ON ANISOTROPY OF THE PRESSURE TENSOR AND THE
FORCE DENSITY FOR A POLARIZABLE FLUID IN AN
ELECTROMAGNETIC FIELD

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By means of a statistical derivation it is shown that the momentum-balance equation of a
polarized fluid contains a force term that is the divergence of an anisotropic tensor \((1/5)PP +
(1/10)P'U\), where \(P\) is the polarization. However, for a fluid in equilibrium this force term is
compensated by an anisotropic part in the pressure tensor. The same is true for a fluid in an
optical field if time-averaged quantities are considered.

1. Introduction

The concepts of pressure and force in a polarized medium have been the
subject of controversies for a long time\(^{1,2}\). In some recent papers\(^3-5\) it has been
argued that the force density contains a term, that is the divergence of an
anisotropic tensor. Neither of these papers consider the associated pressure in
the medium. The divergence of the latter appears in the momentum-balance
equation on a par with the force density. For that reason the divergence of an
anisotropic tensor in the force density can in principle be compensated by an
anisotropic term in the pressure. In this paper we show that this is indeed the case
for a polarized fluid in a static field or in an electromagnetic field of high
frequency.

2. The momentum balance in a polarized fluid

The macroscopic momentum balance for a polarizable medium in an
electric field can be found from the microscopic equations of motion for the
individual molecules of which the system consists. For a molecule \(k\) with
mass \(m\), position \(R_k\), electric dipole moment \(\mu_k\) in a slowly varying external
electric field \(E_e\) the equation of motion reads

\[
m\ddot{R}_k = [\nabla_k E_e(R_k, t)] \cdot \mu_k - \sum_{l\neq k} \nabla_k \phi(R_k - R_l, k, l).
\] (1)
The field $E_e$ is supposed to vary slowly in time and space, so that magnetic interactions may be neglected. The potential $\phi$ depends upon the intermolecular separation $R_k - R_l$ and the internal variables (including the dipole moments) of both of the interacting molecules $k$ and $l$. It may be written as the sum of a long-range and a short-range part:

$$\phi(R, k, l) = \phi^L(R, k, l) + \phi^S(R, k, l) = -\mu_k \cdot \nabla \mu_l \cdot \frac{1}{4\pi R} + \phi^S(R, k, l). \quad (2)$$

For large separations of the molecules, the short-range part $\phi^S$ of the potential falls off more rapidly than $R^{-3}$; it contains the repulsive interactions for small distances and attractive Van der Waals contributions. In the following the explicit form for $\phi^S$ is not needed, although for specific models it can easily be written down (see Appendix A).

When a statistical averaging procedure is carried out, the macroscopic momentum balance becomes

$$\frac{\partial \rho \mathbf{v}}{\partial t} = -\nabla \cdot (\rho \mathbf{v} \mathbf{v} + \mathbf{P}^K) + \mathbf{F}^L + \mathbf{F}^S. \quad (3)$$

Here $\rho$ is the mass density, $\mathbf{v}$ the hydrodynamic velocity and $\mathbf{P}^K$ the kinetic pressure tensor

$$\mathbf{P}^K = \int m \hat{\mathbf{v}}_1 \hat{\mathbf{v}}_1 f_1(R, \mathbf{v}_1; t) \, d\mathbf{v}_1, \quad (4)$$

with $\hat{\mathbf{v}}_1 = \mathbf{v}_1 - \mathbf{v}$ the velocity fluctuation and $f_1$ the one-particle distribution function. Furthermore $\mathbf{F}^L$ and $\mathbf{F}^S$ are the long-range and short-range force densities:

$$\mathbf{F}^L = (\nabla E_e) \cdot \mathbf{P} - \int \nabla_s \phi^L(s, 1, 2) f_2(R, 1, R - s, 2; t) \, ds \, d1 \, d2, \quad (5)$$

$$\mathbf{F}^S = -\int \nabla_s \phi^S(s, 1, 2) f_2(R, 1, R - s, 2; t) \, ds \, d1 \, d2. \quad (6)$$

