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G. L. BRAGLIA and G. L. CARAFFINI (*)

Remarks on the equation for the energy relaxation of a Rayleigh gas. (**)

1. - Introduction.

During a recent investigation of the motions of electrons in a field in a gas, we were led to study the limits of the conventional (first-order) theory and, in particular, to obtain an improved (i.e. a second-order) equation for the electron energy distribution $p(\varepsilon, t)$ [**2**]$_1$, [**3**]. We based our analysis on a very appropriate procedure which starts from the linearized Boltzmann (or master) equation for $p(\varepsilon, t)$. This integro-differential equation is replaced by a series development of the Kramers-Moyal type [**6**]. The coefficients are given in a particularly convenient form [**2**]$_2$, [**3**] allowing us to obtain quickly the appropriate (differential) equation for $p(\varepsilon, t)$ for an arbitrary law of electron-atom interaction (to the desired order of approximation). However, our procedure is not only applicable to the Lorentz gas. In fact, it may advantageously be used also to study relaxation processes of a Rayleigh gas. In particular, it still allows one to obtain easily the equation for $p(\varepsilon, t)$ to higher orders than the first with respect to the ratio between the mass of the subsystem-particles and that of the background-gas particles, for arbitrary law of interaction.

In this paper we present the derivation of the second-order equation for the energy distribution of heavy particles in a gas of light atoms. This means that the terms of higher order than the second with respect to the mass ratio are neglected. We limit ourselves to consider field-free gases and elastic collisions [**2**]$_3$, but *we do not impose restrictions on the interaction law.* To test

(*) Indirizzo: Istituto di Matematica, Università, 43100 Parma, Italia.

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the correctness of our results, we analyze, in particular, the hard-sphere model, in which all the particles of our two-component system are considered to be hard spheres interacting only at the instant of impact. In this case, it is shown that our results are consistent with the (exact) expressions of the first three coefficients of the Kramers-Moyal expansion given by Andersen and Shuler [**1**]. However, even for this simple case, we have been unable to make a comparison between our (fourth-order) equation for $p(\varepsilon, t)$ and corresponding equations of the literature. In fact, it seems that the second-order equation for the energy distribution of a three-dimensional Rayleigh gas has never been derived, not even for the simplest interaction laws. On the contrary, we find in the literature second-order equations for the one-dimensional gas (Rayleigh piston) [**7**]. Really, for a three-dimensional system, it is not even easy to find in the literature the first-order equation, if we do not impose limitations on the interaction law. In any case, the available derivations are very different from, and more complicated than, the derivation given here [**8**].

In this paper we will not be concerned with the solution of the equation for $p(\varepsilon, t)$. However, we shall make some remarks on the temporal behaviour of the energy distribution under special conditions. We shall also dwell a little on the relaxation of the moments of $p(\varepsilon, t)$ and will give some results which are of interest, particulary in the light of the recent progress in this field [**4**].

2. - Equations for $p(\varepsilon, t)$.

2.1. - Our model consists of a subsystem of heavy particles (of mass m), homogeneously dispersed in a heat bath of light particles (of mass M and number density N) at a given temperature T. It is assumed that the temporal behaviour of the subsystem energy distribution $p(\varepsilon, t)$ is properly accounted for neglecting collisions between particles of the subsystem. Moreover, inelastic collisions and action of external fields are excluded.

As in paper [**3**], our starting point is the equation

$$\frac{\partial p(\varepsilon, t)}{\partial t} = \sum_1^\infty {}_r \frac{(-1)^r}{r!} \frac{\partial^r}{\partial \varepsilon^r} \left(b_r(\varepsilon) p(\varepsilon, t)\right) , \tag{1}$$

with ([**2**], [**4**])

$$b_r(\varepsilon) = (-1)^r \left(\frac{mM}{m+M}\right)^r N \int_V \int_s g^{r+1} [\boldsymbol{G} \cdot (\boldsymbol{r} - \boldsymbol{s})]^r \sigma(g, \chi) F(V) \, \mathrm{d}^2 \boldsymbol{s} \, \mathrm{d}^3 \boldsymbol{V} , \tag{2}$$

where we have used the following notations:

$\boldsymbol{v}$ and $\boldsymbol{V}$ are the subsystem-particle and atom velocities in the laboratory frame, respectively;

$\boldsymbol{g} = g\boldsymbol{r} = \boldsymbol{v} - \boldsymbol{V}$ and $\boldsymbol{g}' = g\boldsymbol{s}$ are the relative velocities before and after collision, respectively;

$\boldsymbol{G}$ is the center-of-mass velocity;

$\sigma(g, \chi)\, d^2\boldsymbol{s}$ is the differential scattering cross section;

$F(V)$ is the velocity distribution function relevant to the gas atoms.

An inspection of eq. (2) shows, clearly, that an explicit expression of $b_r(\varepsilon)$ cannot be obtained in the absence of simplifying assumptions. Generally, they concern the g-dependence of the cross section. But the assumption which leads to the most considerable simplification is that of assuming $T = 0$. This assumption is much more interesting in the Lorentz limit than in the Rayleigh limit. However, since our treatment of sect. **2.2** is not appropriate for atoms at rest, it is useful that we give here also the results relevant to this case [**3**].

