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Thermal relaxation and entropy for charged particles in a heat bath with fields

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Abstract. The relaxation back to thermal equilibrium of one very dilute species of charged particle in a heat bath of different neutral particles, with which they collide elastically, is considered by means of the Boltzmann equation for the one-particle distribution function of the test particles. The Boltzmann collision integral is used to describe the collisions. A rigorous proof that relaxation to thermal equilibrium will always take place, even in the presence of a magnetic field, is given, initially for the case when there is no spatial dependence. The proof is based on a functional of the distribution function with properties similar to the Boltzmann entropy. This quantity is shown always to decrease until thermal equilibrium is reached, and to be bounded below by its value in thermal equilibrium. The proof is then generalised to allow for arbitrary spatial dependence of the magnetic field and the initial distribution function. The special role played by states of local thermal equilibrium is emphasised. The thermal distribution function no longer represents equilibrium when an electric field is present, and it is shown how this arises in the present context; the possibility of particle runaway is also considered. The functional employed is then shown to have successive time derivatives of alternate sign when only a magnetic field is present; other functionals which always decrease are derived, both with and without magnetic field. The conjecture that the alternating derivative property singles out the physical entropy is shown to be dubious for this system.

1. Introduction

This paper is concerned with the properties of a very dilute gas of charged test particles in a heat bath of different neutral particles (the 'host' particles) with which they collide elastically. A time-dependent magnetic field may also be present. The neutral particles are in thermal self-equilibrium. A proof is given that, when the collisions between the test and host particles are governed by a collision integral of Boltzmann's form, the test particles will always relax back to thermal equilibrium.

One method of proof for the case of zero magnetic field and no spatial variations is to expand the distribution function for the test particles in the eigenfunctions of the collision operator. It is therefore necessary for the validity of this method that these eigenfunctions comprise a complete integrable set. This has not been proved generally. The demonstration of relaxation presented here does not depend on this result, and also allows a magnetic field and spatial inhomogeneities to be present. It is conceptually similar to the 'generalised H theorem' mentioned by Chapman and Cowling (1970, p 371).

The conjectures of McKean (1966) that, of all the functionals of the test particle distribution function which decrease with time, only one will have successive time derivatives of alternating sign, and that that functional is the physical entropy for the system, are considered in detail. The functional used to prove relaxation takes place is shown to have this property even in the presence of a magnetic field, and alternative functionals are derived.

The notation is set out in table 1. The Boltzmann equation governing the evolution of the test particle distribution function is introduced in § 2; this section also discusses the old eigenfunction expansion approach to the problem. The proof of relaxation in the spatially homogeneous case is given in § 3 by finding a state function Q which always decreases until thermal equilibrium is reached. Section 4 extends the proof to deal with the spatially inhomogeneous case. Section 5 considers the effect of an electric field, in which case the charged test particles do not relax to an equilibrium of thermal type, and may not relax at all. Section 6 shows that successive time derivatives of Q alternate in sign during relaxation with no electric field, irrespective of the magnetic field strength. Section 7 calculates alternative functionals to Q which also decrease, both with and without magnetic field, and discusses the conjecture that the alternating property picks out the physical entropy for the system. Conclusions are presented in § 8.

Table 1. Notation.

t	time
$\boldsymbol{r}$	position vector
$\boldsymbol{v}$	velocity of test particles
$\boldsymbol{B}$	magnetic field
$\boldsymbol{E}$	electric field
q	test particle charge
m	test particle mass
M	host particle mass
T_M	host particle temperature; in general a suffix M will denote a host particle property, and no suffix a test particle property
Δ	$2kT_M/m$
$\boldsymbol{u}$	$\Delta^{-1/2}\boldsymbol{v}$: a dimensionless measure of velocity (also $\boldsymbol{u}_M = \Delta^{-1/2}\boldsymbol{v}_M$)
f	test particle distribution function
h	$\exp(u^2)f$: a quantity related to the distribution function and chosen to be constant in thermal equilibrium
N	test particle concentration
f_M	host particle distribution function. Since the host particles are in thermal self-equilibrium, f_M is given by $$f_M\, d^3v_M = N_M(M/2\pi kT_M)^{3/2}\exp(-Mv_M^2/2kT_M)\, d^3v_M. \quad (1)$$ We work in the frame in which the host particles have zero mean velocity
$\hat{\boldsymbol{\varepsilon}}$	a unit vector in the direction of motion of the test particle after an encounter with a host particle, as seen from the centre-of-mass frame for the encounter. A circumflex will always denote a unit vector
σ	the differential scattering cross section for the encounter, which is taken to be elastic
$'$	The addition of a prime $'$ to a quantity signifies that the value of that quantity is referred to after the collision