The polarization $\mathbf{P}$ is the average dipole density; $f_2$ is the two-particle distribution function, which depends upon the positions $R$, $R - s$ and the internal variables $1, 2$ of a pair of particles. The integrals over $s$ extend over all space. However, since $f_2$ vanishes for small $s$ one may exclude an infinitesimal sphere around the origin so as to avoid the occurrence of divergences in subsequent formulae. In other words, in both (5) and (6) we may insert a principal value symbol $\mathcal{P}$ before the integrals.
The long-range force density falls apart in an uncorrelated and a correlated contribution, if the two-particle distribution function $f_2$ is written as $f_1 f_1 + c_2$, where $c_2$ is called the correlation function. The uncorrelated part of (5) becomes upon using (2)

$$F = (\nabla E_e) \cdot P + \mathcal{P} \int P(R - s, t)P(R, t) \cdot \nabla_s \nabla_s \frac{1}{4\pi s} \, ds.$$  \hspace{1cm} (7)

Instead of the external field $E_e$ we want to introduce the Maxwell field; it has the form

$$E(R, t) = E_e(R, t) + \nabla_R \int P(R - s, t) \cdot \nabla_s \frac{1}{4\pi s} \, ds.$$  \hspace{1cm} (8)

An alternative expression for $E$ is:

$$E(R, t) = E_e(R, t) + \mathcal{P} \int [\nabla_s P(R - s, t)] \cdot \nabla_s \frac{1}{4\pi s} \, ds = E_e(R, t) + \mathcal{P} \int P(R - s, t) \cdot \nabla_s \nabla_s \frac{1}{4\pi s} \, ds - \frac{1}{3} P(R, t).$$  \hspace{1cm} (9)

To obtain the last member a partial integration has been performed and use has been made of the identity

$$\int n^i n^j \, d\Omega/4\pi = \frac{1}{3} \delta^{ij},$$  \hspace{1cm} (10)

where $n$ is a unit vector normal to the surface of the unit sphere.

The first term at the right-hand side of (7) becomes upon using (9)

$$(\nabla E_e) \cdot P = (\nabla E) \cdot P + \mathcal{P} \int [\nabla_s P(R - s, t)]P(R, t) \cdot \nabla_s \nabla_s \frac{1}{4\pi s} \, ds + \frac{1}{6} \nabla P^2.$$  \hspace{1cm} (11)

Performing once more a partial integration and employing the identity

$$\int n^i n^j n^k \, d\Omega/4\pi = \frac{1}{15} (\delta^{ij}\delta^{kl} + \delta^{ik}\delta^{jl} + \delta^{il}\delta^{jk}),$$  \hspace{1cm} (12)
one obtains for (11)

\[
(\nabla E_c) \cdot P = (\nabla E) \cdot P - \nabla \int P(R - s, t)P(R, t): \nabla_s \nabla_t \frac{1}{4\pi s} ds
+ \nabla \cdot (\frac{3}{4}PP + \frac{1}{16}P^2U).
\]

(13)

After insertion into (7) one arrives at an expression for the force density \( F \) from which the external field \( E_c \) has been eliminated:

\[
F = (\nabla E) \cdot P + \nabla (\frac{3}{4}PP + \frac{1}{16}P^2U).
\]

(14)

Let us now consider the correlated part of the long-range force density \( F^L \). The correlation function which is contained in \( F^L \) may be expanded into a Taylor series:

\[
c_2(R, 1, R - s, 2; t) = (1 - \frac{1}{2} s \cdot \nabla + \cdots) c_2(R + \frac{1}{2} s, 1, R - \frac{1}{2} s, 2; t).
\]

(15)

In a fluid the correlation function is of short range in the variable \( s \), so that terms beyond the ones written down can be neglected. After substitution into (5) the leading term of (15) drops out on account of the symmetry of \( \phi^L(s, 1, 2) \) under the change \( s \leftrightarrow -s \). The long-range force density then becomes

\[
F^L = F - \nabla \cdot P^C,
\]

