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Transport properties in a spin polarized gas, II

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Résumé. — Partant des résultats généraux obtenus dans l'article précédent, on étudie les conséquences des effets quantiques d'indiscernabilité sur les propriétés de transport d'un gaz polarisé à basse température. La théorie suppose que l'orientation nucléaire M est quelconque (pas de développement en puissances de M).

On commence par un calcul simple du courant de spin en présence d'un gradient d'orientation, compte tenu des cohérences de spin et de leur évolution due à l'effet de rotation des spins identiques; ce dernier joue en fait un rôle essentiel à la limite des faibles températures. Les équations hydrodynamiques d'évolution de M sont non linéaires et anisotropes. Les effets d'indiscernabilité introduisent également un caractère oscillatoire dans l'évolution des composantes transverses de l'orientation.

Un calcul plus élaboré permet ensuite d'étudier les phénomènes quantiques de couplage entre diffusion de spin et conduction de la chaleur. De tels phénomènes pourraient être à la base de méthodes de surpolarisation thermiques d'un échantillon gazeux.

Enfin, on s'intéresse aux mélanges des deux isotopes ^3He et ^4He où, en sus du couplage classique entre concentration isotopique et conduction thermique, apparaît un couplage supplémentaire quantique avec la diffusion de spin.

Abstract. — The general results obtained in the preceding article are applied to the study of transport phenomena in a spin polarized gas at low temperatures, with particular emphasis on the particle indistinguishability effects in collisions. The effects of the nuclear orientation M are treated exactly (no M expansion).

First, a simple theory of spin diffusion is presented and the response of the gas to a spin orientation gradient is calculated. The spin coherences and their evolution due to the « identical-spin rotation effect » are taken into account; it is found that they can play an important role, especially in the low temperature limit. The hydrodynamic equations of evolution of M are non-linear and anisotropic. Particle indistinguishability effects give an oscillatory character to the evolution of the transverse components of M (spin oscillations).

Then, a more elaborate variational method is used to study the coupling between spin diffusion and heat conduction. This effect is, again, a sheer consequence of quantum interference phenomena introduced by particle indistinguishability.

Finally, isotopic mixtures of ^3He and ^4He are considered. In addition to coupling between isotopic diffusion and heat conduction, which exists for classical systems, quantum collision effects introduce a coupling between these two modes and spin diffusion.

Introduction. — In the preceding article, we have studied the consequences of particle indistinguishability effects on the collision term of the Boltzmann equation for a dilute (non-degenerate) spin polarized gas. We have seen that these effects introduce several terms which have the form of commutators or anti-commutators between spin density operators; the former correspond to what we have called the « identical spin rotation effect ». We have also applied our results to the study of the heat conduction and viscosity coefficients and found that both may depend

strongly on the nuclear polarization M of the gas; the correlations between spin variables and velocities of the atoms have also been discussed. Nevertheless, it so happens that only the anticommutators give a contribution to the viscosity and heat conduction coefficients, the identical spin rotation effect playing no role in both cases. This is because the commutators disappear from the calculations whenever a spin rotation invariance argument ensures that the average spin density operator $\bar{\rho}_s^0$ and the solution $\delta\bar{\rho}_s$ of the linearized Boltzmann equation can be diagonalized

in the same basis. In other words, no spin coherence effects ⁽¹⁾ are involved in the applications presented in the preceding article, and this is why all results where physically interpretable in terms of a semi-classical mixture model (the atoms with up or down spins are considered as two different atomic species, with cross sections obtained from simple considerations concerning quantum effects in collisions).

In the present article, we wish to study situations where spin coherences and identical spin rotation effects do play a role and where the semi-classical model of a gas mixture is not sufficient. In spin diffusion, the average direction of the atomic spins changes over the sample, so that all spin operators do not necessarily commute with each other. Conceptually, the problem of spin diffusion is more complex than, for example, heat conduction, one reason being that the distinguishable or indistinguishable character of the atoms is governed by the spin orientation, which changes in space and time. We have already mentioned these difficulties in the introduction of the preceding article, as well as the contribution of Emery [1] who clarified the situation by pointing out that, for an unpolarized gas, the particle indistinguishability effects in collisions give a negligible contribution to the spin diffusion coefficient. In what follows, we shall confirm this point of view, but we shall also find that the presence of a significant nuclear polarization can radically change the situation : in fact, the spin diffusion phenomenon is then dominated by identical spin rotation effects, and the corresponding hydrodynamic equations become highly non-linear and anisotropic. Instead of remaining a purely dissipative process, the spin diffusion phenomenon also acquires an oscillatory character ; this effect may even become dominant at very low temperatures. Such properties are rather unusual in a gas, and their origin is quantum interference effects during collisions between identical atoms having a high nuclear polarization (they

disappear if $M = 0$). They are reminiscent of the effects predicted by Leggett and Rice [2] and Leggett [3] in normal liquid ^3He at low temperatures, where they are induced by the strong degeneracy of the quantum liquid.

Another aspect of the transport properties in a spin polarized gas is the coupling between modes : since particle indistinguishability effects create correlations between atomic spin orientations and velocities, one can expect that the response of the gas to a heat gradient may include the production of a macroscopic spin current. In the theory of the preceding article, the possibility of such a spin current was ignored from the beginning by the very choice of the trial density operator but, here, we shall develop more elaborate calculations and obtain qualitative predictions for these effects.

The study of gaseous mixtures of ^3He and ^4He offers additional possibilities for studying quantum effects in transport properties. In this case, three modes can be coupled : diffusion of the isotopic concentration, spin diffusion, and heat conduction. This triple coupling is studied in the last section of the present article.

1. Spin diffusion in spin polarized gases : simple theory. — In this section, we study the spin diffusion in a spin polarized gas with non negligible polarization M , in the simple situation where there is no temperature or pressure gradient. To derive the spin diffusion equation, we shall solve by an approximate method the linearized Boltzmann equation obtained in the preceding article, which we recall here for completeness :

$$\frac{d}{dt} \delta \bar{\rho}_s(\mathbf{r}, \mathbf{p}) + \frac{\mathbf{p}}{m} \cdot \nabla_{\mathbf{r}} \{ \bar{\rho}_s^0(\mathbf{r}, \mathbf{p}) \} = I_{\text{coll}}[\delta \bar{\rho}_s(\mathbf{r}, \mathbf{p})] \quad (1a)$$

where the collision integral I_{coll} is given by :

$$\begin{aligned} I_{\text{coll}}[\delta \bar{\rho}_s(\mathbf{r}, \mathbf{p})] = & \int d^3 q' \frac{q'}{m} \int d^2 \hat{q} f_0(\mathbf{p}_2) \left\{ \sigma_k(\theta) (\delta \bar{\rho}_s(\mathbf{p}'_1) - \delta \bar{\rho}_s(\mathbf{p}_1) + \bar{\rho}_s^0 \text{Tr} \{ \delta \bar{\rho}_s(\mathbf{p}'_2) - \delta \bar{\rho}_s(\mathbf{p}_2) \}) + \right. \\ & + \frac{\varepsilon}{2} \sigma_k^{\text{ex}}(\theta) [\bar{\rho}_s^0, \delta \bar{\rho}_s(\mathbf{p}'_2) + \delta \bar{\rho}_s(\mathbf{p}'_1) - \delta \bar{\rho}_s(\mathbf{p}_1) - \delta \bar{\rho}_s(\mathbf{p}_2)]_+ + \frac{i\varepsilon}{2} \tau_k^{\text{ex}}(\theta) [\bar{\rho}_s^0, \delta \bar{\rho}_s(\mathbf{p}'_2) - \delta \bar{\rho}_s(\mathbf{p}'_1)] \left. \right\} \\ & + \frac{i\varepsilon}{2} \int d^3 q \frac{q}{m} \tau_{\text{fwd}}^{\text{ex}}(k) f_0(\mathbf{p} - \mathbf{q}) [\bar{\rho}_s^0, \delta \bar{\rho}_s(\mathbf{p}) - \delta \bar{\rho}_s(\mathbf{p} - \mathbf{q})] \quad (1b) \end{aligned}$$

and :

$$\begin{aligned} \mathbf{p}_1 &= \mathbf{p} & \mathbf{p}'_1 &= \mathbf{p} + \frac{1}{2} \mathbf{q}' - \frac{1}{2} \mathbf{q} \\ \mathbf{p}_2 &= \mathbf{p} - \mathbf{q} & \mathbf{p}'_2 &= \mathbf{p} - \frac{1}{2} \mathbf{q}' - \frac{1}{2} \mathbf{q} \end{aligned} \quad (1c)$$

⁽¹⁾ Following a common usage in optical pumping, « spin populations » or « spin coherences » refer to diagonal or off diagonal elements of the spin density matrix respectively (longitudinal or transverse component of the magnetization).

(θ is the angle between vectors $\mathbf{q}$ and $\mathbf{q}'$, which both have the same modulus ; k is defined by $k = q/2\hbar$). In this expression, the first terms are proportional to $\sigma_k(\theta)$ and do not depend on particle indistinguishability effects (« classical terms »), but all other terms are

direct consequences of these effects and have an opposite sign for bosons ($\varepsilon = +1$) or fermions ($\varepsilon = -1$). The anticommutators are proportional to $\sigma_k^{\varepsilon x}(\theta)$ and they account for the variations of the scattering cross sections between atoms either in the same, or orthogonal, spin states. The commutator in $\tau_k^{\varepsilon x}(\theta)$ corresponds to the « identical spin rotation effect » and the commutator in $\tau_{\text{fwd.}}^{\varepsilon x}$ to the same effect in the forward direction (« nuclear spin Faraday effect »).

It should be emphasized that the collision operator has been linearized with respect to the deviations from a local equilibrium situation, but that the nuclear polarization effects are treated exactly. In other words, we do not restrict ourselves to situations where the nuclear polarization M is near its value at thermal equilibrium, which is ordinarily very low, except in extreme situations [no M expansion has been necessary to obtain equation (1)]. Since the longitudinal relaxation time T_1 is usually very long in a dilute gas [4, 5], a highly polarized sample can be considered to be in a metastable state.

1.1 A FIRST APPROXIMATION FOR THE SPIN CURRENT.

— The mathematical approximation methods we shall use are the same as in the preceding article (first order Chapman-Enskog expansion, truncated basis method). Here, we give only the main steps of the calculation, without dwelling on details.

