ARCHIVES OF ACOUSTICS
32, 4, 933–940 (2007)

ON THE CLASSIFICATION OF DENSE FLUIDS

Sławomir PIEKARSKI

Institute of Fundamental Technological Research
Polish Academy of Sciences
Świętokrzyska 21, 00-049 Warszawa, Poland
e-mail: spiekar@ippt.gov.pl

(*received June 19, 2006; accepted February 19, 2007*)

It is commonly accepted that the existence of entropy imposes restrictions on the constutive functions in the Navier–Stokes–Fourier equations. In the paper: S. Piekarski, "On the Navier–Stokes equation for water" (Archives of Acoustics, **31**, 2, 265–271, 2006) it has been shown that if the energy per unit mass is a function of the temperature T only, then the pressure p is an arbitrary function of the density ρ multiplied by the temperature T.

Now the general form of the relations between the energy density and the pressure is given (both quantities are understood as functions of the mass density and the temperature).

These relations can be approximated in different ways and different approximations suggest different classifications of dense fluids (some of them are similar to the virial expansions).

Keywords: Gibbs identity, thermodynamics.

1. Introduction

For acoustics, the Navier–Stokes–Fourier equations are of a crucial importance. In turn, in order to write these equations explicitly, one has to define such functions like, for example, the energy density (per unit volume) as a function of the mass density ρ and the temperature T and the pressure as a function of ρ and T. It is commonly accepted that these functions are related by the restrictions, imposed by the existence of entropy. Therefore, the explicit form of these restrictions is interesting and in [1] it has been shown that if the energy per unit mass is a function of the temperature T only, then the pressure p is an arbitrary function of the density ρ (which can be denoted $p_0(\rho)$), multiplied by the temperature T. In this paper, the general case of these relations is solved. The form of the solution seems to suggest some scheme of approximate description of the dense fluids, which is similar to the "standard" virial expansions [2].

Explicit calculations are given in the second section. Final results and conclusions are in the last section.

2. The basic equations

The restriction, imposed on the energy density $E\left(\rho, T\right)$ per unit mass and the pressure $p\left(\rho, T\right)$ by the existence of the entropy $S\left(\rho, T\right)$, is

$$\frac{\partial}{\partial T}\left[T^{-1}\frac{\partial E\left(\rho, T\right)}{\partial \rho}-\frac{p\left(\rho, T\right)}{T\rho^{2}}\right]=\frac{\partial}{\partial \rho}\left[T^{-1}\frac{\partial E\left(\rho, T\right)}{\partial T}\right]. \tag{1}$$

In [1], this relation has been obtained directly from the Navier–Stokes–Fourier equations; the alternative approach is to obtain it directly from the Gibbs identity. The relations of the Gibbs identity and the Navier–Stokes–Fourier equations can be investigated also by means of the Lagrange–Liu multipliers (see detailed calculations of WILMAŃSKI [3]).

In order to discuss (1), let us write it in the form

$$\frac{\partial}{\partial T}\left[T^{-1}\frac{\partial E\left(\rho, T\right)}{\partial \rho}\right]+\frac{\partial}{\partial T}\left[-\frac{p\left(\rho, T\right)}{T\rho^{2}}\right]=T^{-1}\frac{\partial^{2}E\left(\rho, T\right)}{\partial \rho \partial T}, \tag{2}$$

which is equivalent to

$$T^{-1}\frac{\partial^{2}E\left(\rho, T\right)}{\partial T \partial \rho}+\frac{\partial E\left(\rho, T\right)}{\partial \rho}\frac{\partial}{\partial T}\left[T^{-1}\right]+\frac{\partial}{\partial T}\left[-\frac{p\left(\rho, T\right)}{T\rho^{2}}\right]=T^{-1}\frac{\partial^{2}E\left(\rho, T\right)}{\partial \rho \partial T}. \tag{3}$$

It can be seen that the first term on the l.h.s. of (3) cancels out the term on the r.h.s. of (3). Therefore one arrives at

$$\frac{\partial E\left(\rho, T\right)}{\partial \rho}\frac{\partial}{\partial T}\left[T^{-1}\right]+\frac{\partial}{\partial T}\left[-\frac{p\left(\rho, T\right)}{T\rho^{2}}\right]=0, \tag{4}$$

that is,

$$-\frac{1}{T^{2}}\frac{\partial E\left(\rho, T\right)}{\partial \rho}+\frac{\partial}{\partial T}\left[-\frac{p\left(\rho, T\right)}{T\rho^{2}}\right]=0. \tag{5}$$

