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HYDRODYNAMICS OF A NORMAL FLUID UP TO HIGH FREQUENCIES AND SMALL WAVELENGTHS
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Résumé. — Nous obtenons des équations d’évolution pour un liquide dense en tenant compte des degrés de liberté rotationnels des molécules et de l’ordre local. Deux tenseurs sont introduits, le premier caractérise l’ordre local des centres de gravité des molécules, le deuxième l’ordre local orientationnel. En couplant ces tenseurs avec le tenseur de contrainte usuel, nous obtenons de nouvelles équations hydrodynamiques. Ces équations montrent que les ondes transverses se propagent pour le nombre d’onde k compris entre deux valeurs.

Abstract. — We obtain equations of evolution for a dense fluid taking into account the orientational degrees of freedom of the molecules and the local order. We introduce two tensors. The first characterizes the local order of the center of gravity of the molecules, the second the orientational local order. Coupling these tensors with the usual stress tensor, we obtain new hydrodynamic equations. These equations show that the transverse waves are propagating for the wave number k between two values.

1. Introduction. — Recent experiments on depolarized light scattering [1] have shown the necessity to obtain new hydrodynamic equations taking into account the orientational degrees of freedom of the molecules. On the other hand investigations on the isotropic phase of a nematic [2] and molecular dynamic calculations on dense liquid nitrogen [3] emphasize the importance of the local order in a dense fluid. The first attempts to obtain hydrodynamic equations taking into account the orientational degrees of freedom neglected the local order [4], so these equations are not valid in a dense fluid. More recent attempts start from the generalized Langevin equations [5, 6] but the great complexity of the calculations does not always bring out clearly the physical ideas behind the phenomena involved, and the importance of the local order is not always stressed. Furthermore, these calculations are to order $k^2$ ($k$ is the wave number), and at this order it is well known [7] that for a non-dense fluid the generalized Langevin equations give the usual Navier-Stokes equation and nothing more. So it does not seem necessary to use such a complex formalism to obtain the equation of evolution for a dense fluid, the classical method [8] should be sufficient. This is the purpose of this paper. A precedent work in this direction was done by De Gennes [2] in the isotropic phase of nematics. This author introduces a tensor characterizing the local orientational order and obtains new equations of evolution by coupling this tensor with the usual stress tensor. By a different approach, it will appear from our calculations that there are not only one but two tensors characterizing the local order. Using then the method proposed by De Gennes, we shall obtain a generalization of his equations. We shall also check that our results are in good agreement with method of broken symmetries proposed by Martin, Parodi, Pershan [12] (M.P.P.). In this paper, some of the calculations are classical and have not been developed. The reader can find the details, for instance, in reference [8].

2. The local order. — In a dense monatomic fluid there exists a local order of the centers of gravity characterized by the pair distribution function [9]. On the other hand in the isotropic phase of a nematic, the local order is essentially orientational [2]. In a typical polyatomic fluid, we must have both the local orientational order and the local order of the center of gravity (c.o.g.). It therefore appears that at least two quantities are necessary to characterize the local order.

Recent molecular dynamic calculations on liquid nitrogen near the triple point [3] show an important
local structure which recalls, for the first shell of neighbours of a given molecule, the structure of the α solid. Since nitrogen is not very elongated the order of the c.o.g. is more important than the orientational order. The correlation length $L_1$ is at least 12 Å. A sphere centered on a molecule with a radius $L_1$ contains about 250 molecules correlated with the central one. Furthermore, there are indications from calculations of pseudo-collective correlation functions [3, 18], that the correlation time $\tau_1$ of the local order, is of the order of $5 \times 10^{-12}$ s. A more complex liquid than nitrogen, in similar conditions of density and temperature has certainly a more important local structure and a larger correlation length and correlation time.

Let $a_j(t)$ be a quantity linked to the molecule $j$; we define the local density $a(r, t)$, as

$$a(r, t) = \frac{1}{L^3} \sum_j a_j(t) \ U(r_j - r) \quad (2.1)$$

where $U(r_j - r)$ equals one if the c.o.g. of the molecule $j$ is in the cubic box of side $L$ centered at $r$, and $U(r_j - r)$ equals zero otherwise. $j$ runs over all the molecules of the fluid.

The size of the box is of great importance in the definition of the local densities when the local order is taken into account. For instance, if we define, in the isotropic phase of a nematic, the density of local order [2] as:

$$Q = \frac{1}{L^3} \sum_j \frac{1}{2} (3 \cos^2 \theta_j - 1) \ U(r - r_j)$$

$Q$ is a function of $L$ which decreases towards zero when $L$ increases and is equal to zero when $L$ is much greater than $L_1$.

Accordingly we shall have to consider two cases:

1. when we are interested in wavelengths larger than $L_1$, we shall take $L$ equal to $L_1$,
2. when we are interested in wavelengths smaller than $L_1$ we shall take $L$ smaller than the wavelength and thus smaller than $L_1$. In such a case the local density defined by (2.1) will be strongly dependent on the size of the box.

Classically, in order to obtain the hydrodynamic equations, the number of molecules in the box must be sufficiently large so that it is possible to define a local thermodynamic equilibrium [10]. From molecular dynamic calculations we know that it is possible to define a thermodynamic equilibrium from about one hundred molecules. Furthermore we know, that for such a number of nitrogen molecules the equilibrium is reached after a time $\tau_2$ of the order of $10^{-13}$ s if the initial conditions are not too far from equilibrium. Performing a time integration on the molecular quantities during a span of time of the order of $\tau_2$, we are also able to define the temperature, the pressure, the entropy, etc... for such a number of molecules.

There are therefore two characteristic times, one is the life-time $\tau_1$ of the local structure and the other is the time $\tau_2$ necessary to define a local thermodynamic equilibrium. In a dense fluid $\tau_1$ is generally much greater than $\tau_2$ ($5 \times 10^{-12}$ s and $10^{-13}$ for nitrogen). For time spans greater than $\tau_2$ and shorter than $\tau_1$, the molecules in the box are in local equilibrium and their relative positions are reminiscent of a loose solid. In the following when we speak of local equilibrium we shall have in mind such a situation.

We now specify what we mean when we perform an average. Suppose that at time $t = 0$ the liquid is not in equilibrium. This could result from an external constraint (wall of a box, electric or magnetic field, gradient of temperature). It can also arise from a natural fluctuation in the liquid. Such an initial condition corresponds to a probability density $p(x)$ in the phase space $I$ and $p(x)$ is different from the usual Boltzmann probability density $\rho(x)$. We define the hydrodynamic average value of a quantity $X(t)$ as

$$\langle X(t) \rangle_H = \frac{1}{\tau_2} \int_{t_1}^{t+\tau_2} X(s) \ ds .$$

The total equilibrium value of $X(t)$ will be written

$$\langle X \rangle_E = \int_I X(x) \rho(x) \ dx .$$

If we release the external constraint or if the initial conditions arise from a natural fluctuation, we have

$$\frac{1}{T} \int_0^T \langle X(t) \rangle_H \ dt \rightarrow \langle X \rangle_E \ \text{when} \ \ T \rightarrow \infty .$$

Let $I(r, t)$ be a quantity characterizing the local order. We suppose that for $t = 0$ and $r = 0$, there is a fluctuation $\delta I(0, 0)$. Qualitatively, we shall have

$$\langle \delta I(r, t) \rangle_H \approx \delta I(0, 0) \ e^{-\eta L_2} e^{-\eta L_2} f(t, r) \quad (2.2)$$

where $f(t, r)$ is a smooth function with regard to the exponentials. It is worth noting that there is no evident relation between $L_2$ and the correlation length $L_1$; $L_2$ can be much larger than $L_1$. If we are interested in frequencies much lower than $1/\tau_1$ and in wavelengths much larger than $L_2$, we can neglect the local order, consider the fluid as homogeneous and isotropic and use the classical Navier-
Stokes equations. But if we are interested in frequencies of the same order or higher than \(1/\tau_1\) or in wavelengths of the same order or smaller than \(L_2\), we must take into account the local order. For instance we shall see in paragraph 6 that when \(\omega \tau_1\) is sufficiently large the viscosity is a function of \(\omega\) and the fluid has a solid like behavior. This is an idea first proposed by Maxwell for the viscous fluids [11].