For the problem of spin diffusion, the local equilibrium density operator (equation (40) of the preceding article) is given by :

$$\rho_s^0(\mathbf{r}, \mathbf{p}) = f_0(\mathbf{p}) \bar{\rho}_s^0(\mathbf{r}) \quad (2a)$$

with, for spin $\frac{1}{2}$ atoms (we simplify the notation $\mathbf{M}_0$ to $\mathbf{M}$) :

$$\bar{\rho}_s^0(\mathbf{r}) = \frac{1}{2}[1 + \boldsymbol{\sigma} \cdot \mathbf{M}(\mathbf{r})] \quad (2b)$$

(in contrast to the case of heat conduction and viscosity, the function f_0 is independent of $\mathbf{r}$). The corresponding drift term for $\delta\bar{\rho}_s$ is then :

$$\frac{1}{m} \mathbf{p} \cdot \nabla_{\mathbf{r}} [\bar{\rho}_s^0(\mathbf{r})] = \frac{1}{2m} \sum_{i=1,2,3} \mathbf{p} \cdot \nabla M_i(\mathbf{r}) \sigma_i \quad (3a)$$

where $i = x, y, z$ and the σ_i 's are the Pauli matrices. Since this expression has no component on the unit 2×2 matrix, the drift term is orthogonal to the atomic number density $n(\mathbf{r})$, linear momentum and energy densities $\mathcal{P}(\mathbf{r})$ and $\mathcal{W}(\mathbf{r})$; since it is an odd function of $\mathbf{p}$, it is also orthogonal to the spin orientation density $\mathcal{M}(\mathbf{r})$. The angular dependence of the drift term is given by spherical harmonics $Y_l^m(\hat{\rho})$, where $\hat{\rho}$ is the unit vector $\mathbf{p}/p$. As a consequence, we can write the first order Chapman-Enskog term of the density operator in the form :

$$\delta\bar{\rho}_s = \frac{1}{2} \left[\mathbf{c}_0(\mathbf{p}) \cdot \mathbf{p} + \sum_i \mathbf{c}_i(\mathbf{p}) \cdot \mathbf{p} \sigma_i \right]. \quad (3b)$$

As in the preceding article, we shall use a simpler variational form. In this section, we choose the following trial density operator :

$$\delta\bar{\rho}_s = \frac{1}{2} \sum_{i=1,2,3} \mathbf{c}_i \cdot \mathbf{p} \sigma_i \quad (3c)$$

which depends only on 9 real parameters (the components of $\mathbf{c}_1$, $\mathbf{c}_2$ and $\mathbf{c}_3$). Two simplifications have been made to write (3c) : first, the p dependence of the vectors $\mathbf{c}$'s has been ignored; second, since the drift term (3a) is traceless (no component on the unit 2×2 matrix), the same property is assumed to be valid for $\delta\bar{\rho}_s$ and the term in $\mathbf{c}_0 \cdot \mathbf{p}$ has been suppressed ⁽²⁾ from (3b). Since the collision operator Γ_c given by (1b) is not in general diagonal in p and can change the trace of operators, expression (3c) is only an approximation, which will be useful to discuss in simple terms the main characteristics of the spin diffusion phenomenon. In the next section, we shall use more elaborate calculations and introduce corrections to the simple approximation (3c).

As in the preceding article, we shall choose a (local) reference frame $Oxyz$ with axis Oz parallel to the nuclear polarization $\mathbf{M}$. An important difference is that this choice does not in general imply that the drift operator [equation (3a)] becomes diagonal; thus, we cannot restrict the summation over i in (3c) to only the term $i = 3$. As a consequence, the commutators, which simply vanished in the case of viscosity and heat conduction, now play a role in the calculations. In fact, with the trial density operator (3c), the cancellation actually occurs for the anticommutators, not the commutators; this is because $\delta\bar{\rho}_s$ is a linear function of $\mathbf{p}$ and

$$\mathbf{p}_1 + \mathbf{p}_2 = \mathbf{p}'_1 + \mathbf{p}'_2$$

(momentum conservation in a collision). Despite these differences, the calculations remain similar to those of the preceding article and give :

$$\begin{aligned} \frac{1}{\beta} \nabla M_x &= nX_1 \mathbf{c}_1 - nX_4 \varepsilon M \mathbf{c}_2 \\ \frac{1}{\beta} \nabla M_y &= nX_4 \varepsilon M \mathbf{c}_1 + nX_1 \mathbf{c}_2 \\ \frac{1}{\beta} \nabla M_z &= nX_1 \mathbf{c}_3 \end{aligned} \quad (4a)$$

⁽²⁾ If the vector $\mathbf{c}_0$ were not zero, it could not be independent of $\mathbf{p}$; this is because the trial density operator has to be orthogonal to the linear momentum density $\mathcal{P}$.

direct consequences of these effects and have an opposite sign for bosons ($\varepsilon = +1$) or fermions ($\varepsilon = -1$). The anticommutators are proportional to $\sigma_k^{\text{ex}}(\theta)$ and they account for the variations of the scattering cross sections between atoms either in the same, or orthogonal, spin states. The commutator in $\tau_k^{\text{ex}}(\theta)$ corresponds to the « identical spin rotation effect » and the commutator in $\tau_{\text{fwd}}^{\text{ex}}$ to the same effect in the forward direction (« nuclear spin Faraday effect »).

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(momentum conservation in a collision). Despite these differences, the calculations remain similar to those of the preceding article and give :

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⁽²⁾ If the vector $\mathbf{c}_0$ were not zero, it could not be independent of $\mathbf{p}$; this is because the trial density operator has to be orthogonal to the linear momentum density $\mathcal{P}$.

where $\beta = (k_B T)^{-1}$ and the X coefficients are defined by ⁽³⁾ :

$$X_1 = -\frac{8}{3} \frac{m}{\beta} \Omega_{[\sigma k]}^{(1,1)}$$

$$X_4 = -\frac{8}{3} \frac{m}{\beta} \{ \Omega_{[\tau^{ex}]}^{(1,1)} + \Xi_{[\tau_{fwd}^{ex}]}^{(1)} \} \quad (4b)$$

and :

$$\Xi_{[\tau_{fwd}^{ex}]}^{(s)} = \frac{1}{\sqrt{\pi m \beta}} \int_0^\infty d\gamma e^{-\gamma^2} \gamma^{2s+3} \tau_{fwd}^{ex} \left(k = \sqrt{\frac{m}{\beta}} \frac{\gamma}{\hbar} \right) \quad (4c)$$

(the Ω integrals have been defined in the preceding article). The linear system (4a) can be easily solved and gives :

$$c_1 = \frac{1}{n\beta\Delta_x} [X_1 \nabla M_x + \varepsilon M X_4 \nabla M_y]$$

$$c_2 = \frac{1}{n\beta\Delta_x} [-\varepsilon M X_4 \nabla M_x + X_1 \nabla M_y]$$

$$c_3 = \frac{1}{n\beta X_1} \nabla M_z \quad (5a)$$

with

$$\Delta_x = X_1^2 + M^2 X_4^2. \quad (5b)$$

On the other hand, the current associated with the M_i component of $\mathbf{M}$ is :

$$\mathbf{J}(M_i) = \frac{1}{n} \int d^3p f_0(p) \frac{\mathbf{p}}{m} \text{Tr} \{ \sigma_i \delta \bar{\rho}_s(\mathbf{p}) \}$$

$$= \frac{1}{\beta} c_i. \quad (6)$$

We therefore finally obtain :

$$\left. \begin{aligned} \mathbf{J}(M_x) &= -\frac{D_0}{1 + \mu^2 M^2} [\nabla M_x + \varepsilon \mu M \nabla M_y] \\ \mathbf{J}(M_y) &= -\frac{D_0}{1 + \mu^2 M^2} [-\varepsilon \mu M \nabla M_x + \nabla M_y] \\ \mathbf{J}(M_z) &= -D_0 \nabla M_z \end{aligned} \right\} \quad (7)$$

⁽³⁾ The calculation of X_4 introduces the angle averaged cross section

$$\tilde{Q}_{[\sigma]}^{(t)}(k) = 2\pi \int_0^\pi \sin \theta d\theta \cos^t \theta \sigma_k(\theta)$$

for $t = 1$ and $\sigma = \tau^{ex}(k)$. In general, $\tilde{Q}_{[\sigma]}^{(t)}$ differs from the classical quantity $Q_{[\sigma]}^{(t)}$ defined by equation (57b) of the preceding article. Nevertheless, we know that the integral $\tau_k^{ex}(\theta)$ over all directions vanishes [equation (21c) of the preceding article]; this is why the introduction of new integrals $\tilde{Q}^{(t,s)}$ is not necessary.

Another way to avoid the introduction of the $\tilde{Q}$'s is to change the first commutator of (1b) into :

$$+ \frac{i\varepsilon}{2} \tau_k^{ex}(\theta) [\bar{\rho}_s^0, \delta \bar{\rho}_s(\mathbf{p}_2) - \delta \bar{\rho}_s(\mathbf{p}_2) + \delta \bar{\rho}_s(\mathbf{p}_1) - \delta \bar{\rho}_s(\mathbf{p}_1)].$$

where D_0 is the « classical » diffusion coefficient :

$$D_0 = \frac{3}{8} \frac{1}{nm\beta} \frac{1}{\Omega_{[\sigma]}^{(1,1)}} \quad (8a)$$

and μ is the parameter :

$$\mu = \frac{X_4}{X_1} = [\Omega_{[\tau^{ex}]}^{(1,1)} + \Xi_{[\tau_{fwd}^{ex}]}^{(1)}] / \Omega_{[\sigma]}^{(1,1)}. \quad (8b)$$

These equations give the spin orientation current associated with the response of the gas to a spin orientation gradient. They are valid only in a local reference frame with the Oz axis parallel to the orientation $\mathbf{M}$, but they are equivalent to the following equation, valid in any reference frame :

$$J_{x_i}(M_j) = -\frac{D_0}{1 + \mu^2 M^2} \left\{ \frac{\partial}{\partial x_i} M_j - \varepsilon \mu \left(\mathbf{M} \times \frac{\partial}{\partial x_i} \mathbf{M} \right)_j + \mu^2 M_j \left(\mathbf{M} \cdot \frac{\partial}{\partial x_i} \mathbf{M} \right) \right\}. \quad (9)$$

1.2 PHYSICAL DISCUSSION. — The simplest situation occurs when the polarization M is very low; equations (7) then become :

$$\mathbf{J}(M_{x_i}) = -D_0 \nabla(M_{x_i}). \quad (10)$$

All particle indistinguishability effects (those depending on the sign of ε) have disappeared from this simple result, where the coefficient D_0 depends only on σ (and not σ^{ex} , τ^{ex} , and τ_{fwd}^{ex}). This is very different from what is obtained in the case of heat conduction and viscosity, where the boson or fermion character of the atoms does indeed affect the transport coefficients of the unpolarized gas. Emery [1] was the first to point out this difference and to give its physical explanation : since collisions between atoms in the same spin state do not affect directly the spin current $\mathbf{J}(M_{x_i})$, the only important collisions for spin diffusion are collisions between atoms in orthogonal spin states (atoms which can, in principle, be recognized from each other by their spin direction, and therefore are not fully indistinguishable).