(16)

with \( F \) given by (14) and with the pressure tensor

\[
P^C = -\frac{1}{2} \nabla \int s[\nabla_s \phi^L(s, 1, 2)] c_2(R + \frac{1}{2} s, 1, R - \frac{1}{2} s, 2; t) ds dl d2.
\]

(17)

In an analogous fashion the short-range force density can be transformed to a divergence if use is made of the short-range character of \( \phi^S(s, 1, 2) \):

\[
F^S = -\nabla \cdot P^S,
\]

(18)

with

\[
P^S = -\frac{1}{2} \nabla \int s[\nabla_s \phi^S(s, 1, 2)] f_2(R + \frac{1}{2} s, 1, R - \frac{1}{2} s, 2; t) ds dl d2.
\]

(19)

The momentum balance (3) may now be written as
\[ \frac{\partial \mathbf{p}_{v \nu}}{\partial t} = - \nabla \cdot (\rho \mathbf{v} \mathbf{v} + \mathbf{P}) + F, \]  
(20)

with the total pressure tensor defined by

\[ \mathbf{P} = \mathbf{P}^K + \mathbf{P}^C + \mathbf{P}^S \]  
(21)

and the force density \( F \) given in (14).

The treatment given so far may be extended easily so as to include the effects of time-dependent fields, at least for the case that the velocities of the electric dipoles are low. Then the equation of motion will contain an additional term of the form \( c^{-1} \frac{\partial}{\partial t} [\mu \cdot \mathbf{B}(R_k, t)] \). (Terms proportional to \( \mu \dot{R}_k/c \) are neglected in the present approximation.) As a consequence \( F^L \) and \( F \) contain an extra term \( c^{-1} \frac{\partial}{\partial t} (\mathbf{P} \cdot \mathbf{B}) \), or \( c^{-1} \frac{\partial}{\partial t} (\mathbf{P} \cdot \mathbf{B}) \) since the medium is not magnetizable. The momentum balance still has the form (20) with the force density \( F \) given by

\[ F = (\nabla E) \cdot \mathbf{P} + c^{-1} \frac{\partial}{\partial t} (\mathbf{P} \cdot \mathbf{B}) + \nabla \cdot (\frac{1}{2} \mathbf{PP} + \frac{1}{10} \mathbf{P}^2 \mathbf{U}), \]  
(22)

instead of (14).

3. Anisotropy of the pressure tensor

The pressure \( \mathbf{P} \) for an unpolarized fluid in equilibrium is an isotropic tensor of the form \( p \mathbf{U} \). However, the pressure tensor \( \mathbf{P} \) for a polarized medium, as defined in (21), does not reduce to diagonal form in equilibrium. In fact we shall prove in the following that the equilibrium form of the pressure is

\[ \mathbf{P} = p' \mathbf{U} + \frac{1}{2} \mathbf{PP}, \]  
(23)

with a scalar \( p' \). For a dilute medium this statement follows from the explicit form of the two-particle distribution function in the low-density limit:

\[ f_2(R + \frac{1}{2}s, 1, R - \frac{1}{2}s, 2) = f_1(R + \frac{1}{2}s, 1)f_1(R - \frac{1}{2}s, 2) e^{-\beta(\phi^L + \phi^S)}, \]  
(24)

with \( \beta = (kT)^{-1} \) and with \( \phi^L \) and \( \phi^S \) depending on \( s, 1 \) and \( 2 \). Insertion of this form into the correlated and the short-range parts (17) and (19) of the pressure tensor yields

\[ \mathbf{P}^C + \mathbf{P}^S = \frac{1}{2} \beta^{-1} \mathcal{P} \int f_1(R + \frac{1}{2}s, 1)f_1(R - \frac{1}{2}s, 2) \times s \nabla_s (e^{-\beta(\phi^L + \phi^S)} - 1 + \beta \phi^L) \, ds \, dl \, d2. \]  
(25)
Since for large $s$ the expression in square brackets starts off with terms of order $s^{-6}$ the integral over $s$ extends effectively over small values of $s$ only, so that the dependence on $s$ in the one-particle distribution functions can be neglected. A partial integration of the integral over $s$ thus gives