2. Introductory analysis

The Boltzmann equation, which describes the evolution of the one-particle distribution function f for the test particles, is

$$\frac{\partial f}{\partial t}+\boldsymbol{v}\cdot\frac{\partial f}{\partial \boldsymbol{r}}+\frac{q}{m}(\boldsymbol{E}+\boldsymbol{v}\times\boldsymbol{B})\cdot\frac{\partial f}{\partial \boldsymbol{v}}=\left(\frac{\partial f}{\partial t}\right)_{\text{coll}} \quad (2)$$

where the term on the right-hand side of (2) represents the effect of collisions involving the test particles. Since the test particles are very dilute ($N \ll N_M$), the dominant term on the right-hand side arises from interactions between test and host particles; collisions involving only test particles can be neglected. This also makes it consistent to assume that the host particles remain at all times in thermal self-equilibrium. The collision term is represented by an integral of Boltzmann's form:

$$(\partial f/\partial t)_{\text{coll}} = \int\!\!\int\!\!\int\!\!\int\!\!\int (f'_M f' - f_M f)|\boldsymbol{v} - \boldsymbol{v}_M|\sigma \, \mathrm{d}^2 \hat{\boldsymbol{\varepsilon}} \, \mathrm{d}^3 \boldsymbol{v}_M \tag{3}$$

(Chapman and Cowling 1970, p 63). The velocities of the test and host particles after the collision are given by

$$\begin{aligned} \boldsymbol{v}' &= (M\boldsymbol{v}_M + m\boldsymbol{v} + M|\boldsymbol{v} - \boldsymbol{v}_M|\hat{\boldsymbol{\varepsilon}})/(M+m), \\ \boldsymbol{v}'_M &= (M\boldsymbol{v}_M + m\boldsymbol{v} - m|\boldsymbol{v} - \boldsymbol{v}_M|\hat{\boldsymbol{\varepsilon}})/(M+m) \end{aligned} \tag{4}$$

(Waldmann 1958, p 335) and satisfy conservation of momentum and energy in the collision.

It is readily verified from (2) and (3) that for zero electric field the thermal (Maxwellian) distribution does represent an equilibrium state. This is a necessary condition for relaxation to the thermal distribution to be possible, and is not a proof that such relaxation must occur. There is nothing in the following proof (§§ 3 and 4) which invalidates it when the magnetic field is allowed to vary with time; the restriction to static magnetic fields is made solely because from Maxwell's equations such a field would induce an electric field, contrary to the above restriction.

We transform the variables of integration in (3) to rewrite it as

$$(\partial f/\partial t)_{\text{coll}} = \int\!\!\int\!\!\int \mathrm{d}^3\boldsymbol{u}' K(\boldsymbol{u}', \boldsymbol{u})(h' - h) \tag{5}$$

where the scattering kernel K is symmetrical in velocities before and after the collision, and is positive definite:

$$K(\boldsymbol{u}', \boldsymbol{u}) = K(\boldsymbol{u}, \boldsymbol{u}') \tag{6}$$

$$K(\boldsymbol{u}', \boldsymbol{u}) \geqslant 0. \tag{7}$$

It can be expressed in terms of the differential collision cross section σ and the mass ratio m/M, and is given in the present notation by Garrett (1982).

We restrict ourselves as yet to the case of spatial independence ($\partial/\partial \boldsymbol{r} = \mathbf{0}$) in which the magnetic field becomes constant everywhere, and the initial distribution function has no spatial gradients. Consequently we are implicitly dealing with a situation pervading all real space. The Boltzmann equation (2) reduces to

$$\partial f/\partial t + [(q/m)\boldsymbol{v} \times \boldsymbol{B}] \cdot \partial f/\partial \boldsymbol{v} = (\partial f/\partial t)_{\text{coll}}. \tag{8}$$

When the magnetic field term in (8) vanishes, which happens either for zero magnetic field or when the initial distribution function f is symmetrical about the field (in which case it is also readily shown to remain so), the proof of relaxation is traditionally given by expansion of f in eigenfunctions of the collision operator (3); all the eigenvalues can be shown to correspond to decaying modes, except for the thermal distribution, which has a zero eigenvalue and therefore persists. Unfortunately a general proof that the eigenfunctions of the collision operator constitute a complete set of expansion functions is lacking, and has only been given for certain special differential cross sections σ: for those for which the cross section integrated over solid angle is finite, by Koppel (1963) and Ferziger (1965), and for a very restricted class of cross sections for which the integrated cross section diverges, by Pao (1974). These works refer to a linearised version of the relaxation problem for a single-species gas, but it should be possible to generalise to the two-species problem considered here.