For $T=0$, all the coefficients $b_r(\varepsilon)$ can be obtained exactly. The result is [**3**]

$$b_r(\varepsilon) = \left(-2\,\frac{mM}{(m+M)^2}\right)^r \varepsilon^r\, \tilde{\nu}_r(\varepsilon)\,, \tag{3}$$

where

$$\tilde{\nu}_r(\varepsilon) = \left\{ Nv\cdot 2\pi \int_0^\pi (1-\cos\chi)^r \sigma(v,\chi)\sin\chi\, d\chi \right\}_{v=\sqrt{2\varepsilon/m}}\,. \tag{4}$$

In particular, we can write

$$b_1(\varepsilon) = -2\,\frac{mM}{(m+M)^2}\,\varepsilon\nu_m(\varepsilon)\,, \tag{5}$$

where $\nu_m(\varepsilon) = \tilde{\nu}_1(\varepsilon)$ is the momentum-transfer cross section relevant to a sub-system particle of energy ε. Moreover,

$$b_2(\varepsilon) = 4\left(\frac{mM}{(m+M)^2}\right)^2 \varepsilon^2\tilde{\nu}_2(\varepsilon) = 4\left(\frac{mM}{(m+M)^2}\right)^2 \varepsilon^2\big(2\nu_1(\varepsilon) - \nu_2(\varepsilon)\big)\,, \tag{6}$$

where use has also been made of the alternative definition [**3**]

$$\nu_r(\varepsilon) = \{Nv\cdot 2\pi\int_0^\pi (1-\cos^r\chi)\,\sigma(v,\chi)\sin\chi\, d\chi\}_{v=\sqrt{2\varepsilon/m}}\,. \tag{7}$$

Thus, if we limit ourselves to consider only second-order terms with respect to the (small) quantity M/m, we obtain that

$$(8)\qquad \begin{cases} b_1(\varepsilon) = -2\left(\dfrac{M}{m}\right)^2\left(\dfrac{m}{M}-2\right)\varepsilon\nu_1(\varepsilon) \\ b_2(\varepsilon) = 4\left(\dfrac{M}{m}\right)^2\varepsilon^2(2\nu_1(\varepsilon)-\nu_2(\varepsilon)) \\ b_r(\varepsilon) = 0 \qquad\qquad (r>2)\,. \end{cases}$$

In other words, only the first two terms of expansion (2) remain different from zero and the equation for $p(\varepsilon, t)$ maintains the Fokker-Planck form.

A further interesting simplification of the coefficients $b_r(\varepsilon)$ is obtained if the scattering processes are isotropic (e.g. if we adopt the hard-sphere model). In this case, in fact, we have that

$$(9)\qquad b_r(\varepsilon) = \left(-2\,\frac{mM}{(m+M)^2}\right)^r \varepsilon^r\nu(\varepsilon)\cdot\frac{1}{2}\sum_0^r{}_j\binom{r}{j}\frac{(-1)^j}{1+j}\left[1-(-1)^{1+j}\right],$$

where $\nu(\varepsilon)$ is the collision frequency

$$(10)\qquad \nu(\varepsilon) = \{Nv\cdot 4\pi\sigma(v)\}_{v=\sqrt{2\varepsilon/m}}\,.$$

As one can see, if $T=0$, the procedure based on eq. (2) allows us to write immediately all the exact coefficients of the Kramers-Moyal expansion, for arbitrary interaction law. This is an important remark when considering the complexity of other treatments based on different methods of approach [**5**].

2.2. - If we renounce the assumption $T=0$ and want to take account of the atom motions correctly, our problem becomes much more difficult. In this case, it becomes necessary to know the g-dependence of $\sigma(g, \chi)$ and only if $\sigma(g,\chi)\propto g^{-1}$ (in which case the frequencies ν_k, or $\tilde{\nu}_k$, are energy-independent) is a remarkable simplification possible. In general, however, it is necessary to have recourse to approximate results.

As we said, we shall limit ourselves to calculate approximate expressions, say $\beta_r(\varepsilon)$, of the exact moments $b_r(\varepsilon)$, by neglecting the terms of higher orders than the second with respect to the mass ratio M/m. In particular, we shall show that

$$(11)\qquad \begin{cases} b_r(\varepsilon) = \beta_r(\varepsilon) + o\big((M/m)^2\big) \qquad \text{for } r=1,\dots,4 \\ b_r(\varepsilon) = o\big((M/m)^2\big) \qquad\qquad \text{for } r>4\,, \end{cases}$$

where $o((M/m)^2)$ means terms of orders $(M/m)^j$, with $j > 2$. Then, as for the Lorentz gas [3], the second-order theory leads to a fourth-order differential equation for $p(\varepsilon, t)$.

As regards the first coefficient of this equation, in [3] it is shown that it can be written in the form

$$(12) \qquad b_1(\varepsilon) = \frac{mM}{(m+M)^2} \int_0^\infty V^2 F(V)\,\mathrm{d}V \left\{ \int_{4\pi} [MV^2 + (m-M)vV\cos\gamma - mv^2] \cdot \right.$$
$$\left. \cdot \nu_1(g) \sin\gamma\,\mathrm{d}\gamma\,\mathrm{d}\eta \right\}_{v=\sqrt{2\varepsilon/m}},$$

where $\gamma \sphericalangle \boldsymbol{v}\boldsymbol{V}$. Clearly, in order to calculate $b_1(\varepsilon)$ we must assign $\nu_1(g)$. Only for $T = 0$, i.e. $g = v$, the knowledge of the speed-dependence of ν_1 is not required.