Actually, these conclusions are not strictly correct : in our calculation, the disappearance of all indistinguishability terms arises from the cancellation of the anticommutators in σ_k^{ex} in the collision term, which in turn is a consequence of the momentum conservation in collisions and of the linear $\mathbf{p}$ dependence of $\delta \bar{\rho}_s$ written in (3c). In the next section, we shall use a less simple trial spin density operator, and the terms in σ_k^{ex} will no longer disappear. Consequently, as also predicted by Emery [1], there are in fact some corrections to the value of the spin diffusion coefficient, which depend on quantum exchange effects for indistinguishable particles. Physically, if these effects cannot directly change $\mathbf{J}(M_{x_i})$, they can do it indirectly by modifying the velocity distribution of

spin up or down atoms separately, so that the subsequent collisions between atoms with opposite spins can eventually be affected.

There is clearly a connection between the preceding physical argument and the model where the gas is considered to be a mixture of two atomic species, corresponding to the two possible spin orientations. It is then natural to expect that, even if M is not small, all preceding conclusions also apply, as long as this distinction between two types of atoms can be done consistently, i.e. when the direction of $\mathbf{M}$ which defines the Oz quantization axis does not change in space. Equations (7) immediately show that this is actually true : in such a situation, ∇M_x and ∇M_y vanish, and $\mathbf{J}(M_z)$ is determined by D_0 only. In other words, whenever « spin coherence » effects are absent, the spin diffusion process can be thought of in very simple terms (as a two component gas mixture).

More interesting situations occur when not only M , but also the direction of $\mathbf{M}$, change in space. Then, equations (7) show that the diffusion equations become anisotropic and non-linear. These features, which are rather unusual in a dilute gas, entirely arise from the « identical spin rotation effect »; the dimensionless coefficient μ introduces the non-linearity and anisotropy into the equations, and equation (8b) implies that spin rotation in both the scattered and transmitted wave are important (we shall see below that the latter, i.e. the identical spin rotation effect, is dominant at low temperatures). It is interesting to note that the spin orientation current (9) is nothing but the expression written by Leggett [3] for a degenerate ^3He liquid. In Leggett's theory, the origin of the terms in μ is somewhat different, since they are introduced by the degeneracy of the liquid; in the frame of Landau's quasiparticle theory of a Fermi liquid at very low temperatures, they arise from the spin orientation dependence of the drift term in Landau's kinetic equation (molecular field effects). The theory of reference [3] uses a relaxation time approximation for the quasiparticle collision term : clearly, no term in μ would have been obtained in (7), if such an approximation had been made for a dilute gas. We have intentionally used the same notation D_0 and μ as in reference [3], but it should be remembered that, here, these coefficients include no phenomenological constant, and can be calculated from first principles as soon as the atom-atom potential is sufficiently well known. Also, equation (9) is not restricted to a quasi-equilibrium situation, and M can be of the order of 1. In light of the many differences between a dilute gas of weakly interacting atoms and a strongly degenerate liquid, it may seem surprising that the spin current should have the same formal expression in both systems; the reason is probably that particle indistinguishability effects can be described, in an approximate fashion, as « transient degeneracy effects » occurring during very short times, when the atoms are very close during a collision. In this sense, the

time averaged effects of collision may be considered as a sort of degeneracy of the dilute gas which affects its transport properties.

The knowledge of all coefficients of the gas in terms of the inter-atomic potential phase shifts [equations (23) of the preceding article] allows one to calculate the temperature dependence of the effects. Let us for example study the low temperature limit; using equations (23) of the preceding article, one easily obtains :

$$\begin{aligned} \Omega_{[\sigma]}^{(1,1)} &\sim \Omega_0 \rightarrow 0 \\ \Omega_{[\text{tr ex.}]}^{(1,1)} &\sim \Omega_0 \frac{35}{8\pi} \left(\frac{\pi m a_0^2}{\beta \hbar^2} \right)^{3/2} \rightarrow 0 \\ \Xi_{[\text{tr ex.}]}^{(1)} &\sim - \frac{3\hbar}{2m} \pi a_0 \end{aligned} \quad (11a)$$

with :

$$\Omega_0 = 4 \pi a_0^2 \left(\frac{k_B T}{\pi m} \right)^{1/2} \quad (11b)$$

(a_0 is the scattering length). The finite limit of $\Omega_{[\text{tr ex.}]}^{(1,1)}$ arises from the divergence of $\tau_{\text{fwd.}}^{\text{ex.}}$ when the collision energy goes to zero. Consequently :

$$\mu \sim T^{-1/2} \rightarrow \infty. \quad (11c)$$

Under these conditions, if the polarization M is not zero (i.e. if $|\mu M| \gg 1$), equations (7) become :

$$\left. \begin{aligned} \mathbf{J}(M_x) &\simeq - D_0 \frac{\varepsilon}{\mu M} \nabla M_y \\ \mathbf{J}(M_y) &\simeq + D_0 \frac{\varepsilon}{\mu M} \nabla M_x \\ \mathbf{J}(M_z) &= - D_0 \nabla M_z \end{aligned} \right\} \quad (12a)$$

with :

$$D_0 \underset{T \rightarrow 0}{\sim} (k_B T)^{1/2} \rightarrow 0. \quad (12b)$$

We see that the M_x and M_y currents have much smaller diffusion coefficients than the M_z current; each of these two currents is proportional to $\varepsilon = +1$ or -1 (bosons or fermions) and depends on the gradient of the other component. Both these facts are consequences of the identical spin rotation effect in the forward direction, which tends to block the transverse diffusion by rotating the currents $\mathbf{J}(M_x)$ and $\mathbf{J}(M_y)$ with respect to the corresponding gradients.

1.3 SPIN OSCILLATIONS; HELICOIDAL DIFFUSION MODES. — Equation (7) shows that, due to the terms in $\varepsilon\mu$, no reciprocal relation exists between the effects of M_x and M_y gradients on the corresponding fluxes. This is due to the antihermitian character of the commutators in the collision operator Γ_c (see Appendix IV of the preceding article). Antihermitian operators have pure imaginary eigenvalues and we expect that the corresponding effects will be non dissipative (no

entropy production by the corresponding collision terms) and have some oscillatory character.

The spin orientation part of the entropy density is :

$$S_M = -k_B \left[\left(\frac{1+M}{2} \right) \text{Log} \left(\frac{1+M}{2} \right) + \left(\frac{1-M}{2} \right) \text{Log} \left(\frac{1-M}{2} \right) \right]. \quad (13)$$

In Appendix III of the present article, we study the time-dependence of the entropy and check that the

currents given by (7) always introduce a positive entropy production (no entropy production being associated with the commutators).

A simple way to see that spin oscillations are indeed predicted by equations (7) is to assume that $\mathbf{M}$ is large and almost constant over the sample :

$$\mathbf{M} = \mathbf{M}_0 + \mathbf{M}'(\mathbf{r}) \quad (14a)$$

$$\mathbf{M}'(\mathbf{r}) \ll M_0$$

and to linearize the equations with respect to $\mathbf{M}'$. Then, the variations of the directions of the axis Ox , Oy and Oz are negligible and we can write :

$$\left. \begin{aligned} \frac{\partial}{\partial t} M'_x &= -\nabla \cdot \mathbf{J}(M'_x) = \frac{D_0}{1 + \mu^2 M_0^2} [\Delta M'_x + \varepsilon \mu M_0 \Delta M'_y] \\ \frac{\partial}{\partial t} M'_y &= -\nabla \cdot \mathbf{J}(M'_y) = \frac{D_0}{1 + \mu^2 M_0^2} [-\varepsilon \mu M_0 \Delta M'_x + \Delta M'_y] \\ \frac{\partial}{\partial t} M'_z &= -\nabla \cdot \mathbf{J}(M'_z) = D_0 \Delta M'_z \end{aligned} \right\} \quad (14b)$$

We then see that the diffusion of the M'_z component is exactly the same as in a classical gas (no particle indistinguishability effects). The diffusion modes can be written :

$$M'_z(\mathbf{r}, t) = e^{i\mathbf{k} \cdot \mathbf{r}} e^{-t/\tau(k)} \quad (15a)$$

with :

$$\frac{1}{\tau(k)} = D_0 k^2 \quad (15b)$$

as usual. The same is not true for the transverse components M'_x and M'_y ; if we set :

$$M'_x \pm iM'_y = M'_\pm \quad (16a)$$

we obtain :

$$\frac{\partial}{\partial t} M'_\pm = \frac{D_0}{1 + \mu^2 M_0^2} [1 + i\varepsilon \mu M_0] \Delta M'_\pm. \quad (16b)$$

The linearized diffusion modes are then :

$$M'_\pm = e^{i\mathbf{k} \cdot \mathbf{r}} e^{-t/\tau'(k)} \quad (16c)$$

where $\tau'(k)$ is the complex number given by :

$$\frac{1}{\tau'(k)} = \frac{D_0 k^2}{1 + \mu^2 M_0^2} [1 + i\varepsilon \mu M_0]. \quad (16d)$$

We see that these modes acquire an oscillatory character provided that $M_0 \neq 0$; the ratio between angular frequency of the oscillation and the damping constant is :

$$R = |\mu M_0| \quad (17)$$

which may, in principle, become very large at low temperatures [equation (11c)]. Also, it is easily seen from equations (16) that the spatial structure of these modes is helicoidal when $\mathbf{k}$ is parallel to $\mathbf{M}_0$; if these vectors are orthogonal, the mode structure corresponds to rotations of the vector $\mathbf{M}'$ inside planes perpendicular to $\mathbf{M}_0$.

Until now, we have assumed that no static magnetic field $\mathbf{B}_0$ acts on the spins. In practice, such fields are often present, but they can trivially be included in the preceding considerations by using a rotating reference frame (for the spin components only, not for the $\mathbf{r}$'s). Then, if $\mathbf{M}_0$ is orthogonal to $\mathbf{B}_0$ (as in a $\pi/2$ pulse experiment), and if the orientation is slightly inhomogeneous, the component of $\mathbf{M}'$ parallel to $\mathbf{B}_0$ should oscillate (« longitudinal oscillation »), with a different phase at different points $\mathbf{r}$ in the sample.

From an experimental point of view, the effects studied here have an important advantage, as compared to heat conduction or viscosity studies : to the lowest order in M , they are linear, instead of quadratic, so that they should not require very high polarizations to be observed.