After multiplying (5) by the temperature T one obtains

$$-\frac{1}{T}\frac{\partial E\left(\rho, T\right)}{\partial \rho}+T\frac{\partial}{\partial T}\left[-\frac{p\left(\rho, T\right)}{T\rho^{2}}\right]=0. \tag{6}$$

After multiplying (6) by the mass density ρ, the result can be written in the following form:

$$\rho\frac{\partial}{\partial \rho}\left[\frac{E\left(\rho, T\right)}{T}\right]+T\frac{\partial}{\partial T}\left[\frac{p\left(\rho, T\right)}{T\rho}\right]=0. \tag{7}$$

In order to get a deeper insight into the nature of this equation, let us define the following symbols:

$$\widehat{E}\left(\rho, T\right)=\frac{E\left(\rho, T\right)}{T}, \tag{8}$$

$$\widehat{p}\left(\rho, T\right)=\frac{p\left(\rho, T\right)}{T\rho}. \tag{9}$$

After taking into account (8) and (9), the Eq. (7) can be written in the form

$$\rho\frac{\partial}{\partial\rho}\widehat{E}\left(\rho,T\right)+T\frac{\partial}{\partial T}\widehat{p}\left(\rho,T\right)=0. \tag{10}$$

It can bee seen that a particular solution of (10) is

$$\widehat{E}\left(\rho,T\right)=\widehat{E}\left(T\right), \tag{11}$$

$$\widehat{p}\left(\rho,T\right)=\widehat{p}\left(\rho\right). \tag{12}$$

In order to interpret (11), (12) in "standard variables", let us invert (8) and (9)

$$E\left(\rho,T\right)=\widehat{E}\left(\rho,T\right)T, \tag{13}$$

$$p\left(\rho,T\right)=\widehat{p}\left(\rho,T\right)T\rho, \tag{14}$$

and after inserting (11) and (12) into (13) and (14), we arrive at:

$$E\left(\rho,T\right)=\widehat{E}\left(T\right)T, \tag{15}$$

$$p\left(\rho,T\right)=\widehat{p}\left(\rho\right)T\rho. \tag{16}$$

This solution has been obtained in [1] in a different way. Its important property is that the energy density per unit mass does not depend on the mass density and that the expression for the pressure is a product of the arbitrary function of the mass density and the linear function of temperature. This solution describes some generalisation of the ideal gas and therefore, the corresponding medium shall be called "a generalized ideal gas". In turn, by the "dense fluid" we shall mean a medium with the energy density (per unit mass) depending not only on the temperature but also on the mass density.

In general, if $\widehat{E}\left(\rho,T\right)$ and $\widehat{p}\left(\rho,T\right)$ satisfies (10), then the other solution is

$$\widehat{E}'\left(\rho,T\right)=\widehat{E}\left(\rho,T\right)+\varphi\left(T\right), \tag{17}$$

$$\widehat{p}'\left(\rho,T\right)=\widehat{p}\left(\rho,T\right)+\gamma\left(\rho\right). \tag{18}$$

This property can be checked easily:

$$\begin{aligned}
&\rho\frac{\partial}{\partial\rho}\widehat{E}'\left(\rho,T\right)+T\frac{\partial}{\partial T}\widehat{p}'\left(\rho,T\right)\\
&\qquad=\rho\frac{\partial}{\partial\rho}\left[\widehat{E}\left(\rho,T\right)+\varphi\left(T\right)\right]+T\frac{\partial}{\partial T}\left[\widehat{p}\left(\rho,T\right)+\gamma\left(\rho\right)\right]\\
&\qquad=\rho\frac{\partial}{\partial\rho}\widehat{E}\left(\rho,T\right)+\rho\frac{\partial}{\partial\rho}\varphi\left(T\right)+T\frac{\partial}{\partial T}\widehat{p}\left(\rho,T\right)+T\frac{\partial}{\partial T}\gamma\left(\rho\right)\\
&\qquad=\rho\frac{\partial}{\partial\rho}\widehat{E}\left(\rho,T\right)+T\frac{\partial}{\partial T}\widehat{p}\left(\rho,T\right).
\end{aligned} \tag{19}$$

The above property means that the solutions of (10) can be divided into the equivalence classes; any two solutions are equivalent if and only if their difference is a solution for the "generalized ideal gas". Since (10) is linear, the set of its solutions forms a vector space, and the above property means the existence of the corresponding quotient space in the space of solutions of (10).