Let \(U(k)\) be the Fourier transform of \(U(r)\). It is easy to see that when \(kL\) tends towards zero, \(U(k)/L^3 \approx 1\). In such a case the equation (2.1) becomes

\[
a(r, t) = \sum_j a_j(t) \delta(r_j - r). \tag{2.3}
\]

This definition of the local density is often used in the literature. But for large \(kL\) such a definition cannot take into account, in a simple way, the local structure.

3. Equations of evolution. — We define now the following densities

\[
\rho(r, t) = \frac{m}{L^3} \sum_j U(r_j - r)
\]

\[
P(r, t) = \frac{1}{L^3} \sum_j P_j U(r_j - r)
\]

\[
e(r, t) = \frac{1}{L^3} \sum_j \times
\]

\[
\times \left( \frac{P_j^2}{2m} + \frac{1}{2} \Omega_j \times \Omega_j + \frac{1}{2} \sum_{ij} U_{ij} \right) U(r_j - r)
\]

\[
M(r, t) = \frac{1}{L^3} \sum_j (r_j - r) \times P_j U(r_j - r)
\]

\[
S(r, t) = \frac{1}{L^3} \sum_j S_j U(r_j - r)
\]

We will now, calculate the time derivatives of these quantities. To do this, we perform the \(k\) Fourier transform, then we differentiate with respect to time and we come back into \(r\) space. Details of the calculations are given in the appendix. We obtain for \(\rho\) and \(P\)

\[
\dot{\rho}(r, t) = -V \cdot P(r, t) \tag{3.2}
\]

\[
\dot{P}(r, t) = -V \cdot \partial(r, t) \tag{3.3}
\]


\[
\partial(r, t) = \frac{1}{mL^3} \sum_j P_j P_j U(r_j - r) + \frac{1}{2L^3} \sum_{j\neq i} r_{ij} F_{ij} f(r, r_{ij}) U(r_j - r)
\]

where \(r_{ij} = r_j - r_i\), \(F_{ij}\) is the force exerted by the molecule \(i\) on the molecule \(j\). \(uv\) is the tensor constructed from the vectors \(u\) and \(v\) \([uv]_{\alpha \beta} = u_\alpha v_\beta\), \(\alpha\) is the row and \(\beta\) is the column index. \(u, v\) is the usual scalar product. \(f * g\) is the convolution product of the function \(f\) with the function \(g\). \(f(r, r_j)\) is given by its Fourier transform:

\[
f(k, r_{ij}) = \frac{1}{\pi} \exp \left\{ -\frac{i \cdot k \cdot r_{ij}}{k} \right\}. \tag{3.4}
\]

If \(1/k\) is much longer than the range of the intermolecular potential \(f(k, r_{ij}) \approx 1 - \frac{1}{2} k \cdot r_{ij}\). \(\partial\) is the usual stress tensor. In the following when it is not ambiguous, we shall write the Fourier transform of a function \(f(r)\) as \(f(k)\).

We now give the derivative with respect to time of the density of spin \(S(r, t)\)

\[
\dot{S}(r, t) = -V \cdot \partial(r, t) - 2 \Sigma(r, t)
\]

\[
\partial(r, t) = \frac{1}{mL^3} \sum_j P_j S_j + \frac{1}{2L^3} \sum_{j\neq i} \times \times \times r_{ij} \epsilon_{ij} f(r, r_{ij}) U(r_j - r)
\]

\[
\Sigma(r, t) = \frac{1}{4L^3} \sum_{ij} r_{ij} \times F_{ij} U(r_j - r)
\]

\(C_j\) is the torque with respect to the c.o.g. of molecule \(j\) exerted on molecule \(j\) by molecule \(l\). Generally \(C_{ij}\) is different from \(-C_{ji}\). More precisely we have

\[
C_{ij} + C_{ji} + r_{ij} \times F_{ij} = 0. \tag{3.6}
\]

This relation comes directly from the conservation of the total angular momentum for two isolated molecules. \(F_{ij}\) is generally not collinear with \(r_{ij}\) for a non-spherical molecule, so \(r_{ij} \times F_{ij}\) is generally different from zero. It is worth noting that this quantity is not the torque between the molecules \(j\) and \(l\), as is sometimes written in the literature.

\(\partial(r, t)\) cannot be written as the gradient of a tensor since \(\Sigma(r, t)\) is generally different from zero. This is the mathematical formulation of the fact that \(\partial(r, t)\) is not conserved.
The equilibrium value of the trace of $\Gamma$ is given by

$$\frac{1}{2 L^3} \left\langle \sum_{j \neq i} r_j \cdot C_{ji} f(r, r_j) \cdot U(r_j - r) \right\rangle_E.$$  

This quantity resembles the virial coefficient with the torque $C_{ji}$ instead of the force $F_{ji}$. This quantity, which is a pseudo-scalar, is equal to zero if the Hamiltonian of the system is invariant under the parity operation. If not, we may have at thermal equilibrium a local torque equivalent to the local pressure.

Before differentiating $M(r, t)$, we shall derive the angular momentum density with regard to the origin of the laboratory frame:

$$J(r, t) = \frac{1}{L^3} \sum_{i} r_i \times P_i U(r_i - r) \quad (3.7)$$

$$\dot{J}(r, t) = \nabla \cdot (\widehat{\sigma} \times r) - \nabla \cdot \dot{\widehat{\sigma}}(r, t) + 2 \Sigma_m(r, t)$$  

$$\dot{\widehat{S}}(r, t) = \frac{1}{mL^3} \sum_{j} \left[ (r_j - r) \times P_j \right] U(r_j - r) + \frac{1}{2 L^3} \sum_{j \neq i} r_j \times [ (r_j - r) \times F_{ji} ] f(r, r_j) \times U(r_j - r)$$  

$$\dot{\widehat{S}}(r, t) = -r \times \nabla \cdot \widehat{\sigma} + \dot{M}(r, t) \quad (3.8)$$

$\widehat{\sigma} \times r$ is a pseudo-tensor. If $v$ is the first row vector of $\widehat{\sigma}$, the first row vector of $\widehat{\sigma} \times r$ is $v \times r$, etc.

As $S$, the intrinsic angular momentum $J$, is not conserved, but as expected from the conservation of the total angular momentum, $S + J$ is conserved. Now, writing $r_j = r_j - r + r$ in (3.7), differentiating with respect to time and using (3.3), we obtain

$$\dot{J}(r, t) = -r \times \nabla \cdot \widehat{S} + \dot{M}(r, t). \quad (3.9)$$

If now, we use (3.8) and the vectorial relation

$$\nabla \cdot (\widehat{\sigma} \times r) = -r \times \nabla \cdot \widehat{\sigma} - 2 \sigma_a$$  

we have

$$\dot{M}(r, t) = -\nabla \cdot \dot{\widehat{S}}(r, t) + 2 \Sigma_m(r, t) - 2 \sigma_a(r, t) \quad (3.10)$$

$\sigma_a$ is a pseudo-vector whose $x$ component is given by $\frac{1}{2}(\sigma_{ax} - \sigma_{ay})$ and the other components by circular permutation. From (3.3), we have

$$\sigma_a(r, t) = \frac{1}{4 L^3} \sum_{j \neq i} r_j \times F_{ji} f(r, r_j) \times U(r_j - r) \quad (3.11)$$

$\sigma_a$ corresponds to the anti-symmetric part of the stress tensor.

If $1/k$ is much longer than the range of the potential, we have:

$$\Sigma_m(k, t) - \sigma_a(k, t) \approx \frac{i e^{i k \cdot r}}{8 L^3} \sum_{j \neq i} r_j \times F_{ji} e^{i k \cdot r} U(k) \quad (3.12)$$

We shall see below that the right hand side of this equation tends towards zero faster than $k$. So when $k$ tends towards zero we can identify $\Sigma_m$ and $\sigma_a$.