2. More elaborate theory : mode coupling. — The heat conduction and spin diffusion processes both introduce drift terms with an angular $\hat{p}$ dependence in $Y_l^m(\hat{p})$; thus, there is no reason why they should not be coupled. The trial density operator written in (3c) does not allow obtaining any heat current since it is traceless; similarly, we have seen in the preceding article that the trial operator then chosen was orthogonal to a spin current. Here, we shall take a broader class of trial density operators, in order to include both phenomena simultaneously :

$$\delta\bar{\rho}_S = \frac{1}{2} \left\{ \sum_{i=1}^3 \mathbf{c}_i \cdot \mathbf{p} \sigma_i + \varphi_0(p) \left[\mathbf{g}_0 \cdot \mathbf{p} + \sum_{i=1}^3 \mathbf{g}_i \cdot \mathbf{p} \sigma_i \right] \right\} \quad (18a)$$

with :

$$\varphi_0(p) = \left[\beta \frac{p^2}{2m} - \frac{5}{2} \right]. \quad (18b)$$

Moreover, we shall assume that the drift term includes at the same time temperature and spin orientation gradients, so that we can write it :

$$\frac{1}{m} \left\{ \frac{1}{2} \sum_{i=1}^3 (\mathbf{p} \cdot \nabla M_i) \sigma_i + \left[\frac{5}{2\beta} - \frac{p^2}{2m} \right] (\mathbf{p} \cdot \nabla \beta) \bar{\rho}_S^0 \right\}. \quad (19)$$

2.1 CALCULATION OF THE CURRENTS. — The method of moments then gives :

$$\begin{aligned} \frac{n}{\beta} \nabla M_x &= n^2 \{ X_1 \mathbf{c}_1 + V_1 \mathbf{g}_1 - \varepsilon M X_4 \mathbf{c}_2 - \varepsilon M V_4 \mathbf{g}_2 \} \\ \frac{n}{\beta} \nabla M_y &= n^2 \{ \varepsilon M X_4 \mathbf{c}_1 + \varepsilon M V_4 \mathbf{g}_1 + X_1 \mathbf{c}_2 + V_1 \mathbf{g}_2 \} \\ \frac{n}{\beta} \nabla M_z &= n^2 \{ M V_2 \mathbf{g}_0 + X_1 \mathbf{c}_3 + V_1 \mathbf{g}_3 \} \\ - \frac{5n}{2\beta} \nabla \text{Log } \beta &= n^2 \{ [W_1 + W_2 + \varepsilon W_3] \mathbf{g}_0 + \varepsilon M W_3 \mathbf{g}_3 \} \\ 0 &= n^2 \{ V_1 \mathbf{c}_1 + [W_1 + \varepsilon W_3] \mathbf{g}_1 - \varepsilon M V_4 \mathbf{c}_2 - \varepsilon M W_4 \mathbf{g}_2 \} \\ 0 &= n^2 \{ + \varepsilon M V_4 \mathbf{c}_1 + \varepsilon M W_4 \mathbf{g}_1 + V_1 \mathbf{c}_2 + [W_1 + \varepsilon W_3] \mathbf{g}_2 \} - \\ - \frac{5n}{2\beta} M \nabla \text{Log } \beta &= n^2 \{ [W_2 + \varepsilon W_3] M \mathbf{g}_0 + V_1 \mathbf{c}_3 + [W_1 + \varepsilon W_3] \mathbf{g}_3 \}. \end{aligned} \quad (20)$$

The coefficients X are defined by (4b), and the coefficients W have been defined in the preceding article [relation (55) and (56)], except W_4 :

$$W_4 = - \frac{m}{\beta} \left\{ \frac{55}{6} \Omega_{[\text{rex.}]}^{(1,1)} - \frac{10}{3} \Omega_{[\text{rex.}]}^{(1,2)} + \frac{2}{3} \Omega_{[\text{rex.}]}^{(1,3)} + \frac{55}{6} \Xi_{[\text{rfwd.}]}^{(1)} - \frac{10}{3} \Xi_{[\text{rfwd.}]}^{(2)} + \frac{2}{3} \Xi_{[\text{rfwd.}]}^{(3)} \right\}. \quad (21a)$$

As for the new coefficients V , their definition is :

$$\begin{aligned} V_1 &= -V_2 = - \frac{m}{\beta} \left[\frac{4}{3} \Omega_{[\sigma]}^{(1,2)} - \frac{10}{3} \Omega_{[\sigma]}^{(1,1)} \right] \\ V_4 &= - \frac{m}{\beta} \left[\frac{4}{3} \Omega_{[\text{rex.}]}^{(1,2)} - \frac{10}{3} \Omega_{[\text{rex.}]}^{(1,1)} + \frac{4}{3} \Xi_{[\text{rfwd.}]}^{(2)} - \frac{10}{3} \Xi_{[\text{rfwd.}]}^{(1)} \right]. \end{aligned} \quad (21b)$$

The system of 7 equations (20) can be split into two subsystems of 3 and 4 equations, respectively, connecting the « scalar » and « longitudinal » parameters $\mathbf{g}_0, \mathbf{g}_3$ and $\mathbf{c}_3$ on one hand, the « transverse » parameters $\mathbf{c}_1, \mathbf{c}_2, \mathbf{g}_1$ and $\mathbf{g}_2$ on the other. Solving the first subsystem gives the heat current $\mathbf{J}_w$ and spin current $\mathbf{J}(M_z)$:

$$\frac{1}{T} \mathbf{J}_w = - \{ \kappa(M) \nabla \text{Log } T + \varepsilon k_B M D'_{TM} n \nabla M_z \} \quad (22a)$$

$$\mathbf{J}(M_z) = - \left\{ \varepsilon M (1 - M^2) D'_{TM} \nabla \text{Log } T + \frac{D_0}{1 - \alpha_1(M)} \nabla M_z \right\}. \quad (22b)$$

The quantity D_0 is the « classical » diffusion coefficient given by (8a), and the diffusion correction parameter α_1 is defined by :

$$\alpha_1(M) = \frac{(V_1)^2}{X_1} \frac{W_1 + W_2 + \varepsilon W_3 (1 + M^2)}{[W_1 + \varepsilon W_3] [W_1 + W_2 + \varepsilon W_3] - \varepsilon M^2 W_3 [W_2 + \varepsilon W_3]}. \quad (23)$$

The heat conduction coefficient $\kappa(M)$ is given by :

$$\kappa(M) = \kappa_0 \frac{1 - \xi'_1 M^2}{1 - \xi'_2 M^2} \quad (24a)$$

with :

$$\xi'_1 = \frac{\varepsilon W_3 X_1}{X_1 [W_1 + \varepsilon W_3] - V_1^2} \quad (24b)$$

$$\xi'_2 = \frac{\varepsilon W_3 [X_1 (W_2 + \varepsilon W_3) + V_1^2]}{(W_1 + W_2 + \varepsilon W_3) [X_1 (W_1 + \varepsilon W_3) - V_1^2]} \quad (24c)$$

[the value of κ_0 is given by equation (61a) of the preceding article]. The coupling coefficient D'_{TM} is given by :

$$D'_{TM} = \frac{5}{2} \frac{D_0}{1 - \alpha_1(M)} \times \frac{W_3 V_1}{[W_1 + \varepsilon W_3] [W_1 + W_2 + \varepsilon W_3] - \varepsilon M^2 W_3 [W_2 + \varepsilon W_3]}. \quad (25)$$

In a similar way, solving the subsystem for the parameters c_1 , c_2 , g_1 and g_2 gives the spin currents relative to the transverse components :

$$J(M_x) = - D'_0 \frac{1 + \lambda M^2}{1 + \lambda'_1 M^2 + \lambda'_2 M^4} [\nabla M_x + \varepsilon M \mu'(M) \nabla M_y] \quad (26)$$

$$J(M_y) = - D'_0 \frac{1 + \lambda M^2}{1 + \lambda'_1 M^2 + \lambda'_2 M^4} [-\varepsilon M \mu'(M) \nabla M_x + \nabla M_y]$$

where :

$$D'_0 = D_0 \frac{(W_1 + \varepsilon W_3) X_1}{[(W_1 + \varepsilon W_3) X_1 - V_1^2]} \quad (27a)$$

$$\mu'(M) = \mu'_0 \frac{1 + \lambda'' M^2}{1 + \lambda M^2}$$

and :

$$\mu'_0 = - \frac{(W_1 + \varepsilon W_3)^2 X_4 - 2 V_1 V_4 (W_1 + \varepsilon W_3) + V_1^2 W_4}{(W_1 + \varepsilon W_3) [(W_1 + \varepsilon W_3) X_1 - V_1^2]} \quad (27b)$$

(the values of the coefficients λ , λ' , λ'_2 and λ'' are given in Appendix II).

2.2 NEW EFFECTS PREDICTED BY THE THEORY. — Several differences with the results of the preceding sections are immediately apparent on the equations that we have obtained.

First, the coefficients which had already been calculated have now a different, more precise, value. In the heat conduction coefficient $\kappa(M)$ for example, the coefficients ξ 's are now given by the more complete expressions (24b) and (24c). The coincidence between our new value of κ when $M = 0$ and the value of the simpler calculation [equation (61a) of the preceding article] is merely a consequence of the choice of the trial operator (18a), where the σ_0 component still has the very simple p dependence assumed before. Such a trial operator is therefore more adapted to the study of the M dependence of the transport coefficients, which is our purpose here, than to a precise calculation for $M = 0$ (which would be possible by taking into account the p dependence of g_0). It is interesting to note that variations of $\kappa(M)$ are still given by the ratio between two linear functions of M^2 ; it would be necessary to include more complicated terms in $\delta \bar{\rho}_s$ to obtain terms in M^4 for instance. In a similar way, the comparison between (22b) and (26) with equations (7) reveals several differences. In this case, we obtain M^4 corrections, and the « spin rotation coefficient » μ is now a function of M^2 . The diffusion correction parameter $\alpha_1(M)$ introduces a M^2 dependence of the diffusion coefficient for M_z ; as already mentioned in the preceding section, this is an indirect effect of particle indistinguishability on collisions between atoms in the same spin state.