In order to get some explicit knowledge about the solutions of (10), let us investigate

$$\frac{\partial}{\partial \rho}\widehat{E}\left(\rho, T\right) = -\frac{T}{\rho}\frac{\partial}{\partial T}\widehat{p}\left(\rho, T\right) \tag{20}$$

and

$$\frac{\partial}{\partial T}\widehat{p}\left(\rho, T\right) = -\frac{\rho}{T}\frac{\partial}{\partial \rho}\widehat{E}\left(\rho, T\right). \tag{21}$$

After integrating (20) and (21) with respect to the mass density and the temperature, correspondingly, one obtains

$$\int\limits_{\rho_0}^{\rho} \frac{\partial}{\partial \rho'}\widehat{E}\left(\rho', T\right) \mathrm{d}\rho' = \widehat{E}\left(\rho, T\right) - \widehat{E}\left(\rho_0, T\right) = -T\frac{\partial}{\partial T}\int\limits_{\rho_0}^{\rho} \frac{\widehat{p}\left(\rho', T\right)}{\rho'}\mathrm{d}\rho' \tag{22}$$

and

$$\int\limits_{T_0}^{T} \frac{\partial}{\partial T'}\widehat{p}\left(\rho, T'\right) \mathrm{d}T' = \widehat{p}\left(\rho, T\right) - \widehat{p}\left(\rho, T_0\right) = -\rho\frac{\partial}{\partial \rho}\int\limits_{T_0}^{T} \frac{\widehat{E}\left(\rho, T'\right)}{T'}\mathrm{d}T'. \tag{23}$$

Now, (22) implies that

$$\widehat{E}\left(\rho, T\right) = \widehat{E}\left(\rho_0, T\right) - T\frac{\partial}{\partial T}\int\limits_{\rho_0}^{\rho} \frac{\widehat{p}\left(\rho', T\right)}{\rho'}\mathrm{d}\rho' \tag{24}$$

and (23) implies that

$$\widehat{p}\left(\rho, T\right) = \widehat{p}\left(\rho, T_0\right) - \rho\frac{\partial}{\partial \rho}\int\limits_{T_0}^{T} \frac{\widehat{E}\left(\rho, T'\right)}{T'}\mathrm{d}T'. \tag{25}$$

From (24) and (25) one can see the general form of the solutions of (10); if $\widehat{p}\left(\rho, T\right)$ is arbitrary, then $\widehat{E}\left(\rho, T\right)$ must be of the form

$$\widehat{E}\left(\rho, T\right) = \widetilde{E}\left(T\right) - T\frac{\partial}{\partial T}\mathit{\Pi}_{\rho}\left(\frac{\widehat{p}\left(\rho, T\right)}{\rho}\right), \tag{26}$$

where $\widetilde{E}\left(T\right)$ is an arbitrary function of the temperature T, and $\mathit{\Pi}_{\rho}$ is the indefinite integral with respect to the variable ρ (with the variable T being a parameter).

In turn, if $\widehat{E}\left(\rho, T\right)$ is arbitrary, then $\widehat{p}\left(\rho, T\right)$ must be of the form

$$\widehat{p}\left(\rho, T\right) = \widetilde{p}\left(\rho\right) - \rho\frac{\partial}{\partial \rho}\mathit{\Pi}_{T}\left(\frac{\widehat{E}\left(\rho, T\right)}{T}\right), \tag{27}$$

where $\widetilde{p}\left(\rho\right)$ is the arbitrary function of the mass density ρ, and $\mathit{\Pi}_{T}$ is the indefinite integral with respect to the variable T (with the variable ρ being a parameter).