3. Proof of relaxation: spatially independent case

We introduce the state function

$$Q=\iiint \mathrm{d}^3\boldsymbol{u}\ \exp(-u^2)h^2=\iiint \mathrm{d}^3\boldsymbol{u}\ \exp(u^2)f^2. \tag{9}$$

The proof of relaxation in the more general case $\boldsymbol{B}\neq\boldsymbol{0}$ is achieved by first showing that Q always decreases as the distribution function evolves, and second that Q is bounded below. It follows from these properties that Q must tend towards a constant value, greater than or equal to the lower bound. It is then shown that this value *is* the lower bound, and that this situation corresponds to thermal equilibrium.

From (9), we have

$$\mathrm{d}Q/\mathrm{d}t=2\iiint \mathrm{d}^3\boldsymbol{u}\ h(\partial f/\partial t). \tag{10}$$

We substitute for $\partial f/\partial t$ from the Boltzmann equation (8), using the form (5) of the collision integral, to give

$$\mathrm{d}Q/\mathrm{d}t=2\iiiint\!\!\iint \mathrm{d}^3\boldsymbol{u}\ \mathrm{d}^3\boldsymbol{u}'\,K(\boldsymbol{u}',\boldsymbol{u})(h'-h)h-2(q/m)\iiint \mathrm{d}^3\boldsymbol{u}\ [(\boldsymbol{u}\times\boldsymbol{B})\cdot(\partial f/\partial\boldsymbol{u})]h. \tag{11}$$

We now show that the second (magnetic field) term in (11) is zero: in suffix notation, it can be rewritten as

$$-(q/m)\varepsilon_{ijk}B_k\iiint \mathrm{d}^3\boldsymbol{u}[\partial(u_j\exp(-u^2)h^2)/\partial u_i-(2u_iu_j+\delta_{ij})\exp(-u^2)h^2]. \tag{12}$$

The first of the terms in the square brackets can be converted to a surface integral at $u=\infty$, and consequently vanishes. The second is zero by virtue of the symmetry properties of the tensors involved when contracted.

The remaining term in (11), due to collisions, is shown to be negative by interchanging $\boldsymbol{u}$ and $\boldsymbol{u}'$, as allowed by the symmetry (6) of the kernel, and adding this to the original formula. The result is

$$\mathrm{d}Q/\mathrm{d}t=-\iiiint\!\!\iint \mathrm{d}^3\boldsymbol{u}\ \mathrm{d}^3\boldsymbol{u}'K(\boldsymbol{u}',\boldsymbol{u})(h'-h)^2 \tag{13}$$

$$\leqslant 0 \tag{14}$$

as a consequence of the positivity property (7) of the kernel. Furthermore, $\mathrm{d}Q/\mathrm{d}t$ is only zero when

$$h(\boldsymbol{u})=\text{constant} \tag{15}$$

which is the thermal distribution.

Next we show how Q is bounded below. Denoting the thermal distribution by a suffix t, we have

$$Q[f]-Q[f_t]=\iiint d^3\boldsymbol{u}\ \exp(-u^2)(h^2-h_t^2) \tag{16}$$

$$=\iiint d^3\boldsymbol{u}\ \exp(-u^2)(h-h_t)^2+2h_t\iiint d^3\boldsymbol{u}\ \exp(-u^2)(h-h_t) \tag{17}$$

where the fact that $h_t(\boldsymbol{u})=$ constant has been used in taking this factor out of the second integral in (17). Now the concentration is given by

$$N=\iiint d^3\boldsymbol{v}\,f=\Delta^{3/2}\iiint d^3\boldsymbol{u}\ \exp(-u^2)h. \tag{18}$$

Since this quantity is conserved, the second integral in (17) vanishes, and we are left with

$$Q[f]-Q[f_t]=\iiint d^3\boldsymbol{u}\ \exp(-u^2)(h-h_t)^2 \tag{19}$$

$$\geqslant 0. \tag{20}$$

Equality only occurs in the thermal state. Chapman and Cowling (1970, p 67) present a more informal proof of the existence of a lower bound for Boltzmann's H function.

The argument given above equation (10) now proves that relaxation must occur. It can readily be seen from (13) that the constant value to which Q tends must be $Q[f_t]$, for only then is dQ/dt vanishingly small. This proof also shows automatically that the thermal distribution is the only equilibrium solution of (8), since any other postulated equilibrium distribution function must eventually evolve to the thermal distribution.