\[
\mathbf{P}^C + \mathbf{P}^S = p^\phi \mathbf{U} - \frac{1}{2} \beta^{-1} \lim_{\epsilon \to 0} \int_{S(\epsilon)} f_1(\mathbf{R}, 1) f_1(\mathbf{R}, 2) \left( \frac{ss}{s} \right) \nu \left( e^{-\beta(\phi^L + \phi^S)} - 1 + \beta \phi^L \right) ds \, dl \, d2.
\]

with

\[
p^\phi = -\frac{1}{2} \beta^{-1} \nu \int f_1(\mathbf{R}, 1) f_1(\mathbf{R}, 2) \left( e^{-\beta(\phi^L + \phi^S)} - 1 + \beta \phi^L \right) ds \, dl \, d2.
\]

The integral in (26) extends over the surface $S(\epsilon)$ of a small sphere of radius $\epsilon$ around $s = 0$, with surface element $dS$ and outward normal $s/s$. In the limit $\epsilon \to 0$ only the term $\nu \phi^L$ in the integrand contributes, since $\phi^S$ tends to infinity and the product $s \, dS$ is proportional to $\epsilon^3$. Employing the identity (12) we obtain therefore

\[
\mathbf{P}^C + \mathbf{P}^S = p^\phi \mathbf{U} + \frac{1}{2} \mathbf{P} \mathbf{P} - \frac{1}{2} \mathbf{P}^2 \mathbf{U}.
\]

In equilibrium the kinetic pressure $\mathbf{P}^K$ has the diagonal form $p^K \mathbf{U}$, so that the total pressure tensor $\mathbf{P}$ for a dilute polarized fluid in equilibrium reads

\[
\mathbf{P} = (p^K + p^\phi) \mathbf{U} + \frac{1}{2} \mathbf{P} \mathbf{P} - \frac{1}{15} \mathbf{P}^2 \mathbf{U}
\]

in accordance with the statement embodied in (23).

For a general polarized fluid in equilibrium the statement (23) can be proved as well if use is made of statistical thermodynamics. In fact, we have shown earlier\(^1\) that under quite general conditions a particular pressure tensor $\hat{\mathbf{P}}$ is diagonal for a fluid in equilibrium. This tensor is connected to the tensor $\mathbf{P}$ of the present paper through the relation

\[
\hat{\mathbf{P}} = \mathbf{P} - \frac{1}{2} \mathbf{P} \mathbf{P} - \frac{1}{10} \mathbf{P}^2 \mathbf{U},
\]

as will be proved in appendix B.

If the fluid is not in equilibrium, as is the case if it is situated in a time-dependent external field, a general statement about the anisotropic part of the pressure tensor cannot be established. However, if fields of optical frequency are considered one is interested not in the pressure as such, but in its time average $\bar{\mathbf{P}}$. For a dilute medium the analogue of (23) may be established.
then by writing the two-particle distribution function as

\[ f_2(R + \frac{1}{2}s, 1, R - \frac{1}{2}s, 2) = f_1(R + \frac{1}{2}s, 1)f_1(R - \frac{1}{2}s, 2) e^{-\beta(\phi^L + \phi^S)}, \] (31)

with the time-averaged interaction potentials \(\overline{\phi^L}\) and \(\overline{\phi^S}\); the symbols 1, 2 denote the time averages and the amplitudes of the oscillating parts of the internal variables for the two atoms. The time-averaged pressure tensor will now contain the contribution (cf. (25))

\[ \overline{P^C} + \overline{P^S} = \frac{1}{2}\beta^{-1}\rho \int f_1(R + \frac{1}{2}s, 1)f_1(R - \frac{1}{2}s, 2) \]
\[ \times s \nabla_s (e^{-\beta(\phi^L + \phi^S)} - 1 + \beta\phi^L_s) \, ds \, dl \, d2. \] (32)

Employing the same steps as above one obtains instead of (28)

\[ \overline{P^C} + \overline{P^S} = \overline{p^s} U + \frac{1}{2}\overline{PP} - \frac{1}{12}\overline{P^2} U, \] (33)

where \(\overline{p^s}\) follows from (27) by adding average bars over \(\phi^L\) and \(\phi^S\). Since the time-averaged kinetic pressure \(\overline{p^K}\) will again be diagonal, one ends up with

\[ \overline{P} = (\overline{p^K} + \overline{p^s}) U + \frac{1}{2}\overline{PP} - \frac{1}{12}\overline{P^2} U \] (34)

instead of (29).