Obviously, the symbols $\mathit{\Pi}_\rho$ and $\mathit{\Pi}_T$ in (26) and (27) satisfy the relations

$$\frac{\partial}{\partial\rho}\left\{\mathit{\Pi}_\rho\left(\frac{\widehat{p}\left(\rho,T\right)}{\rho}\right)\right\}=\frac{\widehat{p}\left(\rho,T\right)}{\rho} \tag{28}$$

and

$$\frac{\partial}{\partial T}\left\{\mathit{\Pi}_T\left(\frac{\widehat{E}\left(\rho,T\right)}{T}\right)\right\}=\frac{\widehat{E}\left(\rho,T\right)}{T}. \tag{29}$$

It is worth to mention that the indefinite integrals are defined up to the additive constants, but the expressions (26) and (27) contain the arbitrary functions of T and ρ, correspondingly. Therefore, the resulting expressions are defined uniquely.

By direct inspection, one can check that (26) is a solution of (10):

$$\begin{aligned}\rho\frac{\partial}{\partial\rho}\widehat{E}\left(\rho,T\right)=\rho\frac{\partial}{\partial\rho}&\left[\widetilde{E}\left(T\right)-T\frac{\partial}{\partial T}\mathit{\Pi}_\rho\left(\frac{\widehat{p}\left(\rho,T\right)}{\rho}\right)\right]\\&=\rho\frac{\partial}{\partial\rho}\left[\widetilde{E}\left(T\right)\right]-\rho\frac{\partial}{\partial\rho}\left[T\frac{\partial}{\partial T}\mathit{\Pi}_\rho\left(\frac{\widehat{p}\left(\rho,T\right)}{\rho}\right)\right]\\=-\rho\frac{\partial}{\partial\rho}T\frac{\partial}{\partial T}\mathit{\Pi}_\rho&\left(\frac{\widehat{p}\left(\rho,T\right)}{\rho}\right)=-\rho T\frac{\partial}{\partial T}\frac{\partial}{\partial\rho}\mathit{\Pi}_\rho\left(\frac{\widehat{p}\left(\rho,T\right)}{\rho}\right)\\&=-\rho T\frac{\partial}{\partial T}\frac{\widehat{p}\left(\rho,T\right)}{\rho}=-T\frac{\partial}{\partial T}\widehat{p}\left(\rho,T\right).\end{aligned} \tag{30}$$

Similarly, one can check that (27) is a solution of (10)

$$\begin{aligned}T\frac{\partial}{\partial T}\widehat{p}\left(\rho,T\right)=T\frac{\partial}{\partial T}&\left[\widetilde{p}\left(\rho\right)-\rho\frac{\partial}{\partial\rho}\mathit{\Pi}_T\left(\frac{\widehat{E}\left(\rho,T\right)}{T}\right)\right]\\&=T\frac{\partial}{\partial T}\left[\widetilde{p}\left(\rho\right)\right]-T\frac{\partial}{\partial T}\left[\rho\frac{\partial}{\partial\rho}\mathit{\Pi}_T\left(\frac{\widehat{E}\left(\rho,T\right)}{T}\right)\right]\\=-T\frac{\partial}{\partial T}&\left[\rho\frac{\partial}{\partial\rho}\mathit{\Pi}_T\left(\frac{\widehat{E}\left(\rho,T\right)}{T}\right)\right]=-T\rho\frac{\partial}{\partial\rho}\frac{\partial}{\partial T}\mathit{\Pi}_T\left(\frac{\widehat{E}\left(\rho,T\right)}{T}\right)\\&=-T\rho\frac{\partial}{\partial\rho}\frac{\widehat{E}\left(\rho,T\right)}{T}=-\rho\frac{\partial}{\partial\rho}\widehat{E}\left(\rho,T\right).\end{aligned} \tag{31}$$

It is well-known that the energy, the pressure and the entropy can be expressed in terms of the free energy (see, for example, [3]):

$$E\left(\rho,T\right)=F\left(\rho,T\right)-T\frac{\partial F\left(\rho,T\right)}{\partial T}, \tag{32}$$

where $F\left(\rho,T\right)$ is the free energy per unit mass,

$$S\left(\rho,T\right)=-\frac{\partial F\left(\rho,T\right)}{\partial T} \tag{33}$$

is the entropy per unit mass, and the pressure is

$$p(\rho,T)=\rho^2\frac{\partial F(\rho,T)}{\partial\rho}. \tag{34}$$

Our solutions of (10) are defined in terms of the variables $\widehat{E}(\rho,T)$ and $\widehat{p}(\rho,T)$ given by (8) and (9); therefore, in order to check whether (32) and (34) satisfy (10), one has to write (32) and (34) in the form

$$\widehat{E}(\rho,T)=\frac{F(\rho,T)}{T}-\frac{\partial F(\rho,T)}{\partial T}, \tag{35}$$

$$\widehat{p}(\rho,T)=\frac{\rho}{T}\frac{\partial F(\rho,T)}{\partial\rho}. \tag{36}$$