The fields $S(r, t)$, $M(r, t)$ and $\Sigma_m(r, t)$ do not appear in the usual hydrodynamic of a normal fluid, which is a theory in the limit of small $k$ where it is possible to neglect the local order. We shall see now that when $k$ tends towards zero our results are in agreement with the usual hydrodynamic.

Let us begin with $\Sigma_m$. For the sake of simplicity we suppose that the molecules are linear. The results should be qualitatively equivalent for non-linear molecules. Let $u_i$ be the unit orientational vector of the molecule $i$. We assume that we have a local thermodynamic equilibrium as defined in section 2 in the neighbourhood of the molecule $j_0$. This will always be the case in hydrodynamic conditions. As in a solid, the relative positions of the neighbours respect the symmetry of the molecule $j_0$. We must therefore have

$$\left\langle \sum_{i \neq j_0} r_{i \beta} \times F_{i \beta} \right\rangle_H = \alpha u_{j_0} \quad (3.14)$$

$\alpha$ is a pseudo-scalar which is equal to zero if the molecule is non polar. So, from the definition of $\Sigma_m$ in (3.5)

$$\left\langle \Sigma_m(r, t) \right\rangle_H = \frac{\alpha}{4 L^3} \left\langle \sum_j u_j U(r_j - r) \right\rangle_H \quad (3.15)$$

If the local order is such that $\left\langle \sum_j U(r_j - r) \right\rangle_H$ is different from zero (this is not the case for example if the local order looks like a loose F.C.C. solid), then $\left\langle \Sigma_m(r, t) \right\rangle_H$ is different from zero. In a nematic liquid the stress tensor is symmetric [13]. This is not in contradiction with our results since the stress tensor is symmetric [13]. This is not in contradiction with our results since the stress tensor is symmetric [13]. This is not in contradiction with our results since the stress tensor is symmetric [13].

The Fourier transform of (3.15) gives:

$$\left\langle \Sigma_m(k, t) \right\rangle_H = \frac{\alpha}{4 L^3} \left\langle \sum_j e^{i k \cdot r_j} U(k) \right\rangle_H \quad (3.16)$$

If $1/k$ is much greater than the correlation length $L_1$ then the right hand side of (3.16) is equal to zero. For example if $L_1 = 10^3 \AA$, and if $1/k = 10^4 \AA$ the right hand side of (3.16) is very small, and the wavelengths of the usual hydrodynamic modes are much more larger than $10^4 \AA$. Thus, if there is no long range order in the liquid $\left\langle \Sigma_m(k, t) \right\rangle_H$ tends towards zero very quickly when $k$ tends towards zero. In a nematic in total thermodynamic equilibrium, there is a long range order but the stress tensor is symmetric [13]. This is not in contradiction with our results since the molecules of a nematic are linear and non polar and in such a case (3.15) shows that $\left\langle \Sigma_m(r, t) \right\rangle_H$ is null since $\alpha$ equals zero.

We will now study the spin density $S(r, t)$. Its equation of motion is given by (3.5), and we have seen that $S(r, t)$ is not a conservative variable since...
\( \Sigma_e(r, t) \) is generally different from zero. But we have shown in the precedent paragraph that \( \Sigma_e(k, t) \) tends quickly towards zero as \( k \) tends towards zero if there is no long range order. This is in contradiction with a result of reference [6]. So for small \( k \), through a redefinition of the tensor \( \mathbf{\tilde{V}} \) it is possible to rewrite (3.5) as

\[
\dot{S}(r, t) \approx - \mathbf{\nabla} \cdot \mathbf{\tilde{V}}(r, t) \tag{3.17}
\]

and the derivative of \( S \) tends towards zero as \( k \) tends towards zero which is characteristic of a hydrodynamic variable. Nevertheless, \( S \) is not a good hydrodynamic variable in the usual sense if there is no long range order for the spin in the fluid, since in such a case \( S(k, t) \) decays very quickly towards zero as \( k \) tends towards zero for the same reason as \( \Sigma_e(k, t) \). If there is a long range order and if \( \Sigma_e(r, t) \) is null, equation (3.5) is the equation of evolution for spin waves.

Let us now study the bulk angular momentum density \( M(r, t) \).

From the definition (3.1) and standard properties of the Fourier transform, \( M(k, t) \) is given by

\[
M(k, t) = - \frac{i}{L^3} \sum_j \mathbf{e}^{i\mathbf{k} \cdot \mathbf{r}_j} \mathbf{P}_j \wedge \mathbf{V} U(k) \tag{3.18}
\]

where \( U(k) \) is given by

\[
U(k) = 8 \prod_i \frac{\sin k_i L/2}{k_i} \tag{3.19}
\]

We now differentiate \( U(k) \) with respect to \( k_1 \)

\[
\frac{1}{L^3} \frac{\partial}{\partial k_1} U(k) = \frac{8 \sin k_2 L/2 \sin k_3 L/2}{L^3 k_2 k_3} \times \left( \frac{L \cos k_1 L/2}{2 k_1} - \frac{\sin k_1 L/2}{k_1^2} \right) \tag{3.20}
\]

and if \( kL \) is small

\[
\frac{1}{L^3} \frac{\partial}{\partial k_1} U(k) \approx - \frac{1}{8} L^2 k_1 \tag{3.21}
\]

In such a case from (3.18) and (3.21)

\[
M(k, t) \approx - \frac{1}{8} L^2 k_1 \mathbf{P}_j \mathbf{e}^{ik \cdot \mathbf{r}_j} U(k) \tag{3.22}
\]

and coming back into \( r \) space

\[
M(k, t) \approx - \frac{I_c}{\rho(r, t)} \frac{1}{2} \mathbf{rot} \mathbf{P}(r, t) \tag{3.23}
\]

where \( I_c = \frac{\rho(r, t) L^5}{4} \) is the moment of inertia of the cube with respect to the c.o.g., if we assume that the liquid is homogeneous. With the same demonstration and using the fact that when \( kL \) is small the stress tensor is symmetric we see from (3.8) that:

\[
\mathbf{\tilde{W}}(r, t) \approx \frac{1}{2} \mathbf{\tilde{V}} \wedge \mathbf{\tilde{S}}(r, t) \tag{3.24}
\]

Also when \( kL \) is small, (3.11) can be obtained directly if we apply the operator \( \frac{1}{2} \mathbf{rot} \) to equation (3.3). \( M(r, t) \) is not an independent variable but is given by (3.23) from the knowledge of \( \mathbf{P}(r, t) \), and (3.11) is not necessary to describe the evolution of the liquid.

Nevertheless this fact which is well known in the usual hydrodynamic regimes, is not true if the correlation length is not negligible compared to \( 1/k \) since in such a case the approximation (3.21) is not valid, and \( M(r, t) \) is not given by \( \frac{1}{2} \mathbf{rot} \mathbf{P}(r, t) \).

We now give the derivative with respect to time of the energy

\[
\dot{e}(r, t) = - \mathbf{\nabla} \cdot \mathbf{J}_e(r, t) \tag{3.25}
\]

\[
\mathbf{J}_e(r, t) = \frac{1}{2 m L^3} \sum_j \mathbf{P}_j \times \left( \mathbf{P}_j \frac{P_j^2}{m} + \mathbf{\Omega}_{j} \cdot \mathbf{L}_{j} + \mathbf{\Omega}_{j} \sum_{i \neq j} U_{ji} \right) U \left( \mathbf{r}_j - \mathbf{r}_i \right) \tag{3.26}
\]

\[
+ \frac{1}{2 m L^3} \sum_j r_j \left( \mathbf{P}_j \cdot \mathbf{F}_j \frac{m}{r_{ji}} + \mathbf{\Omega}_j \cdot \mathbf{C}_j \right) \times f(r, r_{ji}) \ast U(\mathbf{r}_j - \mathbf{r}_i) \tag{3.27}
\]

\( \mathbf{J}_e \) is the energy flux.

Some of the results of this paragraph were given in reference [6].