4. Proof of relaxation: spatially inhomogeneous case

In order to generalise this proof to spatially inhomogeneous situations, it is necessary to integrate not only over velocity space but also over real space. We define the spatial averages

$$\mathcal{Q}=V^{-1}\iiint_V d^3\boldsymbol{r}\,Q. \tag{21}$$

$$\mathcal{N}=V^{-1}\iiint_V d^3\boldsymbol{r}\,N. \tag{22}$$

The advantage of dividing by the volume V is that the analysis remains valid in the important limit $V\to\infty$, $\mathcal{N}$ finite.

It is again shown that the thermal distribution (this time with a spatially independent, truly constant concentration of test particles) is a global minimising function for $\mathcal{Q}$. The calculation of $d\mathcal{Q}/dt$ proceeds by analogy with the above case; the collision term acts to decrease $\mathcal{Q}$ and the magnetic field term leaves it unchanged, as before. The new, spatial inhomogeneity term in the expression for $d\mathcal{Q}/dt$ is, from (2), (9) and (21),

$$-2\Delta^{1/2}V^{-1}\iiint_V \mathrm{d}^3\boldsymbol{r}\iiint \mathrm{d}^3\boldsymbol{u}\, h(\boldsymbol{u}\cdot\partial f/\partial\boldsymbol{r})$$

$$= -\Delta^{1/2}V^{-1}\iiint_V \mathrm{d}^3\boldsymbol{r}\iiint \mathrm{d}^3\boldsymbol{u}\ \partial(u_i \exp(u^2)f^2)/\partial r_i \tag{23}$$

which becomes, on use of the divergence theorem in real space,

$$-\Delta^{1/2}V^{-1}\iint_{\partial V} \mathrm{d}^2\boldsymbol{S}\cdot\iiint \mathrm{d}^3\boldsymbol{u}(\boldsymbol{u}\exp(\boldsymbol{u}^2)f^2). \tag{24}$$

If the region of real space with which we are concerned is infinite, (24) obviously vanishes; even if the surface integral is finite, the division by V ensures this. For finite regions, provided that the test particles are perfectly confined, there can be no flux of test particles in or out of the region in any velocity range:

$$\mathrm{d}^2\boldsymbol{S}\cdot(\boldsymbol{u}f\,\mathrm{d}^3\boldsymbol{u}) = 0 \tag{25}$$

and consequently (24) must vanish. Only the collision term affects the evolution of $\mathcal{Q}$, and as before causes it to decrease until it reaches its lower bound at thermal equilibrium.

It should be noted that there are states other than global thermal equilibrium for which $\mathrm{d}\mathcal{Q}/\mathrm{d}t$ is zero: these are states of *local* thermal equilibrium, in which the local temperature is constant but the concentration varies; the quantity h becomes purely a function of position. It is apparent that the collision term, and therefore $\mathrm{d}\mathcal{Q}/\mathrm{d}t$, vanishes. However, from the Boltzmann equation, the spatial inhomogeneity must cause the distribution function to evolve away from local thermal equilibrium, so the collision term will then become non-zero, and cause $\mathcal{Q}$ to decrease, as before. The zero of $\mathrm{d}\mathcal{Q}/\mathrm{d}t$ in local thermal equilibrium is instantaneous, rather than permanent.

5. Effect of an electric field

In the presence of an electric field, it is readily apparent that the thermal distribution is no longer the equilibrium solution of the Boltzmann equation (2). This is reflected in a breakdown of our proof as follows. For simplicity we consider only the case of zero ambient magnetic field, and spatial homogeneity, so that the electric field is everywhere the same. Then, from (2) and (10), the expression for $\mathrm{d}Q/\mathrm{d}t$ in the presence of the electric field is changed by an amount

$$-2(q/m\Delta^{1/2})\iiint \mathrm{d}^3\boldsymbol{u}\, h(\boldsymbol{E}\cdot\partial f/\partial\boldsymbol{u})$$

$$= -(q/m\Delta^{1/2})\boldsymbol{E}\cdot\iiint \mathrm{d}^3\boldsymbol{u}[\partial(\exp(u^2)f^2)/\partial\boldsymbol{u} - 2\boldsymbol{u}\exp(u^2)f^2]. \tag{26}$$

Again, the first term in the square brackets on the right-hand side can be reduced to a surface integral at $u=\infty$ and neglected. The second term will not vanish since the electric field ultimately induces a drift of charged particles parallel to itself at all velocities: $q\boldsymbol{E}\cdot\boldsymbol{u}$ is always positive (even if q is negative) and so (26) is also positive.