A particularly interesting and simple case is that in which ν_1 is g-independent. Under this condition, in fact, we have immediately that

$$(13) \qquad b_1(\varepsilon) = 2\frac{mM}{(m+M)^2}\left(\frac{3}{2}kT - \varepsilon\right)\nu_1 .$$

But, apart from this and other simple expressions of $\nu_1(g)$, in general the problem is complicated, since the dependence of ν_1 on V cannot be made explicit, even approximately (this is, in fact, the substantial difference one finds between Rayleigh and Lorentz gases [3]). We can, however, make the dependence of $\nu_k(g)$ on γ explicit and go on as follows.

Consider physical situations in which the energy of the subsystem particles may be assumed to be of order kT, i.e. ε/kT of zero order with respect M/m, in almost all collisions. Then we are allowed to consider $v \ll V$ and $v/V \sim \sqrt{M/m}$, and write that

$$(14)_1 \qquad g = |\boldsymbol{v} - \boldsymbol{V}| = \sqrt{v^2 + V^2 - 2vV\cos\gamma} \approx$$
$$\approx V - v\cos\gamma + \frac{1}{2}\frac{v^2}{V}\sin^2\gamma + \frac{1}{2}\frac{v^3}{V^2}\cos\gamma\sin^2\gamma + \dots,$$

that is

$$(14) \qquad \nu_k(g) \approx \nu_k(V) - \frac{\mathrm{d}\nu_k(V)}{\mathrm{d}V}\left(v\cos\gamma - \frac{v^2}{2V}\sin^2\gamma - \frac{v^3}{2V^2}\cos\gamma\sin^2\gamma\right) +$$
$$+ \frac{1}{2}\frac{\mathrm{d}^2\nu_k(V)}{\mathrm{d}V^2}\left(v^2\cos^2\gamma - \frac{v^3}{V}\cos\gamma\sin^2\gamma\right) - \frac{1}{6}\frac{\mathrm{d}^3\nu_k(V)}{\mathrm{d}V^3}v^3\cos^3\gamma + \dots .$$

Let us introduce the notation

$$\langle\varphi(V)\rangle = 4\pi\int_0^\infty \varphi(V)\,V^2 F(V)\,\mathrm{d}V \tag{15}$$

to indicate the average of any arbitrary (scalar) function $\varphi(V)$ of V over the background-particle speed distribution $4\pi V^2 F(V)$. Then, in virtue of eq. (7), if we neglect all the terms of higher order than the second with respect to M/m, after some simple calculations we obtain that (cfr. eq. (2))

$$\beta_1(\varepsilon) = \left(\frac{M}{m}\right)^2 \left\{ \left[-\frac{8}{15}\frac{1}{kT}\langle V\nu_1'\rangle - \frac{2}{5}\frac{1}{M}\langle \nu_1''\rangle - \frac{2}{15}\frac{1}{M}\langle V\nu_1'''\rangle \right]\varepsilon^2 + \right.$$
$$+ \left[-2\left(\frac{m}{M}-2\right)\langle\nu_1\rangle - \frac{2}{3}\left(\frac{m}{M}-4\right)\langle V\nu_1'\rangle + \frac{kT}{M}\left(\langle\nu_1''\rangle + \frac{1}{3}\langle V\nu_1'''\rangle\right)\right]\varepsilon +$$
$$\left. + \left(\frac{m}{M}-2\right)\left(3\langle\nu_1\rangle + \langle V\nu_1'\rangle\right)kT \right\}. \tag{16}$$

As regards the second coefficient, we have [**3**]

$$b_2(\varepsilon) = \left(\frac{mM}{m+M}\right)^2 \left\{ \int_V F(V)\left[\left(2\nu_1(g) - \frac{3}{2}\nu_2(g)\right)(\boldsymbol{G}\cdot\boldsymbol{g})^2 + \right.\right.$$
$$\left.\left. + \frac{1}{2}\nu_2(g)\,G^2 g^2\right]\mathrm{d}^3\boldsymbol{V} \right\}_{v=\sqrt{2\varepsilon/m}}. \tag{17}$$

If we introduce into this equation the quantities

$$\left\{ \begin{aligned} \nu_k(g) &\approx \nu_k(V) - \frac{\mathrm{d}\nu_k(V)}{\mathrm{d}V}\left(v\cos\gamma - \frac{v^2}{2V}\sin^2\gamma\right) + \frac{1}{2}\frac{\mathrm{d}^2\nu_k(V)}{\mathrm{d}V^2}v^2\cos^2\gamma \\ \boldsymbol{G}\cdot\boldsymbol{g} &= -\frac{1}{m+M}\left(MV^2 + (m-M)Vv\cos\gamma - mv^2\right) \\ (Gg)^2 &= \frac{1}{(m+M)^2}\left(m^2v^2 + M^2V^2 + 2MmvV\cos\gamma\right)\left(v^2 + V^2 - 2vV\cos\gamma\right), \end{aligned} \right. \tag{18}$$

after simple calculations we find that (cfr. eq. (11))