It can be checked easily that (35) and (36) satisfy the equation (10); however, our aim here is to investigate explicit relations between the energy and the pressure and therefore expressions formulated in terms of the free energy are not useful for our purposes.

Our results can be approximated in many ways and some of them seem to be related to the virial coefficients [2].

Generally speaking, since the equation (10) is linear, one can choose different bases in the space of its solutions. In order to interpret the integral operators $\mathit{\Pi}_\rho$ and $\mathit{\Pi}_T$ explicitly, it is convenient to use the functions that are products of functions of single variables. For example, one can assume that $\widehat{E}(\rho,T)$ is

$$\widehat{E}(\rho,T)=\widehat{E_0}(T)+\widehat{E_1}(T)\rho+\widehat{E_2}(T)\rho^2+\ldots+\widehat{E_n}(T)\rho^n, \tag{37}$$

and insert (37) into (25):

$$\begin{aligned}
\widehat{p}(\rho,T)&=\widehat{p}(\rho,T_0)\\
&\quad-\rho\frac{\partial}{\partial\rho}\int\limits_{T_0}^{T}\frac{\left[\widehat{E_0}(T')+\widehat{E_1}(T')\rho+\widehat{E_2}(T')\rho^2+\ldots+\widehat{E_n}(T')\rho^n\right]}{T'}\mathrm{d}T'\\
&=\widehat{p}(\rho,T_0)-\rho\frac{\partial}{\partial\rho}\int\limits_{T_0}^{T}\frac{\widehat{E_1}(T')\rho}{T'}\mathrm{d}T'+\ldots+\rho\frac{\partial}{\partial\rho}\int\limits_{T_0}^{T}\frac{\widehat{E_n}(T')\rho^n}{T'}\mathrm{d}T'\\
&=\widehat{p}(\rho,T_0)-\rho\frac{\partial}{\partial\rho}\rho\int\limits_{T_0}^{T}\frac{\widehat{E_1}(T')}{T'}\mathrm{d}T'+\ldots+\rho\frac{\partial}{\partial\rho}\rho^n\int\limits_{T_0}^{T}\frac{\widehat{E_n}(T')}{T'}\mathrm{d}T'\\
&=\widehat{p}(\rho,T_0)-\rho\int\limits_{T_0}^{T}\frac{\widehat{E_1}(T')}{T'}\mathrm{d}T'+\ldots+n\rho^n\int\limits_{T_0}^{T}\frac{\widehat{E_n}(T')}{T'}\mathrm{d}T'.
\end{aligned} \tag{38}$$

In turn, one can assume that

$$\widehat{p}(\rho,T)=\widehat{p_0}(\rho)+\widehat{p_1}(\rho)T+\widehat{p_2}(\rho)T^2+\ldots+\widehat{p_n}(\rho)T^n \tag{39}$$

and insert (39) into (24):

$$
\begin{aligned}
\widehat{E}(\rho,T) &= \widehat{E}(\rho_0,T) \\
&\quad - T\frac{\partial}{\partial T}\int\limits_{\rho_0}^{\rho} \frac{\left[\widehat{p_0}(\rho') + \widehat{p_1}(\rho')T + \widehat{p_2}(\rho')T^2 + \ldots + \widehat{p_n}(\rho')T^n\right]}{\rho'}\mathrm{d}\rho' \\
&= \widehat{E}(\rho_0,T) - T\frac{\partial}{\partial T}\int\limits_{\rho_0}^{\rho}\frac{\widehat{p_1}(\rho')T}{\rho'}\mathrm{d}\rho' - \ldots - T\frac{\partial}{\partial T}\int\limits_{\rho_0}^{\rho}\frac{\widehat{p_n}(\rho')T^n}{\rho'}\mathrm{d}\rho' \\
&= \widehat{E}(\rho_0,T) - T\frac{\partial}{\partial T}T\int\limits_{\rho_0}^{\rho}\frac{\widehat{p_1}(\rho')}{\rho'}\mathrm{d}\rho' - \ldots - T\frac{\partial}{\partial T}T^n\int\limits_{\rho_0}^{\rho}\frac{\widehat{p_n}(\rho')}{\rho'}\mathrm{d}\rho' \\
&= \widehat{E}(\rho_0,T) - T\int\limits_{\rho_0}^{\rho}\frac{\widehat{p_1}(\rho')}{\rho'}\mathrm{d}\rho' - \ldots - nT^n\int\limits_{\rho_0}^{\rho}\frac{\widehat{p_n}(\rho')}{\rho'}\mathrm{d}\rho'. \qquad (40)
\end{aligned}
$$

