3) as explained there.

The boundary condition comes when not all of $j-1, j, j+1$ lie in Λ, and only one term in $\frac{1}{2}(T_{j-1,j} + T_{j,j+1})$ is non zero. So the rate of change of $s_j, j \in \partial\Lambda$, is $\frac{1}{2}\lambda(s_{j+1} - s_j)$. This leads to (1.4) in the continuum limit.

3. The three-atom crystal

Take $\Lambda = \{0, 1, 2\}$ i.e. has three atoms, and suppose the ends $0, 2$ are held fixed at betas $\beta_0, \beta_2 > 0$. This means that after the map (2.2), $(s_0, s_1, s_2) \mapsto (s'_0, s'_1, s'_2)$, we readjust the end occupation numbers s'_0 and s'_2 to be $s_0 = e^{-\beta_0 \hbar\omega}/Z_0, s_2 = e^{-\beta_2 \hbar\omega}/Z_2$. To achieve this physically, we must add heat equal to $\hbar\omega(s_0 - s'_0)$ and $\hbar\omega(s_2 - s'_s)$ at the ends. Mathematically, we just do it.

We are left then with just one variable, $s_1(t)$, obeying the equation

$$\frac{ds_1}{dt} = \frac{\lambda}{2}(s_0 - 2s_1 + s_2) \qquad \frac{ds_0}{dt} = \frac{ds_2}{dt} = 0. \tag{3.1}$$

with a fixed point at $s_1 = s_0 + s_2/2$. Thus the energy density, rather than the temperature, is harmonic at a stationary distribution (reflecting the temperature - dependence of C_v). The entropy of the distribution is given by Shannon's formula (if $k_B = 1$)

$$S = \sum_{k=0}^{2} (-s_k \log s_k - (1 - s_k) \log(1 - s_k)). \tag{3.2}$$

If no heat is added or subtracted from the ends (the adiabatic case), then the instantaneous rate of production of entropy is $\dot{S}$, where (s_o, s_1, s_2) obeys the equation

$$(\dot{s}_0, \dot{s}_1, \dot{s}_2) = \frac{\lambda}{2}(s_1 - s_0, s_0 - 2s_1 + s_2, s_1 - s_2). \tag{3.3}$$

We find

$$\dot{S} = \frac{\lambda}{2}\left\{ (s_1 - s_0) \log\left(\frac{1-s_0}{s_0}\right) + (s_0 - 2s_1 + s_2) \log\left(\frac{1-s_1}{s_1}\right) \right.$$
$$\left. + (s_1 - s_2) \log\left(\frac{1-s_2}{s_2}\right) \right\} \tag{3.4}$$

In the motion (3.1), s_0 and s_2 are replenished and remain fixed (not changing as in (3.3)) but we retain the interpretation of (3.4) as the rate of production of entropy by the crystal. Clearly the centre term in (3.4) is the rate of change of the entropy of the centre atom, and vanishes at the fixed point of (3.1). The first term is

$$\frac{\lambda}{2}(s_1 - s_0) \log \left(\frac{1 - s_0}{s_0}\right) = \frac{\lambda}{2}\beta_0 \hbar \omega (s_1 - s_0) = -\beta_0$$

times the rate of heat flow from 0 to $1 = -\mathrm{d}(\mathrm{d}q_0/T_0)/\mathrm{d}t$, where $\mathrm{d}q_0$ is the heat supplied to keep β_0 constant. Similarly, entropy $\mathrm{d}q_2/T_2$ per unit time is collected at 2 (we speak as if $T_0 > T_2 > 0$). So the interpretation of (3.4) as the rate of entropy production agrees with elementary thermodynamics, and shows, moreover, that at the stationary point, the process is quasistatic.

We can compute $\mathrm{d}/\mathrm{d}t\dot{S}$ using (3.1), i.e. keeping s_0 and s_1 constant. We find

$$\frac{\mathrm{d}\dot{S}}{\mathrm{d}t} = \frac{\lambda^2}{4}\left(-\dot{s}_1^2\left(\frac{1}{s_1} + \frac{1}{1 - s_1}\right) + \dot{s}_1 \log\left[\left(\frac{s_1}{1 - s_1}\right)^2 \frac{(1 - s_0)(1 - s_2)}{s_0 s_2}\right]\right). \tag{3.5}$$

This vanishes at the stationary point, as $\dot{s}_1 = 0$ there, but the non-vanishing linear term ensures that $\dot{S}$ has a point of inflexion, not a minimum, at the fixed point.