4. The collective behaviour. — The densities defined by equations (3.1) are not observable. The experiment gives an average of these quantities. Performing a hydrodynamic average as described in paragraph 2, we shall drop the individual behaviour of the molecules keeping only the collective motion. We call \( \mathbf{v}_j \) the velocity of the molecule \( j \) and we split \( \mathbf{v}_j \) into two parts, a collective one and a random one. The collective part comes from the collective motion of the molecules in the box which is solid like on account of the local order. We therefore write

\[
\mathbf{v}_j = \mathbf{v} + \omega \wedge (\mathbf{r}_j - \mathbf{r}) + \mathbf{a}_j \tag{4.1}
\]

By definition of the random part \( \mathbf{a}_j \) we have

\[
\left\langle \sum_j \mathbf{a}_j U(\mathbf{r}_j - \mathbf{r}) \right\rangle_H = 0 \tag{4.2}
\]

\[
\left\langle \sum_j (\mathbf{r}_j - \mathbf{r}) \wedge \mathbf{a}_j U(\mathbf{r}_j - \mathbf{r}) \right\rangle_H = 0 \tag{4.3}
\]

Furthermore, on the average, the c.o.g. of the molecules in the box is identical with the center of the box

\[
\left\langle \sum_j (\mathbf{r}_j - \mathbf{r}) U(\mathbf{r}_j - \mathbf{r}) \right\rangle_H = 0 \tag{4.4}
\]
Using (3.1), (4.1, 2, 3) and straightforward vectorial algebra, we find
\begin{equation}
\langle \mathbf{P}(\mathbf{r}, t) \rangle_H = \langle \rho(\mathbf{r}, t) \rangle_H \mathbf{v}(\mathbf{r}, t)
\end{equation}
\begin{equation}
\langle \mathbf{M}(\mathbf{r}, t) \rangle_H = \langle \mathbf{G}(\mathbf{r}, t) \rangle_H \Omega(\mathbf{r}, t)
\end{equation}
where
\begin{equation}
\mathbf{G}(\mathbf{r}, t) = \frac{m}{L^3} \sum_j [ (r_j - r)^2 \mathbf{U} - (r_j - r)(r_j - r)] \times U(\mathbf{r}_j - \mathbf{r})
\end{equation}
\text{U is the unit tensor.}

Equation (4.4) defines the linear velocity \( \mathbf{v} \) and the bulk angular velocity \( \omega \).

\( \mathbf{G}(\mathbf{r}, t) \) is the tensor of inertia, with respect to the center of the box, of the molecules inside. We split \( \mathbf{G} \) into the following form
\begin{equation}
\mathbf{G}(\mathbf{r}, t) = \mathbf{G}_i(\mathbf{r}, t) \mathbf{U} + \mathbf{G}_s(\mathbf{r}, t)
\end{equation}
\begin{equation}
\mathbf{G}_i(\mathbf{r}, t) = \frac{m}{L^3} \sum_j (r_j - r)^2 U(\mathbf{r}_j - \mathbf{r})
\end{equation}
\begin{equation}
\mathbf{G}_s(\mathbf{r}, t) = \frac{m}{L^3} \sum_j \left[ \frac{1}{3} (r_j - r)^2 \mathbf{U} - (r_j - r) \times (r_j - r) \right] U(\mathbf{r}_j - \mathbf{r})
\end{equation}
\( \mathbf{G}_i \) is the trace of \( \mathbf{G} \). It is also the moment of inertia with respect to the center of gravity of the molecules in the cube. Its thermodynamic equilibrium value is given by \( \langle \mathbf{G}_i \rangle_E = I_c \) defined in (3.23). For a fixed number of molecules in the box it is possible to find different arrangements of these molecules which give different values for \( \langle \mathbf{G}_i \rangle_H \). This last quantity depends therefore not only on the density but also on the local order.

\( \mathbf{G}_s(r, t) \) is the quadrupolar mass density. \( \langle \mathbf{G}_s(r, t) \rangle_H \) is null if there is no local order of the c.o.g. and its thermodynamic equilibrium value \( \langle \mathbf{G}_s \rangle_E \) is always equal to zero in a normal liquid. It is worth noting that \( \langle \mathbf{G}_s \rangle_E \) is also null in a solid with a cubic array. In such a case the components \( \langle \mathbf{G}_s(r, t) \rangle_H \) are very small and characterize the local deviation from equilibrium due to thermal fluctuations. If we increase the temperature, we are in a dense liquid and it is likely that the local structure look like a smooth cubic solid, so the components of \( \langle \mathbf{G}_s(r, t) \rangle_H \) are greater than in the solid but are still small. If we increase again the temperature there is no more local order and the components of \( \langle \mathbf{G}_s(r, t) \rangle_H \) are null.

We now split the angular velocity \( \Omega \) into a collective part and a random one
\begin{equation}
\Omega_j = \Omega + \mathbf{b}_j.
\end{equation}

By definition of the random part \( \mathbf{b}_j \)
\begin{equation}
\langle \sum_j \mathbf{b}_j U(\mathbf{r}_j - \mathbf{r}) \rangle_H = 0
\end{equation}
\begin{equation}
\langle \sum_j \mathbf{i}_j \mathbf{b}_j U(\mathbf{r}_j - \mathbf{r}) \rangle_H = 0.
\end{equation}

From (3.1) and (4.7, 8) we have
\begin{equation}
\langle \mathbf{S}(\mathbf{r}, t) \rangle_H = \langle \mathbf{I}(\mathbf{r}, t) \rangle_H \Omega(\mathbf{r}, t)
\end{equation}
where
\begin{equation}
\mathbf{I}(\mathbf{r}, t) = \frac{1}{L^3} \sum_j \mathbf{i}_j U(\mathbf{r}_j - \mathbf{r}).
\end{equation}

Equation (4.9) gives the definition of \( \Omega \) which characterizes the collective spin of the molecules. For a linear molecule the tensor of inertia \( \mathbf{I}_j = \beta (\mathbf{U} - \mathbf{u}_j \mathbf{u}_j) \).

We rewrite \( \mathbf{I}(\mathbf{r}, t) \) as :
\begin{equation}
\mathbf{I}(\mathbf{r}, t) = I_r(\mathbf{r}, t) + I_l(\mathbf{r}, t)
\end{equation}
\begin{equation}
I_r(\mathbf{r}, t) = \frac{\beta}{L^3} \sum_j U(\mathbf{r}_j - \mathbf{r})
\end{equation}
\begin{equation}
I_l(\mathbf{r}, t) = \frac{\beta}{L^3} \sum_j \left[ \frac{1}{3} \mathbf{U} - \mathbf{u}_j \mathbf{u}_j \right] U(\mathbf{r}_j - \mathbf{r})
\end{equation}
\( I_r \) is the trace of \( \mathbf{I} \) and is proportional to the density. This can be easily generalized for a non-linear molecule since the trace in the laboratory frame of the tensor of inertia \( \mathbf{I}_j \) is independent of the orientation of the molecule. So \( \langle I_r \rangle_H \) is always proportional to the local density and is independent of the local order which is not the case for \( \langle G_i \rangle_H \).

The tensor \( I_l(\mathbf{r}, t) \) is proportional to the anisotropic part of the polarisability tensor, and is equivalent to the orientational order parameter reference [2].

\begin{equation}
\langle \mathbf{J}_q(\mathbf{r}, t) \rangle_H = \langle \mathbf{J}_l(\mathbf{r}, t) \rangle_H = 0.
\end{equation}

We shall come back, at the end of section 5, to the relations between \( \mathbf{G}, \mathbf{I} \) and the local order.

From (3.25), (4.1, 7) it is easy to show that the average of the energy flux is given by
\begin{equation}
\langle \mathbf{J}_q(\mathbf{r}, t) \rangle_H = \langle \mathbf{J}_s(\mathbf{r}, t) \rangle_H = \langle \mathbf{J}_v(\mathbf{r}, t) \rangle_H = \langle \mathbf{J}_s(\mathbf{r}, t) \rangle_H = \langle \mathbf{J}_s(\mathbf{r}, t) \rangle_H
\end{equation}
where \( \mathbf{J}_q \) is the heat flux. The first term on the right side of (4.12) is the usual term of the Navier-Stokes equations [10] which corresponds to the energy coming from translational motion. The two following terms are new ones. They give the energy coming from the two other collective motions : the bulk rotation and the spin.

