THERMODYNAMIC MODEL OF A DENSE FLUID

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In this paper we derive an approximate equation of state of a dense fluid in which the thermal pressure is completely determined by the pressure dependence of the volume at 0°K. We also consider some generalizations (which take into account the attractive forces of the atoms and the presence of mixtures).

In statistical mechanics the thermodynamic quantities of a material are expressed in terms of the potential of the interatomic interaction, and modern computational techniques (the Monte Carlo method) make it possible to carry out the calculations to the end.

However, calculations (quantum-mechanical) of the interatomic potential itself are extremely difficult. The usual assumption that it does not depend on the density of the material and reduces to a sum of potentials of binary interactions may not be applicable to dense fluids and then even exact statistical calculations made on the basis of these assumptions cannot guarantee accuracy in the description of the thermodynamic properties of a real fluid.

This is why many authors prefer a shorter route: one postulates a certain expression with empirical parameters directly for one of the thermodynamic functions and not for the interatomic potential. This frankly empirical approach is justified by a detailed description of extensive experimental material. However, if only minimal information is available (for example, if one knows only the shock adiabatic curve of a dense fluid), it is desirable to have the simplest and physically most justified equation of state that makes it possible to establish the complete thermodynamics of the fluid with a satisfactory accuracy. The present paper is devoted to this problem.

We note first that there are always regions of higher and lower density in a fluid because of the thermal motion. One can have the extreme case when in a certain microscopic region the atomic nuclei move on the average toward the center of the region (compression) and then away from the center (expansion), i.e., at a certain instant the matter is in a cold state in the microscopic region because the nuclei in the region are instantaneously at rest.

The molar volume V of the region at this instant is determined by the mean pressure in the fluid, i.e., it is equal to the elastic or the cold volume $V_-(p)_p$ at T = 0°K. Here and in what follows, the subscript minus is appended to the quantity for the "cold" state.

The dependence $V_-(p)$ for $p > 0$ reflects the contribution of all the interatomic forces, which, added together, give the repulsive force of the atoms. The interaction of all the elementary charges in regions of higher density is essentially collective and leads to the corresponding bonds: valent, metallic, etc.

Another limiting case is possible when the nuclei are so far apart that they form an ideal gas.

We shall attempt to describe the real case, which is intermediate between these limits, by means of a sensible interpolation. We note first that if $V > V_-(0)$ attractive forces also act; exclusively for the sake of simplicity we shall ignore them. Actually, for a dense fluid (and also in the region of strongly supercritical temperatures), this neglect is completely justified. For simplicity we shall also ignore the excitation of electrons, which can be taken into account by the usual methods.

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We determine the "elastic" volume $V_0(p, T)$ from the identity

$$p = \frac{RT}{V - V_0(p, T)} \tag{1}$$

Here R is the universal gas constant.

In the well-known model of dense fluid with incompressible molecules, V_0 = const. The elastic volume restricts, as it were, the region of motion of the molecules to the free volume, which is equal to

$$V - V_0 = \frac{RT}{p} \equiv V^*(p, T)$$

Here and in what follows, the asterisk denotes the functions of an ideal gas. The molecules in the free volume are themselves regarded as material points. We shall also adopt this interpretation of Eq. (1) for the case of compressible molecules, when V_0 is variable.

Compressibility of a molecule is an internal property that does not depend on the factors producing an internal pressure on the molecule, say, the elastic pressure from the direct contact with immobile neighboring molecules or the kinetic pressure from impacts of the other molecules from all sides (dense fluid, collisions essentially nonbinary !). Therefore, V_0 is assumed to be a function of only the pressure, and the temperature determines only the fraction of the elastic part in the given pressure. Of course, if attractive forces play an important role, V_0 begins to depend on the density as well, i.e., ultimately on the temperature also.

Usually, one ignores discontinuities on melting and the solid phase is not distinguished from the liquid when $V_0(p) = V_-(p)$. We therefore obtain the desired interpolation

$$V = V_-(p) + V^*(p) = V_-(p) + RT / p \tag{2}$$

i.e., the volume is split into two regions in which the limiting states considered above are realized. Note that for a dense fluid the very concept of a molecule is arbitrary and by its dimensions (discussed above) at a given pressure one must understand the mean volume associated with the "molecule" at T = 0 and the same pressure.

