The reestablishment of the van der Waals critical point in fast processes

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The equilibrium distribution of fluctuations of all scales is established slowly near a critical point. If the near-critical state is reached rapidly, a state may be reached which exhibits small fluctuation amplitudes and nonsingular thermodynamic functions.

The thermodynamic behavior of a substance near a second-order phase transition point, e.g., near the liquid-vapor critical point, turned out to be considerably more complicated than originally surmised by van der Waals and Landau.

Superimposed on the classical picture are spatial fluctuations with amplitudes that increase as the critical point is approached. At such a point all wavelengths play identical roles, leading to peculiar power-law behaviors and scaling.

In this note we call attention to the kinetics of the establishment of complete thermodynamic equilibrium, including all kinds of fluctuations. The long-wavelength fluctuations are established slowly, their relaxation time being proportional to the square of the wavelength.

We consider a rapid change of the state which brings the substance under consideration near the critical point. At the first instant following this transition the fluctuations are not yet excited. One may say that full thermodynamic equilibrium does not exist, but equilibria with respect to the interaction of neighboring molecules, and with respect to short-range order (correlations over several molecular distances) are attained rapidly. Thus, in a rapid process one obtains a substance in a sufficiently well-defined state which merits experimental investigation. One may expect that one will obtain the "old" laws of the theory which did not take into account the fluctuations

$$p = p_{cr} + a(T - T_{cr}) + b(T - T_{cr})(\rho - \rho_{cr}) + c(\rho - \rho_{cr})^3 + \ldots,$$

and it is in this sense that we talk of the reestablishment of the van der Waals critical point in fast processes.

It is essential that below the critical point there exists in the van der Waals theory an instability relative to isothermal separation of the phases, but not to adiabatic phase separation. This was noted in the paper by Zel'dovich and Todes,[1] in connection with the problem of the rate of phase separation. It is obvious that an instability with respect only to the isothermal fluc-

tuations has a decisive influence also on the kinetics of the establishment of the fluctuations: what plays an important role is not the hydrodynamic instability, i.e., $\partial p/\partial \rho < 0$, but the thermal instability, namely $\partial p/\partial \rho|_T < 0$, whereas $\partial p/\partial \rho|_S > 0$. The point is that in the van der Waals theory the heat capacity at constant pressure C_p becomes infinite at the critical point and changes sign below it, in distinction from the constant-volume heat capacity C_v, which remains positive and finite. In order to be able to investigate a near-critical state, a decisive role may be played by the rarefaction shock wave which was experimentally observed at the Novosibirsk Institute for Thermophysics,[2] in agreement with Ref. 3.

A rarefaction shock wave makes possible in principle an instantaneous transition from above the critical point, a state which is stable and has small fluctuations, into a state near the critical point which is either stable or unstable. Investigating the behavior of the substance as a function of the distance from the front of the shock wave, one might be able to obtain data on the kinetics of the appearance of fluctuations and phase separation near a critical point.

In this context the method of light reflection from the surface of a shock wave in a condensed medium[4] may turn out to be useful. I use this occasion to express my gratitude to Academician S. S. Kutateladze and his collaborators at the Institute for Thermophysics of the Siberian Section of the USSR Academy of Sciences, for acquainting me with Ref. 2 before its publication.

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