We saw in section 3 that when \( k \) tends towards zero, \( \Omega \) tends very quickly towards zero, \( \omega \) towards \( \frac{1}{2} \mathbf{rot} \mathbf{v} \) and \( \mathbf{b} \) towards \( \frac{1}{2} \mathbf{V} \times \mathbf{E} \). Since the divergence of a rotational quantity is zero. \( \mathbf{V} \cdot \langle \mathbf{J}_q(\mathbf{r}, t) \rangle_H \) which
is the physical quantity which appears in the equations of motion, has the usual form
\[ \mathbf{V} \cdot (\mathbf{E} \nabla)_{\text{H}} + \mathbf{J}_q_{\text{H}} \]
when \( k \) tends towards zero.

In the following, we shall take the hydrodynamic average for all the quantities and we drop the brackets \( \langle \ldots \rangle_{\text{H}} \) when it is not ambiguous. We define now density per unit mass \( \rho_0 = \rho |\rho|, e_0 = e |\rho|, S_0 = S |\rho|, M_0 = M |\rho|, I_0 = I |\rho|, \mathbf{G}_0 = \mathbf{G} |\rho|, \) and we define new tensors \( \mathbf{\sigma}_0 = \mathbf{\sigma} - \mathbf{v} \mathbf{P}, \mathbf{\theta}_0 = \mathbf{\theta} - \mathbf{v} \mathbf{M}, \mathbf{r}_0 = \mathbf{r} - \mathbf{v} \).

\[ \mathbf{S} \mathbf{J}_0 = \mathbf{J} - \mathbf{v} \mathbf{e} \] when we shall use only these quantities and we drop the subscript 0. In summary, in the following the notation \( \mathbf{S} \) for instance has the meaning

\[ \frac{\langle \sum_{j} \mathbf{U}(r_j - r) \rangle_{\text{H}}}{m} \frac{\langle \sum_{j} \mathbf{U}(r_j - r) \rangle_{\text{H}}}{m} \]

We take now the usual time derivative along one flow line:
\[ \frac{d}{dt} a = \mathbf{\dot{a}} + \mathbf{v} \cdot (\nabla a) \]

From classical manipulations [8], we obtain from (3.2, 3, 5, 11, 25) and (4.4, 9, 12) the following equations:

\[ \frac{d}{dt} \rho = - \rho \mathbf{V} \cdot \mathbf{v} \]
\[ \rho \frac{d}{dt} \mathbf{v} = - \mathbf{V} \cdot \mathbf{\sigma} \]
\[ \rho \frac{d}{dt} (\mathbf{G} \cdot \mathbf{c}) = - \mathbf{V} \cdot \mathbf{\theta} \]
\[ \rho \frac{d}{dt} (\mathbf{I} \cdot \mathbf{C}) = - \mathbf{V} \cdot \mathbf{r} - 2 \mathbf{\sigma} \]
\[ \rho \frac{d}{dt} e = - \mathbf{V} (\mathbf{\sigma} \cdot \mathbf{v} + \mathbf{\theta} \cdot \mathbf{c} + \mathbf{r} \cdot \mathbf{C}) \]

In these equations \( \mathbf{C}_a \) disappears. For that, we use (3.3) and a redefinition of \( \mathbf{\tilde{\theta}}, \mathbf{\tilde{r}} \) and \( \mathbf{\tilde{J}}_a \).

The linear velocity density \( \mathbf{v} \), the bulk and spin angular velocity \( \mathbf{c} \) and \( \mathbf{C} \), the corresponding inertial densities \( \mathbf{G} \) and \( \mathbf{I} \), plus the energy density \( e \) describe the collective behaviour of the fluid and their evolution is given by equations (4.13). These equations are exact, there is no approximation in their derivation from molecular quantities. Furthermore, we make no assumption about the state of the matter so they are valid in a solid, a glass, a liquid crystal, a liquid or a gas.

In order to obtain (4.13), we assumed that the molecules are rigid. If the molecules are not rigid, we can handle the problem defining a mass, a linear and angular momentum densities inside the box of side \( L_1 \) and perform integration instead of discrete summation over the molecules. Nevertheless, there is an important difference if the frequency of the intramolecular variables are of the same order as the frequency we are interested with. In such a case it would be necessary to add an extra variable and to handle the problem as in reference [14].

5. Hydrodynamics of a dense fluid. — The equations (4.13) cannot be solved because we have five equations but we have much more than five unknown functions. The fundamental quantities of the problem are \( \mathbf{v}, \mathbf{c}, \mathbf{G}, \mathbf{I} \) and \( e \). We shall express the others unknown quantities \( \mathbf{\sigma}, \mathbf{\theta}, \mathbf{r} \) and \( \mathbf{J}_q \) as function of the first ones. For that we shall use the classical method of irreversible thermodynamics [8] : we compute the rate of change of the entropy and we write that this rate of change is positive.

The energy density can be written as:
\[ e = e_i + \frac{1}{2} \mathbf{v}^2 \]

\( e_i \) is the internal energy. Differentiating (5.1) with respect to time and using (4.13), we find

\[ \frac{d}{dt} e_i = - \mathbf{\nabla} \cdot \mathbf{J}_q - \mathbf{\tilde{\theta}} : (\mathbf{\nabla} \cdot \mathbf{c}) - \mathbf{\tilde{r}} : (\mathbf{\nabla} \cdot \mathbf{C}) + 2 \mathbf{\sigma} \cdot \frac{dM}{dt} + \rho \mathbf{\Omega} \cdot \frac{dS}{dt} \]

where \( \mathbf{\tilde{\theta}} \) is the transpose of \( \mathbf{\tilde{\theta}} \), and

\[ \mathbf{O} : \mathbf{T} = \sum_{jk} O_{jk} T_{kj} \]

We assume now that the molecules in the little box are in thermodynamic equilibrium which, as we saw in section 2, is a quite reasonable assumption if the liquid is not too far from equilibrium, if there are at least one hundred molecules in the box and if we are interested in frequencies lower than or of the same order as \( 10^{13} \) Hz. The fact that the number of molecules in the box must be greater than one hundred imposes a minimum length for the side of the box, and since \( 1/k \) must be greater than this length, it imposes a maximum value for \( k \) beyond which, the local thermodynamic equilibrium assumption is meaningless.

We now write the variation of the internal energy in the frame parallel to the laboratory frame and moving with a velocity \( \mathbf{v} \):

\[ de_i = T dS - P dV + \mathbf{F}_i : d \mathbf{I} + \mathbf{F}_s : d \mathbf{G} + \mathbf{G} \cdot d \mathbf{M} + \mathbf{S} d \mathbf{S} \]

where \( \mathbf{I} = \mathbf{I}_i - \langle \mathbf{I}_i \rangle_\mathbf{E} \) and \( \mathbf{G} = \mathbf{G} - \langle \mathbf{G} \rangle_\mathbf{E} \).

\( \mathbf{F}_i : d \mathbf{I} \) and \( \mathbf{F}_s : d \mathbf{G} \) correspond to the variation of the local order characterized by the tensors \( \mathbf{i} \) and \( \mathbf{g} \) [2, 12]. We do not take into account the trace of \( \mathbf{I} \) since we saw that this trace is proportional to the density. But we must take into account the trace of \( \mathbf{G} \) since, as we saw, this trace depends on the local order. The variation of the internal energy coming from the variation of the bulk angular momentum is given
by $\omega \cdot d\mathbf{M}$ as is shown in reference [19]. The last term corresponds to the variation of the collective spin. $T, S, P, V$ are the local temperature, entropy, pressure and specific volume ($V = 1/\rho$).