If T = const and p → 0, the fluid becomes a perfect gas. We determine the thermodynamic potential from this boundary condition:

$$\Phi(p, T) = \int V(p, T)\, dp = \Phi_-(p) + \Phi^*(p, T) \tag{3}$$

Without complicating Eq. (3), we can also allow for attractive forces approximately by introducing a constant p_0,

$$\Phi(p, T) = \Phi_-(p) + \Phi^*(p + p_0, T) \tag{4}$$

Then a constant term $-p_0$ is added on the right-hand side of (1).

From (4) we obtain the asymptotic behavior as T → 0:

$$E(V, T) = E_-(V) + (1 + {}^1\!/_2 i)\, RT$$

$$p(V, T) = p_-(V) - \frac{RT}{p_0 + p_-(V)} \frac{dp_-(V)}{dV}$$

Here E is the internal energy and i is the number of degrees of freedom of a molecule. For a monotonic substance (i = 3) the thermal energy is 5RT/2 instead of the usual 3RT. This defect is not very important because in gas-dynamical calculations of adiabatic flows and shock waves one only employs the ratio

$$\gamma = (p - p_-)\, V / E - E_-$$

The description of the state of a solid can be improved by choosing p_0 from the condition that γ be equal to its experimental value at $p_- = 0$.

We now give some examples that confirm the model.

1. The Monte Carlo method was used to calculate the equation of state of an idealized material for which the binary potential of the atoms, which repel one another at the distance r, is equal to Ar^{-6}, where A = const. The results can be well described by the one-parametric interpolation formula if the parameter a is set equal to 0.23 in the formula. The formula gives the correct limits as $T \to 0$ (cold state plus the contribution of harmonic oscillations) and as $T \to \infty$ (state of an ideal gas plus the second virial correction):

$$f \equiv \frac{pV}{RT} = \frac{7.1}{x} + 1 + \frac{3 + ax}{1 + ax\,(1 + 1/3.71\sqrt{x})} \tag{5}$$

Here

$$x = \frac{T}{A}\left(\frac{V}{N}\right)^2_{\infty}$$

and N is Avogadro's number. The proposed model gives (for $p_0 = 0$)

$$x = \frac{7.1}{f}\left(\frac{f}{1-f}\right)^3 \tag{6}$$

The two functions $f(x)$ are similar, as can be seen in Fig. 1.

2. In Fig. 2 the functions $V_-(p, T)$ are given for hydrogen in the experimentally investigated region of strongly supercritical states $0 < p < 3$ kbar, $0 \le T \le 150°C$ (see [1]). The difference in the limiting isotherms, which is due to the effect of attractive Van der Waals forces, vanishes for $p > 1.5$ kbar. The difference between V_0 and V_- in the region $1.5 < p < 3$ kbar does not exceed 5%.

3. The cold curve for hydrogen V_- has been measured up to 20 kbar and described by an analytic formula [2]. Extrapolation of the formula to 40 kbar agrees with the approximate calculations of [3]. For a shock wave moving in liquid hydrogen with $V = 14.1$ cm^3/g, calculation in accordance with the model with this cold curve (with $p_0 = 0$) for $p = 39.5$ kbar gives $V = 5.45$ cm^3/g, whereas experimentally [4] we have $V = 5.2$ cm^3/g, i.e., it is only 5% less.

4. There are a series of shock adiabatic curves for ionic salts of different porosity m [5]. The cold curve was determined from the shock adiabatic curve of the continuous material (m = 1) and p_0 from γ at $p_- = 0$. In Table 1 we give the theoretical $V^{(1)}$ and experimental $V^{(2)}$ values of V, and also the calculated temperatures. The greatest systematic discrepancies between $V^{(1)}$ and $V^{(2)}$ (about 5-10%) agree with the corrections for the excitation for electrons estimated in [5].

The main advantage of the proposed model of a fluid over the models in [5] and especially in [4] is the exceptional simplicity of both the calculations and the physical interpretation.

In other materials in the experimentally investigated region of states, Van der Waals forces are more important than for hydrogen. In dynamical experiments with porous metals the excitation of valence electrons is more important than for ionic salts. In these cases, of course, the proposed equation of state must be improved.