This term therefore always opposes the term (13) arising from collisions, which always acts to decrease Q. The crucial monotonicity property (14) of Q is destroyed, and so it is not directly provable from this approach that if an equilibrium exists between the two terms, the system is forced to approach it. Such an equilibrium may very well not exist if collision effects are sufficiently weak for high-energy particles, a situation leading to the phenomenon of particle runaway. These questions are reviewed by Kumar *et al* (1980, section 5b). Nor is it an easy matter to construct a monotonic functional of the distribution function in which the electric fields appear explicitly in the definition, which would be another way of attacking such questions; clearly further work remains to be done in these areas.

6. Alternation of higher derivatives of Q

It will now be shown that, in the absence of electric field and spatial inhomogeneity and for static magnetic field, successive derivatives of Q alternate in sign at all times during the relaxation. This is of interest as a result of the conjecture (McKean 1966) that only one functional of f should possess this property, and that it should be identified as the entropy for the system. There is no *a priori* reason to suppose that our Q is related to entropy; the standard definition of the (negative) entropy in a gas mixture is just the sum of the individual (negative) entropies of the various constituents,

$$\sum_{\text{species } s} \iiint d^3\boldsymbol{v}_s f_s \ln f_s \tag{27}$$

(Chapman and Cowling 1970, p 81), which does not reduce to (9) even in the relevant limit of thermally distributed host particles and infinite dilution of the test particles. Simons (1969) has shown that for a single-species gas sufficiently close to equilibrium, Q and the Boltzmann entropy differ only by a constant, but we are concerned here with arbitrarily large perturbations.

The proof of alternation is inductive, and is based on that of Simons (1969) for the linearised single-species problem. It has been generalised to allow for the magnetic field: this is the first time that the alternating derivative property has been studied for anything other than spatially homogeneous field-free situations.

We define a scalar bracket of two functions α, β of a vector-valued argument:

$$\langle \alpha, \beta \rangle = \iiint d^3\boldsymbol{u} \exp(u^2)\alpha(\boldsymbol{u})\beta(\boldsymbol{u}). \tag{28}$$

From (9), therefore,

$$Q = \langle f, f \rangle. \tag{29}$$

We also rewrite the collision operator (5) as

$$(\partial f/\partial t)_{\text{coll}} = Lf(\boldsymbol{u}) = \iiint d^3\boldsymbol{u}' K^{(1)}(\boldsymbol{u}', \boldsymbol{u}) \exp(u'^2) f(\boldsymbol{u}'). \tag{30}$$

By comparison with (5) and the definition of h, the new kernel $K^{(1)}$ can be written as

$$K^{(1)}(\boldsymbol{u}', \boldsymbol{u}) = K(\boldsymbol{u}', \boldsymbol{u}) - \delta^3(\boldsymbol{u}' - \boldsymbol{u}). \tag{31}$$

Differentiability of $K^{(1)}$ with respect to its arguments will be assumed: although this is not rigorous in view of the delta function in (31), a full analysis would give the same results.

We need as lemmas the following results.

(1)
$$L^n f(\boldsymbol{u}) = \iiint \mathrm{d}^3\boldsymbol{u}_n\, K^{(n)}(\boldsymbol{u}, \boldsymbol{u}_n) \exp(u_n^2) f(\boldsymbol{u}_n) \tag{32}$$

where the iterated kernel $K^{(n)}$ is symmetrical with respect to its two arguments. This is proved by noting from (6) and (31) that $K^{(1)}$ has this property, and that by repeated application of (30)

$$K^{(n)}(\boldsymbol{u}, \boldsymbol{u}_n) = \int \ldots \int \mathrm{d}^3\boldsymbol{u}_1\, \mathrm{d}^3\boldsymbol{u}_2 \ldots \mathrm{d}^3\boldsymbol{u}_{n-1} K^{(1)}(\boldsymbol{u}, \boldsymbol{u}_1) \exp(u_1^2) K^{(1)}(\boldsymbol{u}_1, \boldsymbol{u}_2)$$
$$\times \exp(u_2^2) \ldots K^{(1)}(\boldsymbol{u}_{n-2}, \boldsymbol{u}_{n-1}) \exp(u_{n-1}^2) K^{(1)}(\boldsymbol{u}_{n-1}, \boldsymbol{u}_n), \tag{33}$$

in which form the symmetry is manifest. Furthermore, since no external vector has been introduced into (33), these kernels can only depend on scalar products of the vectors involved:

$$K^{(n)}(\boldsymbol{u}, \boldsymbol{u}_n) = \mathscr{K}^{(n)}(u^2, u_n^2, \boldsymbol{u} \cdot \boldsymbol{u}_n) \tag{34}$$

where $\mathscr{K}^{(n)}$ is symmetrical with respect to its first and second arguments.