Second, we see that M_z and heat diffusion are no longer independent, but become two components of two coupled modes. The coupling coefficient D'_{TM} is proportional to ε , which illustrates the fact that the coupling is a pure consequence of particle indistinguishability effects; nevertheless, some similarity can be found between this coupling and effects occurring in classical gas mixtures where it is well known that a coupling exists between thermal and concentration modes [6, 7]. This is not surprising since, as shown in § 2.2 of the preceding article, the two spin states are very similar to the two components of a classical gas mixture, when there is no transverse magnetization. Also, both crossed terms in (22) are proportional to M : only a gas having a signi-

ficant nuclear polarization will exhibit this coupling. On the other hand, this polarization should not be complete ($M = 1$): then ∇M_z and the $(1 - M^2)$ coefficient in the right hand side of (22b) would vanish ⁽⁴⁾. The physical origin of the mode coupling in a partially polarized gas is clearly the spin-velocity correlations introduced by the spin dependence of the collisions, as already discussed in the preceding article.

When $T \rightarrow 0$, we obtain the following limits [see also equations (11)] :

$$\begin{aligned}\Omega_{[\sigma]}^{(2,2)} &\sim \Omega_{[\sigma^{\text{ex.}}]}^{(2,2)} \sim 2 \Omega_0 \\ \Omega_{[\sigma]}^{(1,2)} &\sim 3 \Omega_0 \\ \Omega_{[\sigma]}^{(1,3)} &\sim 12 \Omega_0\end{aligned}\quad (28)$$

and :

$$\alpha_1(M) \rightarrow \frac{1 - M^2 + (1 + \varepsilon)(1 + M^2)}{43(1 - M^2) + (1 + \varepsilon)(91 + 27 M^2)} \quad (29a)$$

$$\kappa(M) \rightarrow \kappa_0 \frac{21 + 8 M^2 + (1 + \varepsilon)(45 - 16 M^2)}{21(1 - M^2) + (1 + \varepsilon)(45 + 13 M^2)} \quad (29b)$$

$$D'_{TM} \rightarrow \frac{5}{2} \frac{D_0}{1 - \alpha_1(M)} \frac{4}{43(1 - M^2) + (1 + \varepsilon)(91 + 27 M^2)} \quad (29c)$$

$$\mu'_0 \rightarrow \mu \frac{3(16\varepsilon + 59) + 20}{3(16\varepsilon + 59) - 8} \sim (k_B T)^{-1/2}. \quad (29d)$$

For fermions, we then obtain :

$$\left\{ \begin{aligned} \frac{\mathbf{J}_W}{T} &= - \left\{ \kappa_0 \frac{1 + \frac{8}{21} M^2}{1 - M^2} \nabla \text{Log } T - \frac{10}{42} n k_B D_0 \frac{M}{1 - M^2} \nabla M_z \right\} \\ \mathbf{J}(M_z) &= - \left\{ - \frac{10}{42} D_0 M \nabla \text{Log } T + \frac{43}{42} D_0 \nabla M_z \right\}. \end{aligned} \right. \quad (30a)$$

On these results, we see that the heat conduction coefficient $\kappa(M)$ becomes infinite when $M \rightarrow 1$, as in the preceding calculation; this is because the divergence of the atom mean free path in the gas [8] always occurs and introduces a divergence of $\kappa(M)$, whatever the choice of the trial operator $\delta\rho_s$. The same divergence is visible for the coupling coefficient between ∇M_z and $\mathbf{J}_W$, but not for the coupling coefficient between ∇T and $\mathbf{J}(M_z)$. The importance of the non-diagonal coupling coefficient is particularly obvious on (30b): roughly speaking, when $M \simeq 1$, a relative gradient of temperature produces the same effect as a 4 times larger spin orientation gradient. Experimentally, this means that it is possible to maintain a quasi-stationary non-uniform state of the gas by compensating the effect of a spin orientation gradient with a suitable temperature gradient ⁽⁵⁾. To conclude this discussion, we can remark that the M dependence of the (diagonal) spin diffusion coefficient disappears again in the zero temperature limit: no indirect effect of the collisions between atoms in the same spin state is then possible, since the corresponding cross section vanishes.

3. Isotopic mixtures. — Let us now consider a dilute gaseous mixture of the two isotopes ^3He and ^4He . In the preceding section, we have seen that two transport phenomena which have a $Y_l^m(\mathbf{p})$ dependence are coupled by particle indistinguishability effects occurring in collisions. It is therefore natural to expect that, in a mixture of two isotopes, the mass diffusion phenomenon — which has the same angular dependence — will also be coupled to the heat and spin diffusion.

In this section, it is more convenient to use $\mathbf{v}$ (velocity) variables instead of $\mathbf{p}$ (linear momentum). The distribution function for the ^4He atoms is written :

$${}^4f(\mathbf{r}, \mathbf{v})$$

and we keep the same notation $\rho_s(\mathbf{r}, \mathbf{v})$ for the 2×2 density operator of the ^3He atoms, although this operator

⁽⁴⁾ This $1 - M^2$ coefficient is also necessary to satisfy the Onsager symmetry relations (see Appendix III).

⁽⁵⁾ We have only discussed here situations where the spin orientation keeps the same direction over the gas. Nevertheless, if this direction changes, the hydrodynamic equations introduce couplings between longitudinal and transverse components of $\mathbf{M}$, so that the spin oscillations discussed in the preceding sections can affect the heat current.

differs from that used in the preceding section by a factor $(m_3)^3$, where m_3 is the mass of the ^3He atoms. We have :

$${}^3f(\mathbf{r}, \mathbf{v}) = \text{Tr} \{ \rho_S(\mathbf{r}, \mathbf{p}) \}. \quad (31)$$

A straightforward generalization of the considerations developed in the preceding article leads to :

$$\begin{aligned} \frac{\partial}{\partial t} \rho_S(\mathbf{r}, \mathbf{v}) + \mathbf{v} \cdot \nabla_{\mathbf{r}} \rho_S(\mathbf{r}, \mathbf{v}) &= I_{\text{coll}}(3-3) + I_{\text{coll}}(3-4) \\ \frac{\partial}{\partial t} {}^4f(\mathbf{r}, \mathbf{v}) + \mathbf{v} \cdot \nabla_{\mathbf{r}} {}^4f(\mathbf{r}, \mathbf{v}) &= I_{\text{coll}}(4-3) + I_{\text{coll}}(4-4) \end{aligned} \quad (32)$$

where $I_{\text{coll}}(3-3)$ is given by the right hand side of equation (32b) of the preceding article [with the substitutions $\sigma_k \rightarrow \sigma_k^{33}$, $v_r \rightarrow v_{33}$] and :

$$I_{\text{coll}}(3-4) = \int d^3v_2 v_{34} \int d^2\hat{q} \sigma_k^{34}(\theta) [{}^4f(\mathbf{v}'_2) \rho_S(\mathbf{v}'_1) - {}^4f(\mathbf{v}_2) \rho_S(\mathbf{v}_1)] \quad (33a)$$

$$I_{\text{coll}}(4-3) = \int d^3v_2 v_{34} \int d^2\hat{q} \sigma_k^{34}(\theta) [{}^3f(\mathbf{v}'_2) {}^4f(\mathbf{v}'_1) - {}^3f(\mathbf{v}_2) {}^4f(\mathbf{v}_1)] \quad (33b)$$

$$I_{\text{coll}}(4-4) = \int d^3v_2 v_{44} \int d^2\hat{q} \sigma_k^{44}(\theta) [{}^4f(\mathbf{v}'_2) {}^4f(\mathbf{v}'_1) - {}^4f(\mathbf{v}_2) {}^4f(\mathbf{v}_1)]. \quad (33c)$$

We are concerned here with situations where the pressure of the gas is uniform, but where there exists gradients of temperature, isotopic concentration, and spin orientation. The local equilibrium is then described by :

$${}^4f_0(\mathbf{r}, \mathbf{v}) = \left[\frac{m_4 \beta(\mathbf{r})}{2\pi} \right]^{3/2} n_4(\mathbf{r}) e^{-\beta(\mathbf{r})m_4 v^2/2} \quad (34a)$$

$$\begin{aligned} \rho_S^0(\mathbf{r}, \mathbf{v}) &= \left[\frac{m_3 \beta(\mathbf{r})}{2\pi} \right]^{3/2} n_3(\mathbf{r}) e^{-\beta(\mathbf{r})m_3 v^2/2} \bar{\rho}_S^0(\mathbf{r}) \\ &= {}^3f_0(\mathbf{r}, \mathbf{v}) \bar{\rho}_S^0(\mathbf{r}) \end{aligned} \quad (34b)$$

with :

$$\frac{n_3(\mathbf{r}) + n_4(\mathbf{r})}{\beta(\mathbf{r})} = \left[\frac{n}{\beta} \right]_0 \quad (34c)$$

(this condition ensures the uniformity of the pressure). We shall define the isotopic concentration $x(\mathbf{r})$ by :

$$x(\mathbf{r}) = \frac{n_3(\mathbf{r})}{n_3(\mathbf{r}) + n_4(\mathbf{r})} \quad (35)$$

We then have :

$$\begin{aligned} {}^4f_0(\mathbf{r}, \mathbf{v}) &= \left[\frac{n}{\beta} \right]_0 \left(\frac{m_4}{2\pi} \right)^{3/2} [\beta(\mathbf{r})]^{5/2} [1 - x(\mathbf{r})] e^{-\beta(\mathbf{r})m_4 v^2/2} \\ \rho_S^0(\mathbf{r}, \mathbf{v}) &= \left[\frac{n}{\beta} \right]_0 \left(\frac{m_3}{2\pi} \right)^{3/2} [\beta(\mathbf{r})]^{5/2} x(\mathbf{r}) e^{-\beta(\mathbf{r})m_3 v^2/2} \bar{\rho}_S^0(\mathbf{r}). \end{aligned} \quad (36)$$

From this, we obtain the following drift term for the ^4He atom :

$$\mathbf{v} \cdot \nabla_{\mathbf{r}} \{ {}^4f_0(\mathbf{r}, \mathbf{v}) \} = {}^4f_0(\mathbf{r}, \mathbf{v}) \left\{ \left[\frac{5}{2\beta} - \frac{m_4 v^2}{2} \right] \mathbf{v} \cdot \nabla \beta(\mathbf{r}) + \mathbf{v} \cdot \nabla \text{Log} [1 - x(\mathbf{r})] \right\} \quad (37a)$$

and, for the ^3He atoms :

$$\mathbf{v} \cdot \nabla_{\mathbf{r}} \{ \rho_S^0(\mathbf{r}, \mathbf{v}) \} = \mathbf{v} \cdot \nabla \rho_S^0(\mathbf{r}) + \bar{\rho}_S^0(\mathbf{r}, \mathbf{v}) \left\{ \left[\frac{5}{2\beta} - \frac{m_3 v^2}{2} \right] \mathbf{v} \cdot \nabla \beta(\mathbf{r}) + \mathbf{v} \cdot \nabla \text{Log} x(\mathbf{r}) \right\}. \quad (37b)$$