We now split the stress tensor $\mathbf{\tau}$ into two parts:

$$\mathbf{\tau} = \rho \mathbf{U} + \mathbf{\pi}$$  \hspace{1cm} (5.4)

$\mathbf{\pi}$ is the viscous stress tensor, and we write the entropy balance equation [8]

$$\rho \frac{dS}{dt} = - \nabla \cdot \mathbf{J}_s + Q$$  \hspace{1cm} (5.5)

$\mathbf{J}_s$ is the entropy flow and $Q$ is the entropy production which must be positive or zero. From equations (5.2, 3, 4, 5) using classical manipulations [8], we obtain

$$\mathbf{J}_s = \mathbf{J}_s \frac{\rho}{T}$$

$$TQ = - \frac{\nabla T}{T} \cdot \mathbf{J}_s - \mathbf{\pi} : (\nabla \mathbf{v}) - \mathbf{\pi} : (\nabla \omega) - \nabla : (\nabla \mathbf{v}) + 2 \pi_{ij} \Omega_{ij} - \mathbf{F}_{\pi} : \frac{d \mathbf{g}}{dt} - \mathbf{F}_{\pi} : \frac{d \mathbf{i}}{dt}$$  \hspace{1cm} (5.6)

The entropy production $Q$ has the expected structure. A sum of products of two factors, one of these factors in each term is a flow quantity ($\mathbf{J}_s$, $\mathbf{v}$, ..., $d\mathbf{i}/dt$) and the other factor is the conjugate thermodynamic force ($\nabla T/\mathbf{v}$, $\mathbf{\pi}$, $\mathbf{k}$, ..., $\mathbf{F}_{\pi}$).

We assume now that if we are not too far from equilibrium the fluxes and the forces are proportional. One therefore obtains for $Q$ a quadratic expression in the thermodynamic forces or in the fluxes. These relations between flux and force are not sufficient to close equations (4.13) since we do not know the forces $\mathbf{F}_s$ and $\mathbf{F}_{\pi}$. We need new assumptions to obtain these quantities. Following De Gennes [2] we perform an expansion of the free energy $F$ with respect to $\mathbf{i}$ and $\mathbf{g}$ and we limit this expansion to the second order

$$F = F_0 + \frac{a}{2} \mathbf{g} \cdot \mathbf{g} + \frac{b}{2} \mathbf{i} \cdot \mathbf{i} + c \mathbf{g} \cdot \mathbf{i}.$$  \hspace{1cm} (5.7)

For the sake of simplicity, we assume in (5.7) that the symmetric tensor $\mathbf{g}$ is traceless. If it is not, we must introduce in (5.7) one other coefficient.

The equation (5.7) is valid only if the local order is weak enough. This is the case in a liquid or a glass but this is not the case in a solid or a liquid crystal. Henceforth, we shall deal only with normal fluids. From (5.7) we have

$$\mathbf{F}_s = \frac{\partial F}{\partial \mathbf{g}} = a \mathbf{g} + c \mathbf{i}$$
$$\mathbf{F}_i = \frac{\partial F}{\partial \mathbf{i}} = b \mathbf{i} + c \mathbf{g}.$$  \hspace{1cm} (5.8)

Let $a(t, \mathbf{k})$ be one of the densities which have been previously defined. If $1/k$ is greater than the correlation length $L_1$, $a(\mathbf{k}, t)$ depends only on the magnitude of $\mathbf{k}$, but when $1/k$ is smaller than $L_1$, $a(\mathbf{k}, t)$ is also dependent on the orientation of $\mathbf{k}$. So, if we write the proportionality of two tensors, it is possible in the first case to use the Curie principles [8], but in the second case we must take into account the symmetry of the local order as in a solid. Henceforth we shall deal only with wavelengths greater than the correlation length.

We split the tensors in the following way:

$$\mathbf{T} = \frac{1}{3} \mathbf{T}_i \mathbf{U} + \mathbf{T}_s + \mathbf{T}_a$$  \hspace{1cm} (5.9)

where $\mathbf{T}_i$ is the trace of $\mathbf{T}$, $\mathbf{T}_s$ the symmetric part of $\mathbf{T} - \frac{1}{3} \mathbf{T}_i \mathbf{U}$, and $\mathbf{T}_a$ the antisymmetric part of $\mathbf{T}$. We write now the proportionality of the fluxes and forces taking into account the Curie principle

$$\frac{\partial}{\partial t} \mathbf{T}_{s,ij} = - \frac{\partial}{\partial t} \mathbf{g}_{s,ij}$$
$$\mathbf{F}_{s,ij} = - \mathbf{\pi}_{s,ij}$$

$$\frac{\partial}{\partial t} \mathbf{g}_{s,ij} = - \mathbf{\pi}_{s,ij}$$
$$\mathbf{g}_{s,ij} = - \mathbf{\pi}_{s,ij}$$

A sum of products of two factors, one of these factors in each term is a flow quantity ($\mathbf{J}_s$, $\mathbf{V}$, ..., $d\mathbf{i}/dt$) and the other factor is the conjugate thermodynamic force ($\nabla T/\mathbf{v}$, $\mathbf{\pi}$, $\mathbf{k}$, ..., $\mathbf{F}_{\pi}$).

The matrices $\mathbf{\tau}$, $\mathbf{\pi}$, $\mathbf{\eta}$, $\mathbf{\xi}$ and $\mathbf{\phi}$ are symmetric (Onsager relations) so there are 22 phenomenological coefficients.

The equations (4.13, 5.10, ..., 15) give the evolution of a fluid up to high frequencies and short wavelengths.
We come back now to the tensors \( g \) and \( i \) characterizing the local order. Since they are symmetric, we can diagonalize these tensors. The three eigenvectors give the orientation of the local order, and the three eigenvalues the magnitude. Since the eigenvectors are normalized and orthogonal to each other they are given by three independent variables. In a solid these three variables characterize the broken symmetry and are hydrodynamic variables [12]. In a liquid, the magnitude of the local order is in general not a constant and cannot be obtained directly from the knowledge of the local temperature and density. It is clear that in a liquid at equilibrium, the thermodynamic average of the magnitude of the local order is a function of the equilibrium temperature and density and that the local order is more important in a cold and dense liquid than in a hot and non-dense liquid. But if we apply a strong temperature gradient to a liquid, the heat diffusion is not necessarily proportional to the propagation of the intensity of the local order, or if for \( t = 0 \) and \( r = 0 \), there is a crystal seed in a supercooled liquid, this corresponds to the fact that the eigenvalues of \( g(0, 0) \) are very large, and the freezing of the liquid corresponds to a propagation of the intensity of the local order without heat diffusion. So the three eigenvalues of the tensor \( g \) are generally independent variables. The tensor \( i \) being traceless has only two independent eigenvalues.

Let us assume now that the liquid is a set of very small crystals of size \( L_1 \), then the magnitude of the local order is a constant and the bulk rotational velocity \( \omega \) can be obtained from the time derivative, in the laboratory frame, of the eigenvectors of \( g \). In a real liquid, such a picture does not fit well. Amongst other things, it does not take into account the deformation of the local order. The reasons for the variation of the eigenvectors of \( g \) are two-fold, the first comes from the bulk rotational velocity \( \omega \) and the second from the deformation of the structure. So generally \( \omega \) cannot be obtained from the time derivative of the eigenvector of \( g \). For a similar reason there is no trivial relation between the eigenvectors of the tensor \( i \) and the spin velocity \( \Omega \).

So in a liquid the six components of \( g \), the five components of \( i \), the three components of \( \omega \) and the three components of \( \Omega \) are generally independent variables. This is not the case in a molecular solid where the six eigenvalues are constant and where \( \omega \) and \( \Omega \) can be obtained from the time derivative of the eigenfunctions of \( g \) and \( i \), or in a nematic where the three eigenvalues of \( i \) are constant and where \( \Omega \) is proportional to \( \mathbf{n} \wedge \mathbf{n} \), \( \mathbf{n} \) being the director of the nematic characterizing the orientational order.

We shall now compare our results with the broken symmetry method proposed by Martin, Parodi and Pershan (M.P.P.) [12]. At a macroscopic level, a normal fluid is homogeneous and isotropic, so we have translational and rotational symmetry. But at a microscopic level, because of the local structure, the translational and rotational symmetries are broken. Following the ideas of M.P.P. new collective modes should appear for each broken symmetry. These modes should disappear when \( k \) tends towards zero since in such a case we come back to translational and rotational symmetries.