(2)
$$\langle \alpha, L\beta \rangle = \langle L\alpha, \beta \rangle \tag{35}$$

and

$$\langle \alpha, L\alpha \rangle \leqslant 0. \tag{36}$$

These relationships are just the well known self-adjointness property of the collision operator and the statement that its eigenvalues are negative: in view of (29) the latter equation is essentially the statement, at the heart of § 3, that Q cannot increase. They are proved by writing $\langle \alpha, L\beta \rangle$ in full, and adding to it the equal expression given by interchanging $\boldsymbol{u}$ and $\boldsymbol{u}'$ in the integrations, as the symmetry (11) of K allows. This gives

$$\langle \alpha, L\beta \rangle = -\tfrac{1}{2} \iiiiiint \mathrm{d}^3\boldsymbol{u}\, \mathrm{d}^3\boldsymbol{u}'\, K(\boldsymbol{u}', \boldsymbol{u})[\exp(u'^2)\alpha(\boldsymbol{u}') - \exp(u^2)\alpha(\boldsymbol{u})]$$
$$\times [\exp(u'^2)\beta(\boldsymbol{u}') - \exp(u^2)\beta(\boldsymbol{u})]. \tag{37}$$

Since (37) is symmetrical in α and β it could equally well have come from $\langle L\alpha, \beta \rangle$; (35) now follows. Inequality (36) is immediately recovered from (37) by putting $\beta = \alpha$ and using the positivity property (7) of K.

The (inductive) proof that successive derivatives of Q alternate in sign is as follows. Suppose

$$\mathrm{d}^n Q/\mathrm{d}t^n = 2^n \langle f, L^n f \rangle. \tag{38}$$

Then

$$\mathrm{d}^{n+1} Q/\mathrm{d}t^{n+1} = 2^{n+1} \langle \partial f/\partial t, L^n f \rangle \tag{39}$$

using the fact that the operators $\partial/\partial t$ and L commute, and also property (35). If we now substitute for $\partial f/\partial t$ from the Boltzmann equation (8), we find that

$$\mathrm{d}^{n+1} Q/\mathrm{d}t^{n+1} = 2^{n+1} \langle Lf, L^n f \rangle - 2^{n+1} (q/m) \langle \boldsymbol{u} \times \boldsymbol{B} \cdot (\partial f/\partial \boldsymbol{u}), L^n f \rangle. \tag{40}$$

By (35) again, the first of these brackets is $2^{n+1}\langle f, L^{n+1}f\rangle$. Thus if we can establish that the second bracket in (40) vanishes, we will have an inductive chain. Write this term, using h rather than f, and from equation (32), as

$$\langle \boldsymbol{u}\times\boldsymbol{B}\cdot(\partial f/\partial \boldsymbol{u}), L^n f\rangle$$
$$=\varepsilon_{ijk}B_k\iiint \mathrm{d}^3\boldsymbol{u}\ \exp(u^2)u_j\partial(\exp(-u^2)h(\boldsymbol{u}))/\partial u_i\iiint \mathrm{d}^3\boldsymbol{u}_n\,\boldsymbol{K}^{(n)}h(\boldsymbol{u}_n). \quad (41)$$

We rewrite the integrand in (41) as

$$\exp(u^2)u_j\partial(\exp(-u^2)h(\boldsymbol{u}))/\partial u_i\boldsymbol{K}^{(n)}h(\boldsymbol{u}_n)$$
$$=-(2u_iu_j+\delta_{ij})\boldsymbol{K}^{(n)}h(\boldsymbol{u})h(\boldsymbol{u}_n)+h(\boldsymbol{u}_n)\partial\{u_j\boldsymbol{K}^{(n)}h(\boldsymbol{u})\}/\partial u_i$$
$$-u_jh(\boldsymbol{u})h(\boldsymbol{u}_n)\partial\boldsymbol{K}^{(n)}/\partial u_i. \quad (42)$$