We now set :

$$\begin{aligned} {}^4f(\mathbf{r}, \mathbf{v}) &= {}^4f_0(\mathbf{r}, \mathbf{v}) [1 + \delta {}^4\bar{f}(\mathbf{r}, \mathbf{v})] \\ \rho_s(\mathbf{r}, \mathbf{v}) &= \rho_s^0(\mathbf{r}, \mathbf{v}) + {}^3f_0(\mathbf{r}, \mathbf{v}) \delta \bar{\rho}_s(\mathbf{r}, \mathbf{v}). \end{aligned} \quad (38)$$

A linearization of the collision integrals (33) then gives :

$$\begin{aligned} \delta I_{\text{coll}}(3-4) &= \int d^3v_2 v_{34} \int d^2\hat{q} \sigma_k^{34}(\theta) {}^3f_0(\mathbf{v}_1) {}^4f_0(\mathbf{v}_2) [\delta \bar{\rho}_s(\mathbf{v}'_1) - \delta \bar{\rho}_s(\mathbf{v}_1) + \bar{\rho}_s^0 [\delta {}^4f(\mathbf{v}'_2) - \delta {}^4f(\mathbf{v}_2)]] \\ \delta I_{\text{coll}}(4-3) &= \int d^3v_2 v_{34} \int d^2\hat{q} \sigma_k^{34}(\theta) {}^4f_0(\mathbf{v}_1) {}^3f_0(\mathbf{v}_2) [\delta {}^4f(\mathbf{v}'_1) - \delta {}^4f(\mathbf{v}_1) + \text{Tr} \{ \delta \bar{\rho}_s(\mathbf{v}'_2) - \delta \bar{\rho}_s(\mathbf{v}_2) \}] \\ \delta I_{\text{coll}}(4-4) &= \int d^3v_2 v_{44} \int d^2\hat{q} \sigma_k^{44}(\theta) {}^4f_0(\mathbf{v}_1) {}^4f_0(\mathbf{v}_2) [\delta {}^4f(\mathbf{v}'_1) + \delta {}^4f(\mathbf{v}'_2) - \delta {}^4f(\mathbf{v}_1) - \delta {}^4f(\mathbf{v}_2)]. \end{aligned} \quad (39)$$

The trial density operators that we shall use are given by :

$$\delta {}^4\bar{f}(\mathbf{r}, \mathbf{v}) = - \left[\frac{1 - x(\mathbf{r})}{x(\mathbf{r})} \right] \mathbf{c}_0 \cdot \mathbf{v} + {}^4\varphi'_0(v) \mathbf{g}_4 \cdot \mathbf{v}, \quad (40a)$$

$$\delta \bar{\rho}_s = \frac{1}{2} \{ \mathbf{c}_0 \cdot \mathbf{v} + \mathbf{c}_3 \cdot \mathbf{v} \sigma_3 + {}^3\varphi'_0(v) [\mathbf{g}_0 \cdot \mathbf{v} + \mathbf{g}_3 \cdot \mathbf{v} \sigma_3] \}, \quad (40b)$$

with :

$${}^{3,4}\varphi'_0(v) = \left[\frac{\beta}{2} m_{3,4} v^2 - \frac{5}{2} \right]. \quad (40c)$$

In (40a), the factor $(1 - x)/x$ ensures that the linear momentum density $\mathcal{P}_3(\mathbf{r}) + \mathcal{P}_4(\mathbf{r})$ vanishes; in (40b), we have ignored any σ_x or σ_y dependence, because the corresponding terms are not coupled to ∇T and ∇x . With these trial density operators, a calculation similar to that of the preceding section allows one to predict a coupling between three modes : spin orientation diffusion, mass diffusion and heat conduction. The method of moments leads to a system of 5 independent linear equations which determine the values of the 5 constants $\mathbf{c}_0$, $\mathbf{c}_3$, $\mathbf{g}_0$, $\mathbf{g}_3$ and $\mathbf{g}_4$ as a function of the « forces » ∇M_z , $\nabla \text{Log } x$ and $\nabla \text{Log } T$. We shall not give here the details of the calculations, which are somewhat cumbersome; instead, we shall emphasize the M dependence of the coefficients. The mass diffusion current is proportional to $\mathbf{c}_0$, the spin current to $\mathbf{c}_3$ and the heat current to a linear function of $\mathbf{g}_0$ and $\mathbf{g}_4$, and one obtains :

$$\left. \begin{aligned} \mathbf{J}(M_z) &= \frac{A + BM^2}{A + CM^2 + C' M^4} [(D + \varepsilon M^2 E) \nabla M_z + \varepsilon M(1 - M^2) F \nabla \text{Log } T + \varepsilon M(1 - M^2) H \nabla \text{Log } x] \\ \mathbf{J}(x) &= \frac{A + BM^2}{A + CM^2 + C' M^4} [\varepsilon M G \nabla M_z + L \nabla \text{Log } T + N \nabla \text{Log } x] \\ \frac{\mathbf{J}_W}{T} &= \frac{A + BM^2}{A + CM^2 + C' M^4} [\varepsilon M Q \nabla M_z + (\kappa + \varepsilon M^2 I) \nabla \text{Log } T + R \nabla \text{Log } x] \end{aligned} \right\} \quad (41)$$

where the coefficients D , E , ... are homographic functions of M^2 . On these equations, one can remark that all coupling coefficients between spin orientation gradient or flux on one hand, and isotopic or temperature gradient or flux on the other, are proportional to εM . Their origin is purely a particle indistinguishability effect [they arise from the anticommutators in equations (1b)]. There are other coupling coefficients, such as the coupling between $\nabla \text{Log } x$ and $\mathbf{J}_W$ for example, which do not disappear if particle indistinguishability effects are ignored; it is in fact well known [6, 7] that these effects occur in mixtures of classical gases.

4. Conclusion. — The hydrodynamic equations of a dilute spin polarized gas include several non-linear terms which are consequences of the Pauli principle (or symmetrization principle for bosons), and can be calculated from first principles, in terms of the collision phase shifts. Several unusual effects are predicted by the theory. For example the coupling between spin diffusion and heat conduction can, in principle, be used to increase the polarization of a gaseous sample by thermal methods. Conversely, it could also be used to obtain information on thermal processes from spin resonance measurements. It may be hoped that these

effects will be observed, either in $^3\text{He}\uparrow$ or in $\text{H}\uparrow$, in the near future.

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Appendix I. — In this appendix, we study the entropy variations predicted by the spin Boltzmann equation, which is the starting point of our study [equation (32a) of the preceding article], and we show that it is always positive (Boltzmann H theorem).

The total entropy S_T is defined by :

$$S_T = -k_B \text{Tr}_r \text{Tr}_s \{ \rho \text{Log} \rho \} \quad (\text{I.1a})$$

where Tr_r is the trace operation with respect to the external variables, Tr_s the same operation with respect to the spin variables, and ρ the one atom density operator. According to a well known property of the Wigner transform, we have :

$$S_T = -k_B \text{Tr}_s \left\{ \int d^3r \int d^3p (\rho \text{Log} \rho)_w \right\} \quad (\text{I.1b})$$

where $(\rho \text{Log} \rho)_w$ is the Wigner transform of the operator $\rho \text{Log} \rho$. Now, when the variations of $\rho_w(\mathbf{r}, \mathbf{p})$ are sufficiently slow in the phase space, we have :

$$(\rho \text{Log} \rho)_w \simeq \rho_s(\mathbf{r}, \mathbf{p}) \text{Log} \rho_s(\mathbf{r}, \mathbf{p}) \quad (\text{I.2})$$

where $\rho_s(\mathbf{r}, \mathbf{p})$ is the semi-classical $(2I+1) \times (2I+1)$ spin operator which appears in the spin Boltzmann equation [the term neglected in (I.2) involves products of $\mathbf{r}$ and $\mathbf{p}$ derivatives of ρ_s and $\text{Log} \rho_s$, multiplied by $\hbar$]. We then have :

$$S_T = \int d^3r S(\mathbf{r}) \quad (\text{I.3a})$$

where the local entropy $S(\mathbf{r})$ density is defined by :

$$S(\mathbf{r}) = -k_B \int d^3p \text{Tr}_s \{ \rho_s(\mathbf{r}, \mathbf{p}) \text{Log} \rho_s(\mathbf{r}, \mathbf{p}) \} \quad (\text{I.3b})$$

If we set :

$$\rho_s(\mathbf{r}, \mathbf{p}) = f(\mathbf{r}, \mathbf{p}) \bar{\rho}_s^0 \quad (\text{I.4a})$$

with

$$\text{Tr}_s \{ \bar{\rho}_s^0 \} = 1 \quad (\text{I.4b})$$

we also have :

$$S(\mathbf{r}) = -k_B \int d^3p f(\mathbf{r}, \mathbf{p}) \text{Log} f(\mathbf{r}, \mathbf{p}) - k_B n(\mathbf{r}) \times \text{Tr}_s \{ \bar{\rho}_s^0 \text{Log} \bar{\rho}_s^0 \}. \quad (\text{I.5})$$

This is nothing but the sum of a « classical » entropy and a « spin entropy » which, for spin $\frac{1}{2}$ particles, is given by :

$$-k_B \frac{n(\mathbf{r})}{2} \left\{ [1 + M(\mathbf{r})] \text{Log} \left(\frac{1 + M(\mathbf{r})}{2} \right) + [1 - M(\mathbf{r})] \text{Log} \left(\frac{1 - M(\mathbf{r})}{2} \right) \right\}. \quad (\text{I.6})$$

In the full Boltzmann equation, it is easy to show that the drift term does not give rise directly to any total entropy variation [although it can of course produce local changes]; this is because the drift term can be derived from an hamiltonian $\mathbf{p}^2/2m$. Thus, we shall concentrate here on the entropy variations arising from the collision term.

1. Effect of the « classical » collision term. — Let us first ignore the collision terms which are introduced by particle indistinguishability. The local entropy production due to collisions then is [equation (32b) of the preceding article] ⁽⁶⁾ :

$$\left(\frac{dS}{dt} \right)_{\text{cl.}} = -k_B \int d^3p \int d^3q \frac{q}{m} \int d^2\hat{q}' \sigma_k(\theta)$$

$$\text{Tr} \{ [1 + \text{Log} \rho_s(1)] [f(2) \rho_s(1') - f(2) \rho_s(1)] \}. \quad (\text{I.7})$$

In this integral, $\mathbf{q}$ and $\mathbf{q}'$ play a symmetrical role. Since interchanging $\mathbf{q}$ and $\mathbf{q}'$ amounts to interchanging both $\mathbf{p}_1$ and $\mathbf{p}_2$ with $\mathbf{p}'_1$ and $\mathbf{p}'_2$, the trace in the integral can also be written :

$$\text{Tr} \{ [\text{Log} \rho_s(1') - \text{Log} \rho_s(1)] f(2) \rho_s(1) \}.$$

Now a theorem, proved below, states that :

$$\text{Tr} \{ [\text{Log} \rho_s(1) - \text{Log} \rho_s(1')] \rho_s(1) \} \geq [\text{Log} f(1) - \text{Log} f(1')] f(1) \quad (\text{I.8})$$

the equality being valid if and only if $\rho_s(1)$ and $\rho_s(1')$ are proportional.