$$\beta_2(\varepsilon) = \left(\frac{M}{m}\right)^2 \left\{ 4\left[2\langle\nu_1\rangle - \langle\nu_2\rangle + \frac{22}{15}\langle V\nu_1'\rangle - \frac{3}{5}\langle V\nu_2'\rangle + \right.\right. \tag{19}$$

$$+\frac{kT}{M}\left(\frac{3}{5}\langle\nu_1''\rangle-\frac{1}{5}\langle\nu_2''\rangle+\frac{1}{5}\langle V\nu_1'''\rangle-\frac{1}{15}\langle V\nu_2'''\rangle\right)\Bigg]\varepsilon^2+$$

$$+4\left[\frac{m}{M}\left(\langle\nu_1\rangle+\frac{1}{3}\langle V\nu_1'\rangle\right)-12\langle\nu_1\rangle+5\langle\nu_2\rangle-\frac{20}{3}\langle V\nu_1'\rangle+3\langle V\nu_2'\rangle-\right.$$

$$\left.-\frac{kT}{M}\left(2\langle\nu_1''\rangle-\langle\nu_2''\rangle+\frac{2}{3}\langle V\nu_1'''\rangle-\frac{1}{3}\langle V\nu_2'''\rangle\right)\right]kT\cdot\varepsilon+$$

$$+\Bigg[30\langle\nu_1\rangle-15\langle\nu_2\rangle+18\langle V\nu_1'\rangle-9\langle V\nu_2'\rangle+$$

$$\left.+\frac{kT}{M}\left(6\langle\nu_1''\rangle-3\langle\nu_2''\rangle+2\langle V\nu_1'''\rangle-\langle V\nu_2'''\rangle\right)\Bigg](kT)^2\right\}.$$

The third coefficient can be obtained in the same way. We have [**3**]

$$(20)\qquad b_3(\varepsilon)=-\left(\frac{mM}{m+M}\right)^3\int_V F(V)\left\{(3\nu_1(g)-3\nu_2(g)+\nu_3(g))(\boldsymbol{G}\cdot\boldsymbol{g})^3+\right.$$

$$\left.+\frac{3}{2}\left[(\nu_1(g)+\nu_2(g)-\nu_3(g))\,G^2g^2(\boldsymbol{G}\cdot\boldsymbol{g})-(\nu_1(g)+\nu_2(g)-\nu_3(g))(\boldsymbol{G}\cdot\boldsymbol{g})^3\right]\right\}_{v=\sqrt{2\varepsilon/m}}\mathrm{d}^3\boldsymbol{V}.$$

In this case it is sufficient to consider that

$$(21)\qquad \nu_k(g)\approx\nu_k(V)-\frac{\mathrm{d}\nu_k(V)}{\mathrm{d}V}v\cos\gamma$$

to obtain, after simple calculations,

$$(22)\qquad \beta_3(\varepsilon)=\left(\frac{M}{m}\right)^2\Bigg[30\langle\nu_1\rangle-15\langle\nu_2\rangle+18\langle V\nu_1'\rangle-9\langle V\nu_2'\rangle+$$

$$+\frac{kT}{m}\left(6\langle\nu_1''\rangle-3\langle\nu_2''\rangle+2\langle V\nu_1'''\rangle-\langle V\nu_2'''\rangle\right)\Bigg]\left(-\frac{8}{5}kT\varepsilon^2+4(kT)^2\varepsilon\right).$$

At this point, it remains only the calculation of the fourth coefficient. We have

$$(23)\quad b_4(\varepsilon)=\left(\frac{mM}{m+M}\right)^4\int_V F(V)\,\mathrm{d}^3\boldsymbol{V}\left\{\int_0^\pi Ng^5\sigma(g,\chi)\sin\chi\,\mathrm{d}\chi\int_0^{2\pi}[\boldsymbol{G}\cdot(\boldsymbol{r}-\boldsymbol{s})]^4\mathrm{d}\zeta\right\}_{v=\sqrt{2\varepsilon/m}}.$$

The following assumptions

$$(24)\qquad \begin{cases} \left(\dfrac{mM}{m+M}\right)^4 \approx M^4\,, \qquad g \approx V \Rightarrow \nu_k(g) = \nu_k(V) \\[2ex] \boldsymbol{G} \approx \boldsymbol{v}\,, \qquad \boldsymbol{G}\cdot\boldsymbol{r} = \dfrac{1}{g}\,\boldsymbol{G}\cdot\boldsymbol{g} \approx \dfrac{1}{V}\,\boldsymbol{v}\cdot(\boldsymbol{v}-\boldsymbol{V}) = \dfrac{v^2}{V} - v\cos\gamma \end{cases}$$

are now all consistent with the fact that we retain only terms of order $(M/m)^j$ with $j \leqslant 2$. Thus, when noting that

$$(25)\qquad \int_0^{2\pi} [\boldsymbol{G}\cdot(\boldsymbol{r}-\boldsymbol{s})]^4\, d\zeta = 2\pi(\boldsymbol{G}\cdot\boldsymbol{r})^4(1 - 4\cos\chi + 6\cos^2\chi - 4\cos^3\chi + \cos^4\chi) + $$
$$+ 6\pi[G^2 - (\boldsymbol{G}\cdot\boldsymbol{r})^2](\boldsymbol{G}\cdot\boldsymbol{r})^2 \sin^2\chi(1 - 2\cos\chi + \cos^2\chi) +$$
$$+ \frac{3}{4}\pi\,[G^2 - (\boldsymbol{G}\cdot\boldsymbol{r})^2]\sin^2\chi\,,$$