The M.P.P. equations are written for small values of \( k \). We have seen that in such a case, in a normal fluid, the stress tensor is symmetric, the spin velocity \( \Omega \) is zero and the bulk angular velocity \( \omega \) is equal to \( \frac{1}{2} \mathbf{rot} \mathbf{v} \). The M.P.P. equations therefore cannot give information on this point. It would be possible to obtain equations for these quantities by writing angular momentum conservation, which, as we saw, is equivalent to linear momentum conservation only for small values of \( k \).

In our case, the phase variables characterizing the broken symmetries are the three eigenvectors of \( g \) and the three eigenvectors of \( i \). Since the three eigenvectors are normalized and orthogonal to each other they can be characterized by three independent components of the tensor. The M.P.P. theory is dealing only with the phase variables, so we are not sure that the equations of motion for the other components will be correctly given by this theory.

The equations of motions of \( g \) and \( i \) are given by M.P.P. equation (2.2)

\[
\dot{g} = J_g, \quad \dot{i} = J_i. \tag{5.16}
\]

Since there is no long range order \( g(k, t) \) and \( i(k, t) \) tends towards zero when \( k \) tends towards zero. So \( J_g \) and \( J_i \) can be written as a gradient.

The M.P.P. equation (2.3) is

\[
T dS = dE + dW + F_1 : d\mathbf{i} + F_\mathbf{s} : d\mathbf{g} \tag{5.17}
\]

this is equivalent to our equation (5.3) if we do not take into account \( \Omega \) and \( \omega \). From these two equations we can follow exactly the M.P.P. derivation, and we arrive at M.P.P. equation (2.15) which in our case, can be written using the Curie principles

\[
(\mathbf{g}^0)^P = -\eta(\mathbf{v} \mathbf{v}), \\
(\mathbf{g}^D)^P = -\Gamma_1(\mathbf{F}_\mathbf{s})^D - \Gamma_1(\mathbf{F}_\mathbf{s})^D, \\
(\mathbf{g})^P = -\Gamma_2(\mathbf{F}_\mathbf{s})^P - \Gamma_2(\mathbf{F}_\mathbf{s})^P \tag{5.17'}
\]

where \((A)^P\) means the dissipative part of \( A \). The reversible part of \( A \) will be noted \((A)^R\). The reversible part of \( J_g \) and \( J_i \) is given by

\[
(J_g)^R = A_g(\mathbf{v} \mathbf{v}), \\
(J_i)^R = A_i(\mathbf{v} \mathbf{v}), \tag{5.18}
\]

This equation comes from M.P.P. equation (2.16). \( J_g \) and \( J_i \) cannot be proportional to a tensor constructed with the vector \( \mathbf{v} \) since \( J_g \) and \( J_i \) tend towards zero when \( k \) tends towards zero which is not the case for \( \mathbf{v} \).
The reversible part of $J_g$ and $J_i$ must disappear in the entropy production (5.6). For this, we write the reversible part of the viscous stress tensor as:

$$(\mathbf{P}^r) = - A \mathbf{F} - A \mathbf{F}_i.$$  (5.19)

Using (5.17, 18, 19) we have

$$\mathbf{P}^r = - \eta(\mathbf{V}) \mathbf{J} - A \mathbf{F}_s - A \mathbf{F}_i,$$

$$J_{s,i} = A \mathbf{J} - \Gamma_{ij} \mathbf{F}_s - \Gamma_{ij} \mathbf{F}_i,$$  (5.20)

Our equation (5.10) can be written in the following form:

$$\alpha_{11} \mathbf{J}_s = - \alpha \mathbf{J} - \alpha_{12} \mathbf{F}_s - \alpha_{13} \mathbf{F}_i.$$

Equation (5.13) shows that $\mathbf{J}$ is symmetric since $\mathbf{g}$ is meaningless and rot $\mathbf{v} = 0$, then (5.10) gives

$$\alpha_{11} \mathbf{J}_i = \alpha_{12} \mathbf{J} - \alpha_{13} \mathbf{F}_s - \alpha_{13} \mathbf{F}_i,$$  (5.21)

where $\alpha_{11,12,13}$ are the three minors. So for the variables which can be taken into account by the M.P.P. equations, our results are in agreement with their method.

6. An example. — We shall use the previous equations for a monoatomic fluid. In such a case the tensor $\mathbf{I}$ is meaningless and the parameters $b$ and $c$ are zero. Furthermore, we assume that the perturbation from equilibrium is weak and we linearize the equations.

Let us assume that the velocity field is along the $z$ axis and that the variations are along the $x$ axis. The variable of the problem is $v_z(x, t)$ (transverse velocity).

The equation (4.13) gives

$$\rho \ddot{v}_z = - \partial_x \sigma_{zz}.$$  (6.1)

Equation (5.13) shows that $\mathbf{g}$ is symmetric since $\mathbf{g}$ is meaningless and rot $\mathbf{v} = 0$, then (5.10) gives

$$\sigma_{zz} = - \frac{1}{2} \alpha_{11} \partial_x v_z - \alpha_{12} \dot{g}_{zz},$$  \hspace{1cm} (6.2)

$$\sigma_{zz} = - \frac{1}{2} \alpha_{12} \partial_x v_z - \alpha_{22} \dot{g}_{zz}. $$

The positiveness of the entropy production $Q$ and equation (5.6) requires that:

$$\alpha_{11} \sigma_{22} - \alpha_{12}^2 \geq 0.$$  (6.3)

In a fluid at rest (6.2) gives for the relaxation of a fluctuation of the local structure tensor $\mathbf{g}$:

$$\mathbf{g}(t) = \mathbf{g}(0) e^{-\Gamma t}.$$  (6.4)

with $\Gamma = a/\alpha_{22}$.

$1/\Gamma$ is the relaxation time of the local structure when there is no coupling with the shear velocity. Performing now a Fourier transform (time and space) on (6.2), we get (we drop the subscript $x$ and $z$)

$$\sigma(k, \omega) = ik \eta(i \omega) v(k, \omega)$$  (6.5)

where

$$\eta(i \omega) = \frac{1}{2} \left( \alpha_{11} + \frac{\alpha_{12}^2}{\alpha_{22}} \right) \frac{i \omega}{\Gamma - i \omega}. $$  (6.6)

These last equations are equivalent to the equations (4.19) and (4.20) of reference [2]. $\eta(i \omega)$ is the effective viscosity. As expected when $1/\omega$ is much greater than the relaxation time $1/\Gamma$, $\eta(i \omega)$ is the usual shear viscosity. If $\omega$ is much higher than $\Gamma$, we find

$$\sigma(k, \omega) \approx ik \left( \frac{\alpha_{11} \alpha_{22} - \alpha_{12}^2}{2 \alpha_{22}} \right) v(k, \omega) +$$

$$+ ik \frac{\alpha_{12}^2}{2 \alpha_{22}} \Gamma u(k, \omega)$$  (6.7)

where $u$ is the strain ($\dot{u} = \nabla \mathbf{u}$). In a solid the stress tensor is proportional to the strain gradient [11]. Formula (6.7) shows that for high frequencies in a liquid, the stress tensor is proportional both to the strain gradient and to the velocity gradient. The viscoelastic theory of Maxwell [11] assumes that for high frequencies the stress tensor is only proportional to the strain gradient.