The first term on the right-hand side of (42) is symmetrical in indices i and j and consequently vanishes on contraction with ε_{ijk}. The second term vanishes when substituted back into (41) as a consequence of the divergence theorem in $\boldsymbol{u}$ space. We are therefore left with

$$\langle \boldsymbol{u}\times\boldsymbol{B}\cdot(\partial f/\partial \boldsymbol{u}), L^n f\rangle$$
$$=-\varepsilon_{ijk}B_k\iiint \mathrm{d}^3\boldsymbol{u}u_jh(\boldsymbol{u})\iiint \mathrm{d}^3\boldsymbol{u}_n\,h(\boldsymbol{u}_n)\partial\boldsymbol{K}^{(n)}/\partial u_i \quad (43)$$
$$=-\varepsilon_{ijk}B_k\iiint \mathrm{d}^3\boldsymbol{u}\,u_jh(\boldsymbol{u})\iiint \mathrm{d}^3\boldsymbol{u}_nh(\boldsymbol{u}_n)$$
$$\times[2u_i\partial\mathscr{K}^{(n)}(\xi,\eta,\rho)/\partial\xi+(\boldsymbol{u}_n)_i\partial\mathscr{K}^{(n)}/\partial\rho] \quad (44)$$

where $\xi=u^2$, $\eta=u_n^2$ and $\rho=\boldsymbol{u}\cdot\boldsymbol{u}_n$, using (34) to rewrite the kernel. Both terms in the square brackets in (44), when integrated over $\boldsymbol{u}$ and $\boldsymbol{u}_n$, yield forms symmetrical in i and j, which therefore vanish on contraction with ε_{ijk}. The bracket vanishes, and so, from (40), we have established the inductive chain: if (38) holds for some n, it also holds for all successive values. It holds by definition (29) for $n=0$, and for $n=1$ is the subject of § 3. Therefore (38) is established for all values of n. Alternation is assured from (28), (35) and (36): if n is even then

$$\mathrm{d}^nQ/\mathrm{d}t^n=2^n\langle L^{n/2}f, L^{n/2}f\rangle\geqslant 0 \quad (45)$$

while if n is odd

$$\mathrm{d}^nQ/\mathrm{d}t^n=2^n\langle L^{(n-1)/2}f, LL^{(n-1)/2}f\rangle\leqslant 0 \quad (46)$$

in view of (35) with $\alpha=L^{(n-1)/2}f$. It follows as the result of a theorem by Bernstein (1928) that Q can be expressed as the Laplace transform (with respect to time) of a non-negative definite function.

Although the magnetic field drops out of the expressions for time derivatives of Q in terms of the distribution function f, it does still influence the evolution of Q through its effect on the evolution of f, as given by the Boltzmann equation (8).

Note finally that, by making a Taylor expansion of Q about the initial conditions and using (38),

$$Q(t)=\sum_{n=0}^{\infty}\langle f_0, L^nf_0\rangle 2^nt^n/n!=\langle f_0, \exp(2tL)f_0\rangle. \quad (47)$$

7. Other choices of the relaxation state function

The motivation behind McKean's conjectures is dissatisfaction with the standard definition (27) of the (negative) entropy; the fact that this quantity always decreases is only a necessary, rather than a sufficient, condition for the identification of (27) with entropy. Harris (1968a, b) has presented evidence why (27) should not be regarded as the entropy, at least for hard-sphere gases in finite concentrations, and has given different expressions. Rejection of (27) implies spurning the information—theoretical aspects of the problem (Maass 1970).

In this section we find an infinite family of monotonically decreasing functionals of the distribution function f in the field-free case, and show that a (infinite) subset of these functionals still retains this property in the presence of a magnetic field. Among this subset are our own Q, and several functionals closely related to (27). McKean's conjecture that the alternating derivative property for free thermal relaxation serves to pick out the physical entropy seems untenable, at least for this problem, in view of the non-trivial discrepancy between Q and (27). Maass (1970) and Garrett (1983) have also shown that, for particular collision models, the property does not uniquely pick out only one functional. The second of these papers refers to the important case of the single-species nonlinear field-free spatially homogeneous Boltzmann equation, and also shows that the alternating derivative hypothesis breaks down for this collision model.

