

It follows from condition (2) that away from the equilibrium curve $u = u(V, V_0)$. For small deformations u will be a quadratic function of the difference $V - V_0$. To investigate the behaviour of liquids during non-linear deformations, we express the pair interaction energy of the molecules as a Mie potential, for which u can be calculated both for crystals and approximately also for liquids taking into account long-range interactions of the molecules⁵. Equation (1) with the condition (2) then becomes

$$U = u_1(T) - \frac{u(V_0)}{n-m} (mv^n - nv^m); \quad p = \frac{u(V_0)nm}{V_0(m-n)} (v^{n+1} - v^{m+1}), \quad (3)$$

where $v = V_0/V$, n and m are parameters of the Mie potential, and $u(V_0)$ is the value of u on the equilibrium curve.

The second equation (3) is based on the condition⁶ $p_1(T, V) \ll u'_V$, that far from the critical point the vapour pressure is very small in comparison with the external pressure. It has been shown⁷ that, in calculating derivatives from the second equation (1), we can neglect also derivatives with respect to p_1 when the condition $V_1 \geq 10^3 V$ is satisfied, where V_1 is the volume of saturated vapour in equilibrium with the liquid. Thus Eqns. (3) are applicable between the triple point and the temperature at which this condition is satisfied. With most liquids this range constitutes about 30–50% of the range of existence of the liquid phase. From Eqns. (3) we find the isothermal modulus of elasticity K , the thermal coefficient of the pressure β , the heat capacity c_V , and the velocity of sound c :

$$\begin{aligned} K &= \frac{u_0 nm}{(n-m)V_0} [(n+1)v^{n+1} - (m+1)v^{m+1}], \\ \beta p &= \frac{nm}{V(n-m)} [u_0 \alpha_0 (nv^n - mv^m) + u'_{0T} (v^n - v^m)], \\ c_v &= c_{v0} + u'_{0T} + \frac{u_0 \alpha_0 nm}{n-m} (v^n - v^m) + \frac{u'_{0T}}{n-m} (mv^n - nv^m), \\ c^2 &= \frac{VK}{M} \left(1 + \frac{TV\beta^2 p^2}{Kc_v} \right), \end{aligned} \quad (4)$$

where $\alpha_0 = (1/V_0)(dV_0/dT)$, $u_0 = -u(V_0)$, and M is the molecular mass.

Putting $v = 1$ in Eqns. (3) and (4), and denoting quantities on the equilibrium curve by the subscript 0, we obtain

$$\begin{aligned} U_0 &= u_1(T) - u_0; \quad p_0 = 0; \quad K_0 = \frac{nm u_0 \alpha_0}{V_0}; \quad (\beta p)_0 = \frac{nm u_0 \alpha_0}{V_0}; \quad c_0^2 = \\ &= \frac{nm u_0}{M} \left(1 - \frac{T \alpha_0^2 nm u_0}{M c_{v0}} \right)^{-1}. \end{aligned} \quad (5)$$

From the thermodynamic identity $p = T\beta p - (U'_V)_T$ applied to the equilibrium curve and the first, second, and fourth relations (5) we obtain the equation

$$u'_{0T} + T n m \alpha_0^2 u_0 = 0 \quad (6)$$

for computing u_0 . If the exponent n is known, calculations by means of formulae (3)–(6) with $m = 2$, which has a theoretical basis, contain no adjustable parameters. The quantity u_0 , which is required for the calculations, can be computed from experimental values of c_0 , α_0 , and c_{v0} from the last equation (5) or even by integrating Eqn. (6) using only one value of u_0 , found from (5), as an integration constant.

Curve (a) in Fig. 1 illustrates the quantity $\Delta V/V_0 = 1 - v^{-1}$, calculated from Eqn. (2)³ for liquid argon by a method of successive approximations with $n = 3.5$, found by approximate numerical quantum-mechanical calculations of the energy of repulsion based on a power law⁸. Values of n for a few substances, found from their properties in the condensed state, have been collected⁵. Curve (b) in Fig. 1

has been calculated for pentane with $n = 5.5$. The quantities (4) are computed from values of $v(p)$. Curve (a) in Fig. 2 has been calculated for the speed of sound in carbon disulphide with $n = 3.9$. For most liquids n is unknown, and we then have a one-parameter theory. In this case n is found from one experimental value of β with $v \neq 1$ by application of the second equation (3) or even by substitution in the last equation (5) of the semi-empirical formula $u_0 = 2\sigma V_0^{2/3} N^{1/3}$, where σ is the surface tension and N is Avogadro's number¹⁰. Another method requires knowledge of experimental data solely on the equilibrium curve.

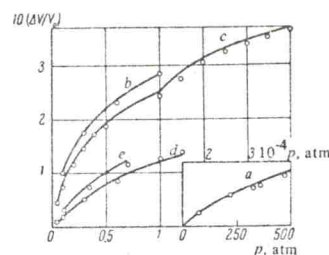


Figure 1. Points for different temperatures from various sources: a) -171.89°C ⁹; b) 0°C ¹¹; c) 25°C ¹²; d) 50°C ¹¹; e) 20°C ¹³.

Values of n which are almost independent of temperature, and agree satisfactorily among themselves and with the above and other independent values, are obtained in such ways. Thus in Fig. 1 curve (c) has been calculated for oct-1-ene ($n = 5.81$), curve (d) for glycerol (7.92), and curve (e) for ethylene glycol (6.17), and in Fig. 2 curve (b) has been calculated for n-butanol (6.16).

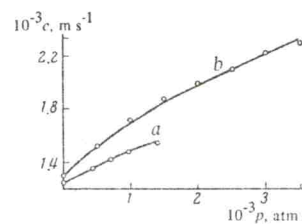


Figure 2. Points for different temperatures: a) 0°C ¹⁵; b) 20°C ¹⁶.

The isotherms of about eighty liquids have now been studied experimentally and will be found in Refs. 9 and 11–13 and in certain other works. Calculations were made for sixteen liquids up to 40 000 atm¹² and for seventeen liquids up to 10 000–12 000 atm¹¹. Data on the equilibrium curve could not be found for other liquids. All calculations agree satisfactorily with experiment, even if the liquid crystallised under the influence of external pressure¹², when the change in $\Delta V/V_0$ on crystallisation is small. Considerable divergence is found only with

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