In [6] an equation of the state in the form (1) is also assumed (specifically for TNT) with

$$V_0 = b + cp + dp^2$$

However, there is no discussion of the physical justification for assuming the temperature independence of the coefficients b, c, and d or the relationship between V_0 and V_- or, finally, the experimental verification of the postulates.

The generalization of the model to the case of a mixture corresponds to the notion of additivity of the volumes of the components (see also [6])

$$\Phi(p, T) = \sum_n \alpha_n \Phi_n(p, T) \qquad \left(\sum_n \alpha_n = 1\right)$$

Here α_n is the concentration of the n-th component of the mixture. All the α_n are determined from the condition of a minimum of Φ subject to additional normalization conditions.

TABLE 1

	m	p, Mbar	$V^{(2)}$, cm^3/g	$V^{(1)}$, cm^3/g	T, °K
LiF	1.55	1.239	0.275	0.272	18000
	2.08	0.935	0.320	0.325	22800
	2.08	0.138	0.368	0.368	5700
	3.00	0.655	0.379	0.403	27200
	4.68	0.430	0.478	0.517	31000
NaCl	1.514	0.915	0.292	0.298	28600
		0.874	0.289	0.300	27300
		0.804	0.302	0.304	25000
		0.645	0.316	0.314	19300
		0.568	0.317	0.320	16500
		0.397	0.333	0.337	10700
		0.162	0.377	0.376	3700
	2.185	0.695	0.366	0.380	39400
		0.659	0.350	0.383	37200
		0.570	0.374	0.389	31400
		0.449	0.384	0.398	24600
		0.424	0.390	0.400	23200
		0.268	0.397	0.416	14000
		0.112	0.436	0.439	5000
KCl	1.41	0.158	0.375	0.374	5000

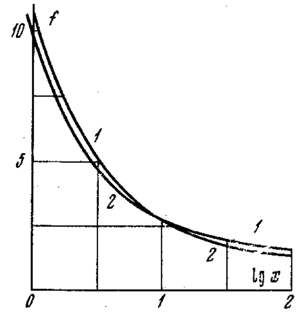

Fig. 1

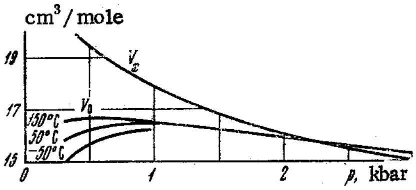

Fig. 2

By way of an example, let us consider a mixture of molecular and atomic hydrogen. The corresponding cold curves can be taken for example, from [7]. The concentration α of atoms is determined by the equation

$$\frac{1}{\alpha^2} - 1 = 4\sum(T)\left(\frac{T_*}{T}\right)^{3/2}\frac{p}{p_*}\exp\,\frac{2\mu_a(p) - \mu_m(p)}{kT}$$

Here $\Sigma(T)$ is the vibrational partition function (we assume that the rotations of the molecules are fully excited), μ_a and μ_m are the chemical potentials at T = 0 of the atom and the molecule, respectively; $p_* = 8.42$ kbar; $T_* = 120.7$°K; k is Boltzmann's constant.

As $p \to 0$ we obtain the usual Saha formulas for an ideal gas (dissociation by the "temperature") and as $T \to 0$ we obtain the usual condition for the coexistence of atomic and molecular phases at T = 0 (disassociation by the "pressure"):

$$2\mu_a(p) = \mu_m(p)$$

However, corrections must be made in the formulas at low temperatures to take into account the freezing of the rotation of the molecules and the vibrations of the centers of mass of the molecules and the atoms.

Note that in the adopted model a phase transition of the first kind from the molecular to the atomic phase is absent since the concentration α varies continuously for $T > 0$. However, pronounced nonmonotonicity is possible in this variation. Then, for example, the passage of a shock wave at fairly low temperatures would reveal effects very similar to a phase transition (in effect, a point of inflection of the adiabatic curve). This gives an alternative qualitative explanation of the point of inflection of the shock adiabatic curve for ionic salts discovered in a definitely liquid state [5]. The components of the "phases" are here liquids with coordination numbers as in the corresponding solid modifications.

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