We shall now compare our results with the memory function formalism. Following Mori [15], since the perturbation is weak, $v(k, t)$ obeys the equation

$$i v(k, t) + \int_0^t K(t - \tau) v(\tau) d\tau = 0.$$  (6.8)

The Laplace transform gives

$$v(k, Z) = \frac{\nu_0}{Z + K(Z)}.$$  (6.9)

Performing a Fourier transform with respect to $x$ and a Laplace transform with respect to $t$ on (6.1) and (6.2), and assuming that $v(x, 0) = v_0 \delta(x)$ and $g(x, 0) = 0$ we obtain

$$v(k, Z) = \frac{\nu_0}{Z + k^2 \eta(Z)}.$$  (6.10)

Using (6.6, 9, 10) and coming back to the time space, we find

$$K(t) = \frac{k^2}{2 \rho \alpha_{22}} \left[ (\alpha_{11} \alpha_{22} - \alpha_{12}^2) \delta(t) + \Gamma \alpha_{22} \frac{e^{-\Gamma t}}{\Gamma} \right].$$  (6.11)

This last equation and (6.7) shows that the Maxwell theory is equivalent to the relaxation approximation for the memory function, since in both cases $\alpha_{11} \alpha_{22} - \alpha_{12}^2 = 0$. The experimental memory function for liquid argon near the triple point is given from molecular dynamics in reference [16]. This
memory function is well fitted by two exponentials, one with a short relaxation time and the second with a much longer relaxation time. The equation (6.11) is qualitatively in agreement with these results, the short relaxation time exponential being equivalent to $\delta(t)$, and the long tail of the memory function coming from local structure relaxation.

From (6.6) and (6.10) $v(k, Z)$ is given as the ratio of two polynomials, the denominator being of degree two. The roots of the denominator are imaginary if

$$2 \rho \Gamma a_{22} \left(\frac{\alpha_{11} a_{22}^2 - \alpha_{12}^2}{(\alpha_{11} a_{22} - \alpha_{12}^2)^2}\right) \leq k^2 \leq \frac{2 \rho \Gamma a_{22} \left(\frac{\alpha_{11} a_{22}^2 + \alpha_{12}^2}{(\alpha_{11} a_{22} - \alpha_{12}^2)^2}\right)}{\left(\frac{\alpha_{11} a_{22} - \alpha_{12}^2}{\alpha_{11} a_{22} + \alpha_{12}^2}\right)^2}.$$

(6.12)

In such a case the transverse velocity is propagative. Recent molecular dynamic calculations [16, 17] show a similar behaviour for the transverse currents.

7. Conclusion. — In this paper, we give hydrodynamics equations for a normal fluid, available up to high frequencies and small wavelengths. More precisely there is a characteristic length and a characteristic time beyond which these equations are not valid. The characteristic length is the side of the cubic box which contains the minimum number of molecules necessary to define a local equilibrium (this number is of the order of hundred which give a characteristic length of about 10 Å for dense liquid nitrogen). The characteristic time is the time necessary to reach a local thermal equilibrium, after a small perturbation, for such a number of molecules (it is of the order of $10^{-13}$ s for dense liquid nitrogen). One other characteristic length and one other characteristic time are the correlation length $L_1$ and the life time $\tau_1$ of the local structure.

Beside the usual densities of the usual hydrodynamic, it is necessary to define new densities to take into account the local order. Those quantities are the bulk angular velocity density $\omega$, the spin density $\Omega$, and the conjugate inertial densities $G$ and $I$ which characterize respectively the local order of the center of gravity and the local orientational order. In order to obtain the equations of motion for those quantities it is necessary to use the angular momentum conservation which is equivalent to the linear momentum conservation only when $kL_1$ tends towards zero. Furthermore, we saw that for the great values of $k$ the stress tensor is generally non symmetric and we are able to link this fact with the Kirkwood factor $g$ in the case of polar molecules. As expected those equations give the usual hydrodynamic equations for a normal fluid when $kL_1$ tends towards zero.

Up to equation (5.7) no assumptions were made concerning the state of the matter, but the equation (5.7) assumes that the local order is weak, which is the case in a fluid or a glass. A part of the work is therefore already done to obtain hydrodynamic equations for high frequencies and short wavelengths for the other states of the matter. At this level it should be necessary to obtain other equations than (5.8) for the thermodynamic forces $F_\omega$ and $F_\Omega$.

The equations (5.10, ..., 15) are valid only if $kL_1$ is smaller than one. If $kL_1$ is greater than one we cannot use the Curie principle but it should be very easy, knowing the space group of the local structure, to write equivalent equations.

From our point of view, our equations will be useful to understand the phenomena involving the local collective behaviour. For instance, the smaller $k$ value data of the molecular dynamic computation could be understood by this theory. We have still shown that some results are in qualitative agreements. Our theory should be also useful to compute the long tail of the correlation functions.

One of the applications of this paper is also the light scattering and more precisely the depolarized light scattering as we shall see in a following paper.

It should be also interesting to check our equations in the viscous fluids. In such a case the life time of the structure can be of the order of $10^{-7}$ or $10^{-8}$ s and the usual ultrasonic frequencies should couple with the local order.

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Appendix. — In this appendix, we shall give the details of the calculations of paragraph 3

1. DERIVATION OF (3.3)

\[
P(k, t) = \frac{1}{L^3} \sum_j P_j \exp(ik \cdot r_j) U(k)
\]

\[
\dot{P}(k, t) = \frac{1}{L^3} \sum_j \left(\frac{ik \cdot P_j}{m} + \dot{r}_j\right) \exp(ik \cdot r_j) U(k).
\]

We study now the last expression

\[
\sum_j \dot{P}_j \exp(ik \cdot r_j) = \sum_j \sum_{i \neq j} F_{ij} \exp(ik \cdot r_j)
\]
$F_{ij}$ is the force exerted by the molecule $i$ on the molecule $j$. Since $F_{ij} = - F_{ji}$, we have

$$\sum_j \hat{F}_{ij} \exp(ik \cdot r_j) = \frac{1}{2} \sum_j F_{ij} (1 - \exp(-ik \cdot r_j)) \exp(ik \cdot r_j) = \frac{1}{2} \sum_j r_{ij} F_{ij} \frac{1}{ik \cdot r_{ij}} \exp(ik \cdot r_j).$$

Coming back to $r$ space, we get equation (3.3).

2. DERIVATION OF (3.5)

$$\hat{S}(k, t) = \frac{1}{L^3} \sum_j \left( \frac{ik \cdot P_j}{m} \right) \exp(ik \cdot r_j) U(k).$$

We study the last expression

$$\sum_j \hat{S}_j \exp(ik \cdot r_j) = \frac{1}{2} \sum_j (c_{ij} + c_{ji} \exp(-ik \cdot r_{ij})) \exp(ik \cdot r_j),$$

where $c_{ij}$ is the torque exerted by the molecule $i$ on the molecule $j$.

Since the angular momentum of two isolated molecules is conserved we have

$$c_{ij} + c_{ji} + r_{ij} \wedge F_{ij} = 0,$$

and

$$\sum_j \hat{S}_j \exp(ik \cdot r_j) = \frac{1}{2} \sum_j (1 - \exp(-ik \cdot r_{ij})) \exp(ik \cdot r_j) = \frac{1}{2} \sum_j r_{ij} \wedge F_{ij} \exp(ik \cdot r_j).$$

Coming back to $r$ space, we find (3.3).

3. DERIVATION OF (3.7)

$$\dot{S}(k, t) = \sum_j \left[ ik \cdot P_j (r_j \wedge P_j) + (r_j \wedge \dot{P}_j) \right] \exp(ik \cdot r) U(k).$$

The last expression gives

$$\sum_j r_j \wedge \dot{P}_j \exp(ik \cdot r_j) = \frac{1}{2} \sum_j (r_j \wedge F_{ij} - r_i \wedge F_{ij} \exp(ik \cdot r_{ij})) \exp ik \cdot r_j

= \frac{1}{2} \sum_j \left[ r_j \wedge F_{ij} (1 - \exp(ik \cdot r_{ij})) + r_{ij} \wedge F_{ij} \exp(ik \cdot r_{ij}) \right] \exp(ik \cdot r_j)$$

and

$$\dot{S}(k, t) = \frac{ik}{L^3} \sum_j \left[ \frac{P_j}{m} (r_j \wedge P_j) + \frac{1}{2} \sum r_{ij} r_{ij} \wedge F_{ij} f(k, r_{ij}) \right] \exp(ik \cdot r) U(k) + 2 \Sigma_0(k, t).$$

If we now put $r_{ij} = r_j - r + r$ in this last equation and if we use (3.3), we get (3.7).

4. DERIVATION OF (3.25). — This derivation is essentially given in reference [6].

References