Consequently, the classical collision term gives rise to an entropy variation which is greater than :

$$k_B \int d^3p \int d^3q \frac{q}{m} \int d^2\hat{q}' \sigma_k(\theta) f(1)f(2) [\text{Log} f(1) - \text{Log} f(1')]$$

⁽⁶⁾ Here, we simplify the notations $f(\mathbf{p}_i)$ into $f(i)$ and $\rho_s(\mathbf{p}_i)$ into $\rho_s(i)$.

which is nothing but the classical entropy creation rate corresponding to the motion of the atoms. The rest of the reasoning is well known : a symmetrization with respect to the $\mathbf{p}_1$, $\mathbf{p}_2$, $\mathbf{p}'_1$ and $\mathbf{p}'_2$ variables allows one to change the integrated function into :

$$\frac{1}{4}[f(1)f(2) - f(1')f(2')] \times \\ \times [\text{Log} f(1) + \text{Log} f(2) - \text{Log} f(1') - \text{Log} f(2')] \quad (\text{I. 9})$$

which is either positive or zero, this second possibility occurring only if :

$$f(1)f(2) = f(1')f(2')$$

that is if the translation degree of freedom of the atoms are described by the Boltzmann equilibrium function $f_0(\mathbf{p})$. Consequently, we see that the « classi-

cal » collision term always introduces a positive local entropy creation, which can vanish only if the Boltzmann equilibrium is reached for the velocities, and if the internal spin state described by $\bar{\rho}_s(\mathbf{p})$ is independent of $\mathbf{p}$ [this second condition is introduced because (I. 8) reduces to an equality for any $\mathbf{p}_1$ and $\mathbf{p}'_1$]. Then the local equilibrium density operator :

$$\rho_s^0(\mathbf{p}) = f_0(\mathbf{p}) \bar{\rho}_s^0 \quad (\text{I. 10})$$

depends on the arbitrary spin density operator $\bar{\rho}_s^0$; this is a consequence of our assumption that there is no spin relaxation due to collisions.

Although it is not necessary here, it is convenient for the next section to use a more symmetrical form of the « classical » term in the collision creation of entropy. Using the $\mathbf{p}_1$, $\mathbf{p}_2$, $\mathbf{p}'_1$, $\mathbf{p}'_2$ symmetries, we can change (I. 7) into :

$$\left(\frac{dS}{dt}\right)_{\text{cl.}} = \frac{k_B}{16} \int d^3p \int d^3q \frac{q}{m} \int d^2\hat{q} [\sigma_k(\theta) + \sigma_k(\pi - \theta)] \\ \text{Tr} \left\{ [\text{Log} \rho_s(1) - \text{Log} \rho_s(1')] [f(2) \rho_s(1) - f(2') \rho_s(1')] + \right. \\ + [\text{Log} \rho_s(1) - \text{Log} \rho_s(2')] [f(2) \rho_s(1) - f(1') \rho_s(2')] \\ + [\text{Log} \rho_s(2) - \text{Log} \rho_s(1')] [f(1) \rho_s(2) - f(2') \rho_s(1')] \\ \left. + [\text{Log} \rho_s(2) - \text{Log} \rho_s(2')] [f(1) \rho_s(2) - f(1') \rho_s(2')] \right\}. \quad (\text{I. 11})$$

PROOF OF THE THEOREM. — Let us consider two hermitian definite positive operators ρ and ρ' , with respective eigenvalues p_m and p'_m and eigenkets $|p_m\rangle$ and $|p'_n\rangle$. The traces of ρ and ρ' are :

$$f = \text{Tr} \{ \rho \} = \sum_m p_m \quad f' = \text{Tr} \{ \rho' \} = \sum_n p'_n.$$

If λ is any positive number, the inequality :

$$x \text{Log} x \geq x - 1 \quad (\text{I. 12a})$$

can be written with $x = p_m/\lambda p'_n$ and gives :

$$p_m [\text{Log} p_m - \text{Log} p'_n] \geq p_m (1 + \text{Log} \lambda) - \lambda p'_n. \quad (\text{I. 12b})$$

Let us now multiply both sides of this inequality by the real positive number $\langle p_m | p'_n \rangle \langle p'_n | p_m \rangle$ and sum over m and n . Since :

$$\sum_n \langle p_m | p'_n \rangle \langle p'_n | p_m \rangle = 1$$

the term in $p_m \log p_m$ introduces the number $\text{Tr} \{ \rho \log \rho \}$; similarly, the terms p_m and p_n introduce the traces f and f' . Finally, since :

$$\sum_{mn} \langle p_m | p'_n \rangle \langle p'_n | p_m \rangle p_m \log p'_n = \sum_m \langle p_m | \rho \text{Log} \rho' | p'_n \rangle \langle p'_n | p_m \rangle = \text{Tr} \{ \rho \text{Log} \rho' \}$$

we obtain :

$$\text{Tr} \{ \rho [\text{Log} \rho - \text{Log} \rho'] \} \geq (1 + \text{Log} \lambda) f - \lambda f'. \quad (\text{I. 13})$$

This relationship is true whatever the choice of the positive number λ . If we set :

$$\lambda = \lambda_0 = f/f'$$

we obtain :

$$\text{Tr} \{ \rho [\text{Log} \rho - \text{Log} \rho'] \} \geq f \text{Log} f/f'. \quad (\text{I. 14})$$

The equality occurs only if $p_m = \lambda_0 p'_n$ (that is $x = 1$) whenever $\langle p_m | p'_n \rangle$ is not zero; if we introduce the operator :

$$\tilde{\rho}' = \lambda_0 \rho'$$

we can readily check that any eigenvalue of ρ is then an eigenvalue of $\tilde{\rho}'$, and conversely; the eigenspaces are the same, and we see that (I. 12) becomes an equality if and only if :

$$\rho = \tilde{\rho}' = \lambda_0 \rho'.$$

2. Effect of the particle indistinguishability term. — In equation (32a) of the preceding article, the term proportional to ε introduce an entropy variation :

$$\left(\frac{dS}{dt}\right)_\varepsilon = -k_B \frac{\varepsilon}{2} \int d^3p \int d^3q \frac{q}{m} \int d^2\hat{q}' \sigma_k^{\text{ex}}(\theta) \text{Tr} \left\{ \left[1 + \text{Log } \rho_s(1) \right] \left[[\rho_s(1'), \rho_s(2')]_+ - [\rho_s(1), \rho_s(2)]_+ \right] \right\} + \\ + i\tau_k^{\text{ex}}(\theta) \text{Tr} \left\{ \left[1 + \text{Log } \rho_s(1) \right] [\rho_s(1'), \rho_s(2')] \right\} + i\tau_{\text{fwd}}^{\text{ex}} \text{Tr} \left\{ \left[1 + \text{Log } \rho_s(1) \right] [\rho_s(1), \rho_s(2)] \right\}. \quad (\text{I. 15})$$

The two last terms are introduced by the « identical spin rotation effect » and they give rise to no entropy production. This result can easily be checked for the term in $\tau_k^{\text{ex}}(\theta)$ since it changes sign when $\mathbf{p}'_1$ and $\mathbf{p}'_2$ are exchanged (inversion of $\mathbf{q}$ and $\mathbf{q}'$ which leaves θ unchanged). As for the terms in $\tau_{\text{fwd}}^{\text{ex}}$, it is also zero, since $1 + \text{Log } \rho_s(1)$ commutes with $\rho_s(1)$ (circular permutation of the operators inside the trace). In fact $\rho_s(2)$ plays the role of an effective hamiltonian, and it is well known that the entropy does not change in an hamiltonian evolution.

We are now left with the two anticommutators in $\sigma_k^{\text{ex}}(\theta)$. Using the $\mathbf{p}_1, \mathbf{p}_2, \mathbf{p}'_1, \mathbf{p}'_2$ symmetries, the integrated function can be transformed into

$$- \varepsilon \frac{q}{8m} \sigma_k^{\text{ex}}(\theta) \text{Tr} \left\{ \left[\text{Log } \rho_s(1) + \text{Log } \rho_s(2) - \text{Log } \rho_s(1') - \text{Log } \rho_s(2') \right] \left[[\rho_s(1), \rho_s(2)]_+ - [\rho_s(1'), \rho_s(2')]_+ \right] \right\}. \quad (\text{I. 16})$$

Now, a theorem (proved below) states that :

$$\pm \text{Tr} \left\{ \left[\text{Log } \rho_1 + \text{Log } \rho_2 - \text{Log } \rho_3 - \text{Log } \rho_4 \right] \left[[\rho_1, \rho_2]_+ - [\rho_3, \rho_4]_+ \right] \right\} \leq \\ \leq \text{Tr} \left\{ [\text{Log } \rho_1 - \text{Log } \rho_3] [f_2 \rho_1 - f_4 \rho_3] + [\text{Log } \rho_1 - \text{Log } \rho_4] [f_2 \rho_1 - f_3 \rho_4] \right. \\ \left. + [\text{Log } \rho_2 - \text{Log } \rho_3] [f_1 \rho_2 - f_4 \rho_3] + [\text{Log } \rho_2 - \text{Log } \rho_4] [f_1 \rho_2 - f_3 \rho_4] \right\}. \quad (\text{I. 17})$$

Using (I. 11), we therefore obtain :

$$\left(\frac{dS}{dt}\right)_{\text{cl.}} + \left(\frac{dS}{dt}\right)_\varepsilon \geq \frac{k_B}{16} \int d^3p \int d^3q \frac{q}{m} \int d^2\hat{q}' [\sigma_k(\theta) + \sigma_k(\pi - \theta) - 2 |\sigma_k^{\text{ex}}(\theta)|] F(\rho_1, \rho_2, \rho'_1, \rho'_2) \quad (\text{I. 18})$$

where $F(\rho_1, \rho_2, \rho'_1, \rho'_2)$ is the trace written on the right hand side of (I. 11). But the combination of cross sections between brackets is always positive [equation (20) of the preceding article], as well as the function F . Consequently :

$$\left(\frac{dS}{dt}\right)_{\text{cl.}} + \left(\frac{dS}{dt}\right)_\varepsilon \geq 0 \quad (\text{I. 19})$$

the equality occurring if and only if the atomic velocities are in the Boltzmann equilibrium and the spin state is velocity independent [equation (I. 10)].

