XI. STATISTICAL THERMODYNAMICS[*]

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A. THE THERMODYNAMIC THEORY OF LINE SINGULARITIES IN ONE-COMPONENT SYSTEMS

According to the theory of thermodynamic stability, the experimentally observed λ-anomalies are manifestations of singularities in the thermodynamic formalism (1). Thus for a one-component system the second derivatives of the Gibbs function $G = G(p, T)$ tend to infinity, as the λ-line is approached in the pressure-temperature plane.

The phenomenological theory does not allow us to calculate the nature of the above-mentioned singularity. However, it is possible to develop a scheme for the analysis and correlation of the experimental data.

We shall tentatively assume that the Gibbs function can be represented as

$$G(p, T) = f(p) + h(T-T_\lambda) \tag{1}$$

where $f(p)$ is a slowly varying function representing the Gibbs function along the λ-line, and $h(t)$ is a singular function with the properties that

$$h(0) = 0, \quad h'(0) = \text{finite}, \quad h''(0) = -\infty \tag{2}$$

We confine ourselves to a region in the p,T-plane that is small enough to ensure that the slope of the λ-line is constant. We denote this slope by

$$\zeta = \left(\frac{dp}{dT}\right)_\lambda = \left(\frac{dT_\lambda}{dp}\right)^{-1} \tag{3}$$

The idea of separating the regular and singular parts of the thermodynamic functions, which was first advanced by Pippard (2), has been discussed in an earlier progress report (3). Pippard's point of departure was the entropy $S = S(p,T)$. However, it is advantageous to start instead from the Gibbs function, since this constitutes a fundamental equation and contains implicitly the answer to every thermostatic question.

The special form of Eq. 1 is the simplest that is consistent with the broad features of the experimental facts. An increased precision and an extended range of the experiments will presumably call for a more elaborate functional form.

We note that general thermodynamic principles bring about further restrictions for the functions $f(p)$ and $h(t)$:

$$f' > 0, \quad h' < 0, \quad f'' < 0, \quad h'' < 0 \tag{4}$$

where the primes denote differentiation.

We shall show that the significant thermostatic functions can be obtained from Eq. 1 through direct computation.

First we obtain the entropy and the volume:

$$S = -\left(\frac{\partial G}{\partial T}\right)_p = -f'\zeta - h' \tag{5}$$

$$V = \left(\frac{\partial G}{\partial p}\right)_T = f' - h'\frac{1}{\zeta} \tag{6}$$

The specific heat C_p, expansion coefficient a, and the isothermal compressibility κ_T are given by

$$\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T} = -f''\zeta^2 - h'' \tag{7}$$

$$-\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p = Va = f''\zeta - h''\frac{1}{\zeta} \tag{8}$$

$$-\left(\frac{\partial V}{\partial p}\right)_T = V\kappa_T = -f'' - h''\frac{1}{\zeta^2} \tag{9}$$

After eliminating the singular function h'' from Eqs. 7, 8, and 9 we obtain the analogs of Ehrenfest's relations:

$$Va\zeta = \frac{C_p}{T} + 2f''\zeta^2 \tag{10}$$

$$V\kappa_T\zeta = Va - 2f''\zeta \tag{11}$$

Eliminating f'', we have

$$\zeta^2 = \frac{C_p}{VT\kappa_T} \tag{12}$$

From Eqs. 7, 8, and 9 we obtain by standard thermodynamic methods the specific heat at constant volume, the ratio of the specific heats, and the adiabatic compressibility:

$$\frac{C_V}{T} = -\frac{4f''h''}{f'' + h''\frac{1}{\zeta^2}} \tag{13}$$

$$\gamma = \frac{C_p}{C_V} = \frac{(f'' \zeta + h'' \, 1/\zeta)^2}{4f'' h''} \tag{14}$$

$$V \kappa_S = \frac{1}{\gamma} V \kappa_T = - \frac{4f'' h''}{f'' \zeta^2 + h''} \tag{15}$$

It is apparent that $\gamma \to \infty$, and C_V and κ_S remain finite as $h'' \to -\infty$. This is in accordance with the general theory of stability.

The foregoing relations can be used to express the derivatives of the functions f and h in terms of measurable quantities. This can be achieved in a number of ways, and the resulting identities serve as checks for the consistency of the theory.

We shall now enumerate the formulas corresponding to the choice of V, S, ζ, C_p, and κ_S as measurable quantities:

$$f' = \frac{1}{2} V - \frac{1}{2\zeta} S \tag{16}$$

$$h' = - \frac{\zeta}{2} V - \frac{1}{2} S \tag{17}$$

$$- f'' \zeta^2 = \frac{C_p}{2T} \left[1 - \left(1 - \frac{V T \kappa_S \zeta^2}{C_p} \right)^{1/2} \right] \tag{18}$$

$$- h'' = \frac{C_p}{2T} \left[1 + \left(1 - \frac{V T \kappa_S \zeta^2}{C_p} \right)^{1/2} \right] \tag{19}$$

In the vicinity of the λ-line, with

$$\frac{V T \kappa_S \zeta^2}{C_p} \ll 1 \tag{20}$$

Eqs. 18 and 19 reduce to

$$- f'' \approx \frac{\kappa_S V}{4} \tag{21}$$

$$- h'' \approx \frac{C_p}{T} - \frac{V \kappa_S \zeta^2}{4} \tag{22}$$

Finally, we note that, for certain substances, such as liquid helium, $a < 0$ close to the λ-line. In such cases, there is a line in the p,T-diagram where $a = 0$, and hence according to Eq. 8

$$\left(\frac{dp}{dT}\right)_{\lambda}^{2} = \left(\frac{h''}{f''}\right)_{\alpha=0} \tag{23}$$

Equations 10-12 and 21-23 offer numerous possibilities for experimental verification, although the existing data are usually not accurate enough for an extensive check.

Pippard (2) has shown that the linear relation between α and C_p (Eq. 10) is in agreement with experiment. C. E. Chase and E. Maxwell, of Lincoln Laboratory, came to the same conclusion for helium (4).

It would be desirable to perform experiments that are designed to check the finer features of the theory.

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References

1. L. Tisza, Phys. Rev. 110, 587 (1958).

2. A. B. Pippard, Phil. Mag. (8) 1, 473 (1956).

3. L. Tisza, On the nature of the λ-line of liquid helium, Quarterly Progress Report No. 51, Oct. 15, 1958, p. 92.

4. Private communication, June 1958.

B. DISTRIBUTION FUNCTIONS IN STATISTICAL THERMODYNAMICS

Certain questions left open in the author's thesis (1) were solved, and the material of the thesis has been revised for future publication.

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References

1. P. M. Quay, Distribution functions in statistical thermodynamics, Ph.D. Thesis, Department of Physics, M.I.T., September 1958.