We see that $\dot{S}$ is decreasing in time in a neighbourhood of the fixed point $\dot{s}_1 = 0$ only if the argument of the logarithm is 1, which is possible only if $\beta_0 = \beta_2$ or $s_1 = \frac{1}{2}$. The latter corresponds to infinite temperature.

We conclude that the minimum entropy production conjecture does not apply to this model.

4. Comparison with the model of M J Klein

The principle of minimal entropy production was critically analysed in 1956 by M J Klein; this work has been described by Kittel [4]. A two-level atom is in contact with a heat bath, and is maintained away from equilibrium by exchanging energy (called ϵ in [4]) with a radiation field. Klein shows that at the stationary distribution the rate of production of entropy is not a minimum. In this rate he included the rate of production by the system (analogous to the middle term of (3.4)) and the rate of increase of entropy of the heat bath (analogous to the last term in (3.4)). But he did not include the loss in entropy of the radiation field. This omission might puzzle some readers of [4]. It is similar to omitting the first term in (3.4).

However, no mistake was made. Although the radiation field near the stationary point makes a net positive energy transfer per unit time to the system, this transfer is at infinite temperature, and so does not change the entropy of either the radiation field or the system. It is analogous to choosing $\beta_0 = 0$ in our model, i.e. $s_0 = \frac{1}{2}$. In this case the first term of (3.4) is zero.

This explanation is not clear in Kittel's text, and is hidden in the assumption that the forward and backward transfer rates with the radiation field, called b in [4], are equal. This is only physically correct if the radiation field is at infinite temperature.

In fact, Klein's model can be mapped into a slight generalization of ours. Suppose in our 3-atom crystal, the diffusion rates from 0 to 1, say λ_1, and from 1 to 2, say λ_2, are unequal. Then instead of (3.1.) we would get

$$\frac{\mathrm{d}s_1}{\mathrm{d}t} = \frac{\lambda_1}{2}(s_0 - s_1) + \frac{\lambda_2}{2}(s_2 - s_1). \tag{4.1}$$

Make the following change of notation in (4.1):

$$s_1 = p_2 \qquad (1 - s_1) = p_1 \qquad s_2 = \frac{e^{-\beta \epsilon}}{1 + e^{-\beta \epsilon}} \qquad \hbar \omega = \epsilon$$

$$\beta = \frac{1}{\tau} \qquad \frac{\lambda_2}{2} = a(1 + e^{\beta \epsilon}) \qquad s_0 = \tfrac{1}{2} \qquad \lambda_1 = 4b.$$

Then (4.1) becomes identical to Klein's dynamics as given in (35.1) of [4]. Namely, we get Klein's equation $dp_1/dt = (a\alpha + b) \, p_2 - (a + b) \, p_1$, $\alpha = e^{\beta \epsilon}$, which is thus the special case of (4.1) when the point 0 is maintained at infinite temperature (and the point 2 at Klein's heat- bath temperature τ).

The subsequent calculations in [4] of the rate of entropy production also agree with ours—if $\beta_0 = 0$ the first term of (3.4) is zero. It is this term that corresponds to the loss of entropy by the radiation field.

Kittel concludes from this example that the principle of minimal entropy production is nearly valid at high temperature. This is a misleading conclusion. In our model, the principle is (trivially) exactly valid if $\beta_0 = \beta_2$, since then the stationary point is $\beta_1 = \beta_0 = \beta_2$, thermal equilibrium. The same point is made by Denbigh [3]. The further β_0 and β_2 are apart, the worse the 'theorem' is. In Klein's case $\beta_0 = 0$, $\beta_2 = \beta = 1/\tau$: the smaller β_2, the less the error. But if $\beta_0 \neq 0$ the principle gets worse as $\beta_2 \to 0$. We conclude that there is no reliable domain that is not near thermal equilibrium.

Acknowledgments

References

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