PROOF OF THE THEOREM. — Let us consider 4 kets $|1\rangle, |2\rangle, |3\rangle, |4\rangle$; a first step in the proof is to show that

$$\pm [\langle 1|3\rangle \langle 3|2\rangle \langle 2|4\rangle \langle 4|1\rangle + \langle 2|3\rangle \langle 3|1\rangle \langle 1|4\rangle \langle 4|2\rangle] \\ \leq |\langle 1|3\rangle|^2 |\langle 2|4\rangle|^2 + |\langle 1|4\rangle|^2 |\langle 2|3\rangle|^2 \quad (\text{I. 20})$$

To do this, we can introduce 2 similar particles a and b, with density operators :

$$\rho_a^1 = |a:1\rangle \langle a:1| \quad \rho_b^2 = |b:2\rangle \langle b:2|$$

or :

$$\rho_b^2 = |a:2\rangle\langle a:2| \quad \rho_b^1 = |b:1\rangle\langle b:1|$$

(we may assume that the kets are normed to one, but this is not essential). A possible density operator of the system is :

$$\rho(a, b) = \frac{1}{2}[\rho_a^1 \otimes \rho_b^2 + \rho_a^2 \otimes \rho_b^1]. \quad (I.21)$$

Since this operator is positive, we have :

$$\langle \psi(a, b) | \rho(a, b) | \psi(a, b) \rangle \geq 0 \quad (I.22)$$

whatever the choice of the 2 particle ket $|\psi(a, b)\rangle$. If we set :

$$|\psi(a, b)\rangle = x |a:3; b:4\rangle + |a:4; b:3\rangle$$

we obtain for the right hand side of (I.21) a polynomial in x of degree two, of which the discriminant has to be negative. A very simple calculation shows that this condition can be written :

$$|\langle 1|3\rangle\langle 3|2\rangle\langle 2|4\rangle\langle 4|1\rangle + \text{c.c.}| \leq |\langle 1|3\rangle|^2 |\langle 2|4\rangle|^2 + |\langle 1|4\rangle|^2 |\langle 2|3\rangle|^2$$

from which inequality (I.19) is readily obtained.

We can now multiply (I.20) by the positive number

$$[p_m^1 p_n^2 - p_q^3 p_r^4] [\text{Log } p_m^1 + \text{Log } p_n^2 - \text{Log } p_q^3 - \text{Log } p_r^4]$$

where p_m^1, p_n^2, p_q^3 and p_r^4 are the respective eigenvalues of operators ρ_1, ρ_2, ρ_3 and ρ_4 . After a summation over the indices m, n, p and r , a simple calculation then leads to inequality (I.17).

Appendix II

$$D_0 = -\frac{1}{n\beta^2} \cdot \frac{1}{X_1} \frac{1 - \frac{V_1^2}{X_1(W_1 + \varepsilon W_3)}}{\left[1 - \frac{V_1^2}{X_1(W_1 + \varepsilon W_3)}\right]^2}$$

$$\mu'_0 = \frac{(W_1 + \varepsilon W_3)^2 X_4 - 2 V_1 V_4 (W_1 + \varepsilon W_3) + V_1^2 W_4}{(W_1 + \varepsilon W_3)^2 X_1 - V_1^2 (W_1 + \varepsilon W_3)}$$

$$\lambda'' = \frac{W_4^2 X_4 - W_4 V_4^2}{(W_1 + \varepsilon W_3)^2 X_4 - 2 V_1 V_4 (W_1 + \varepsilon W_3) + V_1^2 W_4}$$

$$\lambda = \frac{W_4^2 X_1 - 2 V_1 V_4 W_4 + V_4^2 (W_1 + \varepsilon W_3)}{(W_1 + \varepsilon W_3)^2 X_1 - V_1^2 (W_1 + \varepsilon W_3)}$$

$$\lambda'_1 = \frac{(X_1 W_4 - V_1 V_4)^2 + \{(W_1 + \varepsilon W_3) X_4 - V_1 V_4\}^2 + 2(V_4 X_1 - V_1 X_4) \{V_4 (W_1 + \varepsilon W_3) - V_1 W_4\}}{[(W_1 + \varepsilon W_3) X_1 - V_1^2]^2}$$

$$\lambda'_2 = \frac{W_4^2 X_4^2 - V_4^4}{[(W_1 + \varepsilon W_3) X_1 - V_1^2]^2}.$$

Appendix III. — In this appendix, we study the entropy changes of the gas in the hydrodynamic regime (mean free path $l \ll$ macroscopic distance L), obtained within a first order Chapman-Enskog expansion. We know from appendix I that the local entropy creation introduced by collisions reaches its minimum zero value if (and only if) the local equilibrium is obtained. Since the difference between $\rho_s(\mathbf{r}, \mathbf{p})$ and the equilibrium density operator $\rho_s^0(\mathbf{r}, \mathbf{p})$ is a first order quantity in l/L , the collision entropy production will be a second order quantity which is negligible to our first order approximation. Then, all entropy variations will come from the changes in time of the macroscopic quantities which define the local equilibrium [energy density $\mathcal{W}(\mathbf{r})$, spin orientation $M(\mathbf{r})$].

As an example, let us study the entropy variations corresponding to the hydrodynamic spin orientation currents written in (7). These currents have been obtained for a physical situation when the density n and tempe-

perature T are uniform, the only non-uniform quantity being the spin orientation $\mathbf{M}(\mathbf{r})$. It has been assumed [equation (3c)] that the translational degrees of freedom remain in the Boltzmann equilibrium. Equations (I.5) then becomes, for spin $\frac{1}{2}$ particles :

$$\begin{aligned} S_M(\mathbf{r}) &= -k_B n \text{Tr} \{ \bar{\rho}_s(\mathbf{r}) \text{Log} \bar{\rho}_s(\mathbf{r}) \} \\ &= -\frac{k_B n}{2} \left\{ [1 + M(\mathbf{r})] \text{Log} \left(\frac{1 + M(\mathbf{r})}{2} \right) + [1 - M(\mathbf{r})] \text{Log} \left(\frac{1 - M(\mathbf{r})}{2} \right) \right\}. \end{aligned} \quad (\text{III.1})$$

The function S_M depends on M only and :

$$\frac{dS_M}{dM} = -\frac{k_B n}{2} \text{Log} \left(\frac{1 + M}{1 - M} \right) \leq 0. \quad (\text{III.2})$$

The time dependence of S is due to the variation of M :

$$\frac{\partial}{\partial t} M = \frac{M_x}{M} \frac{\partial M_x}{\partial t} + \frac{M_y}{M} \frac{\partial M_y}{\partial t} + \frac{M_z}{M} \frac{\partial M_z}{\partial t}$$

where :

$$\frac{\partial M_{x_i}}{\partial t} = -\nabla \cdot \mathbf{J}(M_{x_i}). \quad (\text{III.3})$$

Then :

$$\begin{aligned} \frac{dS_M}{dt} &= -\frac{dS_M}{dM} \sum_{i=1}^3 \frac{M_{x_i}}{M} \nabla \cdot \mathbf{J}(M_{x_i}) \\ &= -\nabla \cdot \left\{ \frac{dS_M}{dM} \sum_{i=1}^3 \frac{M_{x_i}}{M} \mathbf{J}(M_{x_i}) \right\} + \sum_{i=1}^3 \mathbf{J}(M_{x_i}) \cdot \nabla \left(\frac{M_{x_i}}{M} \frac{dS_M}{dM} \right). \end{aligned} \quad (\text{III.4})$$

On the right hand side of this equation, the first term is an exact divergence and corresponds to a conservative entropy flux (its integral over the whole gas vanishes, except of course if there are other causes for entropy creation, e.g. a nuclear relaxation on the walls). We shall therefore concentrate on the second term. Since it does not contain any space derivative of the currents $\mathbf{J}$, it can be calculated in the local reference frame $Oxyz$ with axis Oz parallel to $\mathbf{M}$, and we obtain :

$$\left(\frac{dS_M}{dt} \right)_{\text{non conservative}} = -\frac{k_B n}{2} \sum_i \mathbf{J}(M_{x_i}) \cdot \left\{ \left(\frac{1}{M} \text{Log} \frac{1 + M}{1 - M} \right) \left(\nabla M_{x_i} - \frac{M_{x_i}}{M} \nabla M_z \right) + \frac{2}{1 - M^2} \frac{M_{x_i}}{M} \nabla M_z \right\}. \quad (\text{III.5})$$

Using equations (7), we then obtain :

$$\left(\frac{dS_M}{dt} \right)_{\text{non conservative}} = \frac{k_B n}{2} D_0 \left\{ \left[\frac{\nabla M_x^2 + \nabla M_y^2}{1 + \mu^2 M^2} \right] \frac{1}{M} \text{Log} \left(\frac{1 + M}{1 - M} \right) + \nabla M_z^2 \frac{2}{(1 - M^2)} \right\}. \quad (\text{III.6})$$

It is then easy to see that the entropy production is always positive.

Let us now consider the more elaborate theory of section 2, and study the consequences of the couplings between ∇M_z and ∇T on the entropy production. If we use equation (22b) for the current $\mathbf{J}(M_z)$, and result (III.5), we obtain a crossed term in ∇M_z and $\nabla \text{Log } T$ which is equal to :

$$\begin{aligned} \left(\frac{dS_M}{dt} \right)_{MT} &= \frac{k_B n}{2} M(1 - M^2) D'_{TM} \nabla(\text{Log } T) \left[\frac{2}{1 - M^2} \nabla M_z \right] \\ &= D'_{TM} k_B n M \nabla \text{Log } T \cdot \nabla M_z. \end{aligned} \quad (\text{III.7})$$

On the other hand, the time derivative of the thermal entropy of the gas is :

$$\begin{aligned} \frac{d}{dt} S_T &= \frac{dS_T}{d\mathcal{W}} \frac{d\mathcal{W}}{dt} = -\frac{1}{T} \nabla \cdot \mathbf{J}_W \\ &= -\nabla \cdot \left\{ \frac{\mathbf{J}_W}{T} \right\} - \frac{1}{T} \mathbf{J}_W \cdot \nabla \text{Log } T. \end{aligned} \quad (\text{III.8})$$

Using (22a), the crossed term in the dissipative part of this variation can be written :

$$k_B n M D'_{TM} \nabla M_z \cdot \nabla \log T \quad (\text{III.9})$$

which is nothing but (III.7). The two crossed terms in the entropy creation are therefore equal (Onsager relations).

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