TEMPERATURE DEPENDENCE OF THE SPEED OF SOUND IN SATURATED VAPOR AND IN LIQUID NEAR THE CRITICAL POINT

I. S. Radovskii

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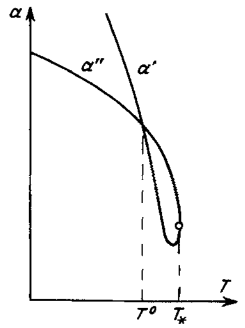
It has been observed [1, 2] that the speed of sound as a function of temperature T for saturated vapor meets that for liquid near the critical point, i.e., there is a range (0.3-0.5° K) near that point where the velocity in the liquid is less than that in the saturated vapor. This apparently anomalous effect has not received a satisfactory explanation, and it has been asserted [3] that the curves cannot actually intersect, the apparent intersection being due to experimental error. However, a study of the data [2] shows that the difference between the two velocities near the critical point substantially exceeds the possible error of the experiments.



We cannot accept as entirely reliable the conclusion [4] that these curves for some substances meet at only one point (the critical point) but for other substances may meet at two points, since this conclusion is based on the assumption that the thermodynamic functions can be expanded as Taylor series near the critical point. The critical state is special to some extent, so great care should be taken over such an assumption [5].

The present analysis is based not on series expansion but on application of the usual mathematical methods of thermodynamics.

Laplace's equation for the speed of sound

$$a^2 = -v^2\left(\frac{\partial p}{\partial v}\right)_s \tag{1}$$

gives us the derivative with respect to T along the saturation line as

$$\frac{da}{dT} = -\frac{a}{v}\frac{dv}{dT} - \frac{v^2}{2a}\frac{d}{dT}\left(\frac{\partial p}{\partial v}\right)_s. \tag{2}$$

On the other hand, that derivative is

$$\frac{da}{dT} = \left(\frac{\partial a}{\partial T}\right)_v + \left(\frac{\partial a}{\partial v}\right)_T\frac{dv}{dT}. \tag{3}$$

The value of $(\partial a/\partial v)_T$ at the critical point is [6]

$$\left(\frac{\partial a}{\partial v}\right)_{T_*} = \frac{a_*}{v_*}, \tag{4}$$

where the subscript $_*$ is used to denote quantities at the critical point.

Then

$$\left(\frac{da}{dT}\right)_* = \left(\frac{\partial a}{\partial T}\right)_{v_*} + \frac{a_*}{v_*}\left(\frac{dv}{dT}\right)_*. \tag{5}$$

Comparison of (5) with (2) for the critical point gives

$$\left[\frac{d}{dT}\left(\frac{\partial p}{\partial v}\right)_s\right]_* = -\frac{2a_*}{v_*^2}\left(\frac{\partial a}{\partial T}\right)_{v_*}. \tag{6}$$

It has been shown [6] that

$$\left(\frac{\partial a}{\partial T}\right)_{v_*} > 0. \tag{7}$$

Since $a_* \neq 0$, we have from (6) and (7) that

$$\left[\frac{d}{dT}\left(\frac{\partial p}{\partial v}\right)_s\right]_* < 0. \tag{8}$$

Inequality (8) is correct on approaching the critical point along the saturation line from the vapor side or from the liquid side; in particular, it means that $(\partial p/\partial v)_s$ for the liquid near T_* increases in absolute value with T, i.e., there is a region in which $|(\partial p/\partial v)_s'| < |(\partial p/\partial v)_{s*}|$. On the other hand, the specific volume of the liquid also decreases away from the critical point, i.e., $v' < v_*$.

Equation (1), with these inequalities, shows that the speed of sound in the liquid for $T \leq T_*$ becomes less than that for $T = T_*$, i.e., $a' < a_*$. It has also been shown [6] that

$$\left(\frac{da''}{dT}\right)_* = -\infty, \tag{9}$$

i.e., the speed of sound in the saturated vapor for $T < T_*$ is always greater than that for $T = T_*$, so near $T = T_*$ there is a range in which $a' < a''$. On the other hand, it is known that $a' \gg a''$ at some distance from T_*, on account of marked reduction in the compressibility of the liquid.

Therefore, intersection occurs near the critical point for all substances without exception.

This conclusion may be reached in a somewhat different way, by using (5) for da'/dT at T_*:

$$\left(\frac{da'}{dT}\right)_* = \left(\frac{\partial a}{\partial T}\right)_{v_*} + \frac{a_*}{v_*}\left(\frac{dv'}{dT}\right)_*. \tag{10}$$

As $(dv'/dT)_* = +\infty$, we have from (7) that

$$\left(\frac{da'}{dT}\right)_* = +\infty. \tag{11}$$

It follows from (11) and (9) that the curves for a' and a'' join smoothly (Fig. 1) at T_*, with a' initially falling for $T < T_*$, then passing through a minimum and rising monotonically, to equal a'' at T_0 (point of intersection of the curves).

The range $T_* - T_0$ in which $a' < a''$ may vary from substance to substance; if it does not exceed the error in measuring T in measurements on the speed of sound, the intersection of the curves will not be detected by experiment. This would appear to be the case in [7], where very detailed measurements were made of the speed of sound in both phases near the critical point.

The deduction about the intersection is correct if $a_* \neq 0$, i.e., $c_{V*} \neq \infty$; hence, observation of the intersection provides experimental proof that c_V at T_* is finite.

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