These expressions can be used for an approximate classification of the “dense fluids”. As it has been already mentioned, by a dense fluid we mean here any medium, in which the energy density per unit mass is a function not only of the temperature T but also of the mass density ρ. In particular, (37) can be interpreted as a perturbational scheme with the “generalized ideal gas” as a background. Obviously, one can discuss similar approximations with the “dense fluid” taken as a background.

3. Final remarks and conclusions

The aim of this text is to describe a general approach, which could be potentially useful for numerical experiments and for classifications of dense fluids. In [1] it has been shown that if the energy per unit mass is a function of the temperature T only, then the pressure p is an arbitrary function of the density ρ multiplied by the temperature T. In the present paper, the general form of the relations between the energy density and the pressure is given. It can be observed that the results of [1] can be derived directly from the Gibbs identity in an elementary way and this derivation is as follows:

- the Gibbs identity reads

$$T\mathrm{d}S = \mathrm{d}E + p\mathrm{d}\left[\frac{1}{\rho}\right] = \mathrm{d}E - \frac{p}{\rho^2}\mathrm{d}\rho, \qquad (41)$$

and if E and p are considered as functions of ρ and T, one can see that (41) is equivalent to

$$\mathrm{d}S = \mathrm{d}E + p\mathrm{d}\left[\frac{1}{\rho}\right] = \frac{1}{T}\mathrm{d}E(\rho,T) - \frac{p(\rho,T)}{T\rho^2}\mathrm{d}\rho. \qquad (42)$$

From the form of (42) it can be seen that for $E = E(T)$ and $p(\rho, T) = p_0(\rho)T$, the above expresssion simplifies to

$$\mathrm{d}S = \frac{1}{T}\mathrm{d}E(T) - \frac{p_0(\rho)T}{T\rho^2}\mathrm{d}\rho = \frac{1}{T}\frac{\partial E(T)}{\partial T}\mathrm{d}T - \frac{p_0(\rho)}{\rho^2}\mathrm{d}\rho. \tag{43}$$

From (43), the explicit expression for the entropy per unit mass can be integrated:

$$S(\rho, T) = \int\limits_{T_0}^{T} \frac{1}{T'}\frac{\partial E(T')}{\partial T'}\mathrm{d}T' - \int\limits_{\rho_0}^{\rho} \frac{p_0(\rho')}{\rho'^2}\mathrm{d}\rho'. \tag{44}$$

Therefore, the entropy of a "generalized ideal gas" can be written as a sum of a term depending only on T and a term depending only on ρ. The above "derivation" is very simple but it should be stressed that in [1] the restrictions for the allowed form of $E(\rho, T)$ and $p(\rho, T)$ have been derived from the field equations and not from the Gibbs identity.

We hope to make a more detailed discussion later.

References

[1] PIEKARSKI S., *On the Navier–Stokes equation for water*, Archives of Acoustics, **31**, 2, 265–271 (2006).

[2] DYMOND J. H., SMITH E. B., *The virial coefficients of pure gases and mixtures. A critical compilation*, Clarendon Press, Oxford 1980.

[3] WILMAŃSKI K., *Thermodynamical models of continuous media* [in Polish], Poznań University of Technology, 1985.

[4] SMITH E. B., *Basic chemical thermodynamics*, Oxford University Press, 1982.

[5] WILMAŃSKI K., *Thermomechanics of continua*, Springer, Berlin 1998.