one proves, without difficulties, that

$$(26)\qquad \beta_4(\varepsilon) = \frac{16}{5}\left(\frac{M}{m}\right)^2 \Big[30\langle\nu_1\rangle - 15\langle\nu_2\rangle + 18\langle V\nu_1'\rangle - 9\langle V\nu_2'\rangle +$$
$$+ \frac{kT}{M}\left(6\langle\nu_1''\rangle - 3\langle\nu_2''\rangle + 2\langle V\nu_1'''\rangle - \langle V\nu_2'''\rangle\right)\Big]\,(kT)^2\varepsilon^2\,.$$

As one can see, $\beta_3(\varepsilon)$ and $\beta_4(\varepsilon)$ involve only terms of order $(M/m)^2$. Similarly, one might show that $b_5(\varepsilon)$ does not involve terms of this order. Then, the second-order theory is characterized by the following equation for $p(\varepsilon, t)$

$$(27)\qquad \frac{\partial p(\varepsilon, t)}{\partial t} = \sum_1^4{}_r \frac{(-1)^r}{r!}\,\frac{\partial^r}{\partial\varepsilon^r}\left(\beta_r(\varepsilon)p(\varepsilon, t)\right)\,.$$

This equation becomes a second-order differential equation only for $T = 0$ or if we neglect the terms of order $(M/m)^2$. In the latter case, the temporal behaviour of $p(\varepsilon, t)$ is described by a Fokker-Planck equation with the following coefficients

$$(28)\qquad \begin{cases} \beta_1(\varepsilon) = -2\,\dfrac{M}{m}\left(\langle\nu_1\rangle + \dfrac{1}{3}\,\langle V\nu_1'\rangle\right)\left(\varepsilon - \dfrac{3}{2}\,kT\right) \\[2ex] \beta_2(\varepsilon) = 4\,\dfrac{M}{m}\left(\langle\nu_1\rangle + \dfrac{1}{3}\,\langle V\nu_1'\rangle\right) kT\cdot\varepsilon\,. \end{cases}$$

These equations generalize to an arbitrary interaction law the coefficients given by Andersen and Shuler for the rigid sphere model and agree, as we shall see, with the results of the literature obtained by different procedures.

2.3. - Three different tests have been made to confirm the correctness of our results. First of all, we have verified that the distribution

$$p(\varepsilon) = p(\varepsilon, \infty) = \left(\frac{m}{2\pi kT}\right)^{3/2} \varepsilon^{\frac{1}{2}} \exp\left[-\frac{\varepsilon}{kT}\right] \tag{29}$$

is the steady-state solution of eq. (27), and that

$$\langle\beta_1(\varepsilon)\rangle = \int_0^\infty \beta_1(\varepsilon) p(\varepsilon)\, d\varepsilon = 0 \,. \tag{30}$$

Then, we have made a comparison between our results and the first three exact coefficients of the Kramers-Moyal expansion, given by Andersen and Shuler, for the sphere model [1]. We have followed the same procedure of Appendix B of our paper [3]. When noting that for Rayleigh gases $\lambda^2 = M/m \ll 1$, so that

$$\frac{1}{x^{\frac{1}{2}}} \operatorname{erf}(\lambda x^{\frac{1}{2}}) = \lambda \exp[-\lambda^2 x]\left[1 + \frac{2}{3}\lambda^2 x + \frac{4}{15}(\lambda^2 x)^2 + \frac{8}{105}(\lambda^2 x)^3 + \dots\right] \tag{31}$$

(where $x = \varepsilon/(kT)$ is treated as a zero-order quantity with respect to λ), we have obtained

$$\left\{\begin{aligned}
\beta_1(\varepsilon) &= -4\left(\frac{M}{m}\right)^2 \left\{\frac{2}{15}\frac{\varepsilon^2}{kT} - \left(\frac{5}{3} - \frac{2}{3}\frac{m}{M}\right)\varepsilon + \left(2 - \frac{m}{M}\right) kT\right\} Z(T)\\
\beta_2(\varepsilon) &= 8\left(\frac{M}{m}\right)^2 \left\{\frac{6}{5}\varepsilon^2 + \frac{2}{3}\left(\frac{m}{M} - 10\right) kT\cdot\varepsilon + 4(kT)^2\right\} Z(T)\\
\beta_3(\varepsilon) &= -128\left(\frac{M}{m}\right)^2 \left\{\frac{2}{5} kT\cdot\varepsilon^2 - (kT)^2\varepsilon\right\} Z(T)\,,
\end{aligned}\right. \tag{32}$$

where

$$Z(T) = N\pi d^2 \sqrt{\frac{8kT}{\pi M}} \tag{33}$$

(d being the sum of the sphere radii).