For a fluid in equilibrium we have seen in (29) and (30) that the anisotropic part of the pressure has the same form for a dilute and a dense medium. For that reason it is plausible to assume that the time-averaged pressure tensor of a fluid in an oscillating field of an optical frequency has the form (34) for a dense fluid as well.

4. An alternative form for the momentum balance

The balance equation (20) as derived in section 2 is slightly inconvenient because it contains anisotropic terms in the pressure (23) and the force density (14) that cancel out in equilibrium. For a dilute medium in equilibrium an alternative form of the balance equation follows by inserting (29) into (20) with (14):

\[ \frac{\partial \rho v}{\partial t} = - \nabla \cdot (\rho vv) - \nabla (p^K + p^s - \frac{1}{2}P^2) + (\nabla E) \cdot P \]
\[ = - \nabla \cdot (\rho vv) - \nabla (p^K + p^s) + F', \] (35)
The momentum balance for a general polarized fluid in equilibrium may likewise be written in a different form by substituting (30) into (20) with (14):

$$\frac{\partial \rho v}{\partial t} = -\nabla \cdot (\rho vv + \hat{P}) + \hat{F},$$

(37)

with the force density

$$\hat{F} = (\nabla E) \cdot P.$$  

(38)

This form of the balance equation is equal to that used before\(^1\), if magnetic terms are deleted in conformity with the present treatment.

If the fluid is situated in a field of optical frequency its time-averaged momentum balance follows from (20) with (22) and (34):

$$\nabla \cdot (\rho vv - \bar{v}) + \nabla (-\bar{P} + -\bar{P}) = \bar{F},$$

(39)

with \(\bar{F}\) given in (36).

The transitions from (20) with (14) to (35-36), to (37-38) or to (39) are illustrations of the possibility of shifting terms from the pressure gradient to the force density. The definition of the force density by itself is thus not unique: only the combination of the force density and the associated pressure has a physical meaning.

In recent papers\(^3,4\) a force density was studied which is equivalent to (22) if the electric field is transverse. However, in writing the momentum-balance equation the pressure tensor was not taken into account. The occurrence of anisotropic terms in the pressure tensor thus escapes the attention. In fact we have shown that the time average of the pressure tensor for a fluid in an optical field contains an anisotropic term \(\bar{P}\) which compensates the anisotropic part \(\nabla \cdot (\frac{1}{2}PP)\) in the force density.

**Appendix A**

**Pressure tensor for hard-sphere molecules carrying electric dipoles**

The short-range part of the interaction for a pair of hard-sphere dipole molecules is given by the hard-sphere potential \(\phi^{HS}(R)\) which vanishes for \(R > \sigma\).
and is infinite for $R < \sigma$. The long-range part is for $R > \sigma$ equal to $\phi^L(R)$, defined in (2), while it vanishes for $R < \sigma$. The correlation part of the pressure tensor has a form analogous to (17):

$$P^C = -\frac{1}{s} \int_{s > \sigma} s[\nabla_s \phi^L(s, 1, 2)] c_2(R + \frac{1}{2}s, 1, R - \frac{1}{2}s, 2; t) \, ds \, ds \, d^2l. \tag{A.1}$$

Furthermore the short-range part of the pressure tensor (cf. (19)) becomes

$$P^S = -\frac{1}{s} \int s[\nabla_s \phi^{HS}(s)] f_2(R + \frac{1}{2}s, 1, R - \frac{1}{2}s, 2; t) \, ds \, ds \, d^2l, \tag{A.2}$$

where owing to the singular character of $\phi^{HS}$ the integrand is different from zero only at the surface of the sphere $s = \sigma$. For a dilute fluid of dipolar hard-spheres in equilibrium the two-particle distribution function can be approximated as in (24). Then the sum of (A.1) and (A.2) becomes

$$P^C + P^S = \frac{1}{3}\beta^{-1} \int f_1(R + \frac{1}{2}s, 1)f_1(R - \frac{1}{2}s, 2)$$

$$\times \left[ \theta(s - \sigma)s\nabla_s (e^{-\beta\phi^L} - 1 + \beta\phi^L) + e^{-\beta\phi^L}s\nabla_s e^{-\beta\phi^{HS}} \right] \, ds \, ds \, d^2l. \tag{A.3}$$