It is easily shown that, in the absence of fields and spatial inhomogeneities, *any* functional

$$\Phi=\iiint \mathrm{d}^3\boldsymbol{u}\,\exp(-u^2)\phi[h(\boldsymbol{u})] \tag{48}$$

for which ϕ is an algebraic function of h with positive curvature:

$$\mathrm{d}^2\phi/\mathrm{d}h^2\geqslant 0,\qquad \forall h\geqslant 0 \tag{49}$$

can never increase:

$$\mathrm{d}\Phi/\mathrm{d}t\leqslant 0. \tag{50}$$

This is proved as follows. For ease define

$$\psi=\mathrm{d}\phi/\mathrm{d}h. \tag{51}$$

Then

$$\mathrm{d}\Phi/\mathrm{d}t=\iiint \mathrm{d}^3\boldsymbol{u}\psi(\partial f/\partial t). \tag{52}$$

If we now substitute for $\partial f/\partial t$ from the Boltzmann equation, and then use the standard trick of interchanging $\boldsymbol{u}$ and $\boldsymbol{u}'$ and adding the original and interchanged equations, we find

$$\mathrm{d}\Phi/\mathrm{d}t=-\tfrac{1}{2}\iiiint\!\!\iint \mathrm{d}^3\boldsymbol{u}\,\mathrm{d}^3\boldsymbol{u}'K(\psi'-\psi)(h'-h) \tag{53}$$

in an obvious shorthand notation. The property (50) of uniform decrease follows immediately from (49), (52) and (53). It can also be shown that the thermal distribution (15) is the only stationary distribution for Φ: this is accomplished by considering small variations in Φ induced by varying the distribution function. Only variations which preserve the concentration (18) are permitted; this is dealt with by introducing a Lagrange multiplier. Care should be taken to check that the stationary, thermal distribution is a minimum, and a global rather than just a local one.

The functionals Φ given by (48) and (49) are complete in that they are the only functionals which decrease uniformly and are made stationary by the thermal distribution: for if there were a region in which (49) were not satisfied, h could be chosen as a very sharp peak in that region, and, from (53), Φ would increase. Also, if Φ were permitted to have dependence on $\boldsymbol{u}$ other than through h, the analysis would show that the thermal distribution no longer makes it stationary. It remains open whether our Q is the only state function Φ with all derivatives alternating in sign.

In the presence of a magnetic field, there is an extra term

$$\varepsilon_{ijk}B_k \iiint \mathrm{d}^3\boldsymbol{u}\, \psi u_j \partial f/\partial u_i$$

$$= \varepsilon_{ijk}B_k \iiint \mathrm{d}^3\boldsymbol{u}[\partial(u_j f\psi)/\partial u_i - \delta_{ij} f\psi - u_j f(\mathrm{d}\psi/\mathrm{d}h)(\partial h/\partial u_i)] \tag{54}$$

in the expression (53) for the evolution of Φ. The first two terms on the right-hand side of (54) vanish by virtue of the divergence theorem and tensor symmetry respectively. The third term, after further manipulation, simplifies to

$$\varepsilon_{ijk}B_k \iiint \mathrm{d}^3\boldsymbol{u}\; u_j(\partial f/\partial u_i)(-\mathrm{d}\psi/\mathrm{d}(\ln h)). \tag{55}$$

This is the same as the left-hand side of (54) except that ψ has been differentiated with respect to $-\ln h$. By repeated application of this prescription, the term can clearly be written as

$$\varepsilon_{ijk}B_k \iiint \mathrm{d}^3\boldsymbol{u}\; u_j(\partial f/\partial u_i) \sum_{n=0}^{\infty} \lambda_n(-\mathrm{d}/\mathrm{d}(\ln h))^n\psi \tag{56}$$

provided only that the sum of the coefficients λ_n is unity. The term will vanish if $\psi(h)$ satisfies the differential equation

$$\sum_{n=0}^{\infty} \lambda_n(-\mathrm{d}/\mathrm{d}(\ln h))^n\psi = 0 \tag{57}$$

for some such set $\{\lambda_n\}$. Even with the magnetic field present there is a vast freedom of choice of decreasing functionals Φ!

Evidently the choice

$$\phi = h^2, \qquad \psi = 2h, \qquad \lambda_0 = \lambda_1 = \tfrac{1}{2}, \qquad \lambda_2 = \lambda_3 = \ldots = 0 \tag{58}$$

corresponds to our own functional, Q. Other possibilities include any positive power of h, and various combinations of powers and logarithms, quite similar to (27). They must still satisfy (49) in order to be potential candidates for the physical entropy, and would then serve as well as Q in proving that relaxation occurs.

8. Conclusions

It has been demonstrated with full rigour that relaxation to thermal equilibrium of a very dilute species of charged particle in a heat bath of other particles must always occur, even in the presence of a magnetic field. This result is of potential use in all applications of dilute plasmas (Kumar *et al* (1980) give a summary). The conflicting definitions of entropy for the problem have been examined by means of McKean's conjecture that successive time derivatives of the entropy should alternate in sign; a functional possessing this property has been found, and the property persists even with magnetic field. The conjecture seems to be of dubious validity in this example.

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