But these results agree with ours. In fact, for the rigid sphere model,

$$(34) \qquad \begin{cases} \langle \nu_1(V)\rangle = \langle V\nu_1'(V)\rangle = \langle \nu(V)\rangle = N\pi d^2 \langle V\rangle = N\pi d^2 \int_V V F(V)\,\mathrm{d}^3 V = Z(T) \\ \nu_2(V) \quad = \dfrac{2}{3}\nu_1(V)\,, \qquad \nu_K''(V) = \nu_K'''(V) = 0\,. \end{cases}$$

Andersen and Shuler do not calculate the explicit expression of $b_4(x)$. For this reason we shall only note that, for the rigid sphere model, eq. (26) yields (cf. eq. (33))

$$(35) \qquad \beta_4(\varepsilon) = \frac{512}{5}\left(\frac{M}{m}\right)^2 (kT)^2 \varepsilon^2 Z(T)\,.$$

Finally, we have tested if our (first-order) coefficients (28) are consistent with the equation for the velocity distribution function of Brownian particles given by Wang Chang and Uhlembeck [**8**]. In the absence of spatial gradients and external fields, the said equation is [**8**]

$$(36) \qquad \frac{\partial f}{\partial t} = \eta \left\{ \sum_j \frac{\partial}{\partial v_j}(v_j f) + \frac{kT}{m}\sum_j \frac{\partial^2 f}{\partial v_j^2} \right\},$$

where f is here an isotropic function of v and t, and η is the friction coefficient [**8**]

$$(37) \quad \eta = \frac{16\sqrt{\pi}}{3}\frac{NM}{m}\left(\frac{M}{2kT}\right)^{5/2}\int_0^\pi (1-\cos\chi)\sin\chi\,\mathrm{d}\chi\int_0^\infty V^5 \exp\left[-\frac{MV^2}{2kT}\right]\sigma(V,\chi)\,\mathrm{d}V\,.$$

But eq. (36) can be written in the form

$$(38) \qquad \frac{\partial f}{\partial t} = \eta\left\{\left(3f + v\frac{\partial f}{\partial v}\right) + \frac{kT}{m}\left(\frac{2}{v}\frac{\partial f}{\partial v} + \frac{\partial^2 f}{\partial v^2}\right)\right\},$$

from which it follows that the equation for $p(v,t) = 4\pi v^2 f(v,t)$ is a Fokker-Planck equation with the coefficients

$$(39) \qquad \beta_1(v) = -\left(v - \frac{2kT}{mv}\right)\eta\,, \qquad \beta_2(v) = 2\frac{kT}{m}\eta\,.$$

Therefore, the coefficients of the Fokker-Planck equation for $p(\varepsilon, t)$ are

$$(40)\quad \begin{cases} \beta_1(\varepsilon) = \left\{ mv\beta_1(v) + \dfrac{m}{2}\beta_2(v) \right\}_{v=\sqrt{2\varepsilon/m}} = -2\left(\varepsilon - \dfrac{3}{2}kT\right)\eta\,, \\ \\ \beta_2(\varepsilon) = \{m^2v^2\beta_2(v)\}_{v=\sqrt{2\varepsilon/m}} = 4kT\varepsilon\eta\,. \end{cases}$$

Then, we must prove that (cfr. eq. (28))

$$(41)\quad \eta = \frac{M}{m}\left(\langle\nu_1\rangle + \frac{1}{3}\langle V\nu_1'\rangle\right) = \frac{1}{3}\frac{M}{m}\left\langle \frac{1}{V^2}\frac{\mathrm{d}}{\mathrm{d}V}(V^3\nu_1)\right\rangle .$$

But in virtue of eq. (7), eq. (37) can be written as follows:

$$(42)\quad \eta = \frac{8}{3}\frac{1}{\sqrt{\pi}}\frac{M}{m}\frac{kT}{M}\left(\frac{M}{2kT}\right)^{5/2}\int_0^\infty V^4 \exp\left[-\frac{MV^2}{2kT}\right]\nu_1(V)\,\mathrm{d}V\,,$$

i.e., after an integration by parts,

$$(43)\quad \eta = \frac{1}{3}\frac{M}{m}4\pi\left(\frac{M}{2\pi kT}\right)^{3/2}\int_0^\infty \exp\left[-\frac{MV^2}{2kT}\right]\frac{\mathrm{d}}{\mathrm{d}V}(V^3\nu_1)\,\mathrm{d}V\,,$$

which agrees with our result (41).

3. - Remarks on relaxation processes.

In this paper we shall not be concerned with the solution of eq. (27) for $p(\varepsilon, t)$. However, we want to make some remarks on the relaxation processes governed by this equation.

Under rather general conditions, from eq. (27) it follows that

$$(44)\quad \frac{\mathrm{d}\mu_1(t)}{\mathrm{d}t} = B(t)\,,$$

with

$$(45)\quad \mu_r(t) = \int_0^\infty \varepsilon^r p(\varepsilon, t)\,\mathrm{d}\varepsilon\,, \qquad B(t) = \int_0^\infty \beta_1(\varepsilon)p(\varepsilon, t)\,\mathrm{d}\varepsilon\,.$$

Thus, $B(t)$ will be a linear function of $\mu_1(t)$ if $\beta_1(\varepsilon)$ is a linear function of ε. But eq. (16) shows that this happens only if we neglect the terms of order $(M/m)^2$ or if $\nu_1(V)$ is V-independent (i.e. $\sigma(V, \chi) \propto V^{-1}$), in which case $B(t)$ is a linear function of $\mu_1(t)$ for arbitrary mass ratio (cfr. eq. (13)). But under this condition, $\mu_1(t)$ relaxes according to a simple exponential law [**1**], [**2**]$_4$. Therefore, we must conclude that, contrary to what happens for the first-order theory [**1**], if we consider also the terms of order $(M/m)^2$, $\mu_1(t)$ relaxes according to a simple exponential law only when ν_1 is a constant.