As in Section 3 the dependence of the one-particle distribution function on $s$ may be neglected. In the first term between square brackets a partial integration is performed and in the second term one uses the identity $\exp(-\beta\phi^{HS}) = \theta(s - \sigma)$. With the use of (12) one then obtains a relation like (28) with $p^\phi$ given by

$$p^\phi = \frac{2\pi}{3} n^2 \beta^{-1} \sigma^3 - \frac{1}{3} \beta^{-1} \int_{s > \sigma} f_1(R, 1)f_1(R, 2)(e^{-\beta\phi^L} - 1 + \beta\phi^L) \, ds \, ds \, d^2l. \tag{A.4}$$

The first term is the low-density hard-sphere pressure, while the second represents the pressure due to electric-dipole interactions. Such a decomposition of the pressure was not feasible in the general case treated in Section 3.

Appendix B

Connexion between the pressure tensors $P$ and $\dot{P}$

To be able to discuss the relation (30) we shall start by defining $\dot{P}$ as it appears in our book"). For a dipole fluid in a slowly-varying electric field the
pressure tensor \( \hat{\mathbf{p}} \) is of the form (21), but with \( \mathbf{p}^C \) replaced by \( \hat{\mathbf{p}}^C \) defined without a principal value symbol:

\[
\hat{\mathbf{p}}^C = -\frac{1}{2} \int s[\nabla_s \phi^L(s, 1, 2)]c^2(R + \frac{1}{2}s, 1, R - \frac{1}{2}s, 2; t) \, ds \, dl \, d2. \tag{B.1}
\]

Upon comparing with (17) one gets

\[
\hat{\mathbf{p}}^C = \mathbf{p}^C + \lim_{\epsilon \to 0} \int_{U(\epsilon)} s[\nabla_s \phi^L(s, 1, 2)]f_1(R, 1, t)f_1(R, 2, t) \, ds \, dl \, d2, \tag{B.2}
\]

where \( U(\epsilon) \) represents a small sphere of radius \( \epsilon \) around \( s = 0 \). We could replace the correlation function \( c_2 \) by the product \(-f_1f_1\) since \( f_2 \) reduces to zero when the interparticle distance vanishes. Introducing the explicit expression for \( \phi^L \) given in (2), we may write (B.2) as

\[
\hat{\mathbf{p}}^C = \mathbf{p}^C + \lim_{\epsilon \to 0} \int_{U(\epsilon)} s \nabla_s \mathbf{P} \cdot \nabla_s \mathbf{P} \cdot \nabla_s \frac{1}{8\pi s} \, ds, \tag{B.3}
\]

with \( \mathbf{P} \) the macroscopic polarization. With the use of the auxiliary relation

\[
\lim_{\epsilon \to 0} \int_{U(\epsilon)} s^k \nabla_s^i \nabla_s^j \nabla_s^l \frac{1}{4\pi s} \, ds = \frac{1}{2}(\delta^{ij}\delta^{kl} + \delta^{ik}\delta^{jl} + \delta^{il}\delta^{jk}), \tag{B.4}
\]

which follows from partial integration and formula (12), the connexion between \( \hat{\mathbf{p}}^C \) and \( \mathbf{p}^C \) becomes

\[
\hat{\mathbf{p}}^C = \mathbf{p}^C - \frac{1}{2} \mathbf{P} \mathbf{P} - \frac{1}{10} \mathbf{P}^2 \mathbf{U}, \tag{B.5}
\]

which proves (30).

References

2) I. Brevik, Phys. Reports 52 (1979) 133.