Another interesting result of the first-order theory is the following: if $p(\varepsilon, 0)$ is a Maxwellian distribution at a given temperature $T_0 > 0$, then $p(\varepsilon, t)$ is a Maxwellian distribution, with temperature $T(t) = (2/3k)\mu_1(t)$, for any arbitrary interaction law [**1**], [**2**]$_4$. For $T = 0$, it is the δ-distribution which preserves its form during the relaxation process, according to the fact that the diffusion coefficient in the energy space vanishes if $T \to 0$ (cfr. eq. (28)) [**2**]$_4$. However, if we do not neglect the terms of order $(M/m)^2$, all these results are no longer maintained, even for $\sigma(V, \chi) \propto V^{-1}$. In this last case, in particular, $p(\varepsilon, t)$ satisfies the equation

$$\text{(46)} \qquad \frac{\partial p(\varepsilon, t)}{\partial t} = 2\frac{M}{m}\frac{\partial}{\partial \varepsilon}\left\{\left(1 - 2\frac{M}{m}\right)\nu_1 \varepsilon p(\varepsilon, t) + \frac{M}{m}(2\nu_1 - \nu_2)\frac{\partial}{\partial \varepsilon}\left[\varepsilon^2 p(\varepsilon, t)\right]\right\},$$

whose fundamental solution is found to be the Mc Alister, or lognormal, distribution

$$\text{(47)} \quad p(\varepsilon, t) = \left(\frac{1}{8\pi(M/m)^2(2\nu_1 - \nu_2)t}\right)^{1/2}\frac{1}{\varepsilon}\exp\left\{-\frac{[\ln(\varepsilon/\varepsilon_0) + 2(M/m)(\nu_1 - (M/m)\nu_2)t]^2}{8(M/m)^2(2\nu_1 - \nu_2)t}\right\}.$$

(A lognormal distribution was also found for Lorentz gases and isotropic scattering processes by Eaton and Holway [**5**]). According to eq. (47), $p(\varepsilon, t) \to \delta(\varepsilon - \varepsilon_0)$ for $t \to 0$. But one can easily prove, also, that the moments of $p(\varepsilon, t)$ relax according to the simple exponential law

$$\text{(48)} \qquad \mu_r(t) = \varepsilon_0^r \exp\left[-2\frac{M}{m} r\nu_1\left\{1 - \frac{M}{m}\left[\frac{\nu_2}{\nu_1} + r\left(2 - \frac{\nu_2}{\nu_1}\right)\right]\right\}t\right].$$

Note that, as for the Lorentz gas [**5**], they diverge for very large r, in our case for

$$\text{(49)} \qquad r > \frac{1 - (M/m)(\nu_2/\nu_1)}{(M/m)(2 - \nu_2/\nu_1)}.$$

As one can see, if we make use of a second-order theory, a number of simple and important results of the first-order theory is lost. For this reason, it may be of interest to see what we can say on the approximate relaxation of the subsystem-energy when $\sigma(V, \chi)$ is an arbitrary function of V. For the sake of brevity, we shall write, here also, $x = \varepsilon/(kT)$ and shall continue to use angular brackets to indicate the averages over equilibrium distributions, e.g. $p(x, \infty) = 2/\sqrt{\pi}\, x^{\frac{1}{2}} \exp[-x]$ (cfr. also eq. (15)). Averages over $p(x, t)$ and, in particular, $p(x, 0)$, will be denoted by a bar.

According to Cukier and Hynes [4], if we want to represent the relaxation of the first moment $\bar{x}(t)$ of $p(x, t)$ or the equilibrium correlaxion function

$$C(t) = \frac{\langle \delta x\, \delta x(t)\rangle}{\langle (\delta x)^2\rangle} \qquad (\delta x = x - \langle x\rangle)\,, \tag{50}$$

by simple exponential laws, i.e. to write that

$$\frac{\bar{x}(t) - \langle x\rangle}{\bar{x}(0) - \langle x\rangle} = \exp[-r' t]\,, \qquad C(t) = \exp[-rt]\,, \tag{51}$$

the appropriate choices of r' and r are

$$r' = -\frac{\bar{\beta}_1(x)(0)}{\bar{x}(0) - \langle x\rangle} \tag{52}$$

and

$$r = -\frac{\langle \delta x\, \beta_1(x)\rangle}{\langle (\delta x)^2\rangle}\,. \tag{53}$$

But we have (cfr. eq. (16))

$$\begin{aligned}\beta_1(x) = \left(\frac{M}{m}\right)^2 \Bigg\{ \Bigg[-\frac{8}{15}\langle V\nu_1'\rangle - \frac{2}{5}\frac{kT}{M}\left(\langle \nu_1''\rangle + \frac{1}{3}\langle V\nu_1'''\rangle\right)\Bigg] x^2 + \\ + \Bigg[4\left(\langle \nu_1\rangle + \frac{2}{3}\langle V\nu_1'\rangle\right) - 2\frac{m}{M}\left(\langle \nu_1\rangle + \frac{1}{3}\langle V\nu_1'\rangle\right) + \\ + \frac{kT}{M}\left(\langle \nu_1''\rangle + \frac{1}{3}\langle V\nu_1'''\rangle\right)\Bigg] x + \left(\frac{m}{M} - 2\right)(3\langle \nu_1\rangle + \langle V\nu_1'\rangle)\Bigg\}\,,\end{aligned} \tag{54}$$

which, also in virtue of eq. (30), allows us to write that

$$r = -\frac{\langle x\beta_1(x)\rangle}{\langle x^2\rangle - \langle x\rangle^2} = -\frac{2}{3}\langle x\beta_1(x)\rangle = \tag{55}$$

$$= \frac{2}{3}\left(\frac{M}{m}\right)^2 \left\{\frac{m}{M}\left(3\langle\nu_1\rangle + \langle V\nu_1'\rangle\right) - 6\langle\nu_1\rangle + \frac{3}{2}\frac{kT}{M}\left(\langle\nu_1''\rangle + \frac{1}{3}\langle V\nu_1'''\rangle\right)\right\}.$$

If ν_1 is V-independent, we have immediately that

$$r = 2\frac{M}{m}\left(1 - 2\frac{M}{m}\right)\nu_1\,, \tag{56}$$

while for the rigid sphere model we obtain that (cfr. eq. (10))

$$r = 4\frac{M}{m}\left(\frac{2}{3} - \frac{M}{m}\right)\langle\nu\rangle\,. \tag{57}$$

This result is easily seen to agree with that given by Cukier and Hynes [**4**], that is (cfr. eq. (34))

$$r = \frac{8}{3}\frac{M}{m}\left(1 + \frac{M}{m}\right)^{-3/2} Z\,, \tag{58}$$

if only the terms of orders $(M/m)^j$ with $j \leqslant 2$ are retained.

As regards the calculation of r', we must choose, first of all, the initial energy distribution. We shall assume that

$$p(x, 0) = \frac{2}{\sqrt{\pi\delta^3}}\, x^{\frac{1}{2}} \exp\left[-x/\delta\right] \qquad \left(\delta = \frac{T_0}{T}\right), \tag{59}$$

from which it follows that $\bar{x}(0) = (3/2)\,\delta$ and $\bar{x}^2(0) = (15/4)\,\delta^2$. Thus, we obtain that

$$\overline{\beta_1(x)}(0) = \left(\frac{M}{m}\right)^2 \left\{\left[-2\langle V\nu_1'\rangle - \frac{1}{2}\frac{kT}{M}\left(3\langle\nu_1''\rangle + \langle V\nu_1'''\rangle\right)\right]\delta^2 + \right. \tag{60}$$

$$+ \left[2\left(3\langle\nu_1\rangle + 2\langle V\nu_1'\rangle - \frac{m}{M}(3\langle\nu_1\rangle + \langle V\nu_1'\rangle) + \right.\right.$$

$$\left.\left. + \frac{1}{2}\frac{kT}{M}\left(3\langle\nu_1''\rangle + \langle V\nu_1'''\rangle\right)\right]\delta + \left(\frac{m}{M} - 2\right)\left(3\langle\nu_1\rangle + \langle V\nu_1'\rangle\right)\right\},$$

which permits immediately to calculate r' by means of eq. (52), i.e. of the equation

$$r' = \frac{2}{3}\frac{1}{1-\delta}\,\overline{\beta_1(x)}(0)\ . \tag{61}$$

For constant ν_1 these equations yield

$$r' = 2\frac{M}{m}\left(1-2\frac{M}{m}\right)\nu_1 = r\ , \tag{62}$$

while, for the rigid sphere model, after some simple calculations, we obtain that

$$r' = \frac{4}{3}\frac{M}{m}\left(2-3\frac{M}{m}\right)\langle\nu\rangle\ . \tag{63}$$

Also this result is easily seen to agree with that given by Cukier and Hynes [**6**], i.e.

$$r' = r\left(\frac{1+(M/m)\,\delta}{1+M/m}\right)^{\frac{1}{2}} \tag{64}$$

if the terms of higher orders than the second with respect to M/m are neglected.

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Summary.

A derivation of the equation for the energy distribution $p(\varepsilon, t)$ of particles (mass m) homogeneously dispersed in a heat bath of atoms (mass M) is presented. The procedure. extremely simple, is based on a particularly convenient expansion of the master equation, We work in the limit $m/M \gg 1$ and derive an equation for $p(\varepsilon, t)$ which is correct to the second order with respect to the mass ratio M/m. This equation is then used to study some relaxation processes.

Sommario.

Viene dedotta un'equazione per la distribuzione energetica $p(\varepsilon, t)$ di particelle (di massa m) disperse omogeneamente in un gas di atomi (di massa M). Il procedimento, estremamente semplice, è basato su un'espansione particolarmente conveniente dell'equazione di Boltzmann linearizzata. Ci poniamo nell'ipotesi in cui $m/M \gg 1$ e deduciamo un'equazione per $p(\varepsilon, t)$ corretta al secondo ordine rispetto al rapporto fra le masse M/m. Questa equazione è successivamente usata per studiare alcuni processi di rilassamento.

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