PHYSICAL REVIEW VOLUME 155, NUMBER 1 5 MARCH 1967

Generalization of the Maxwell Criterion for Van der Waals Equation

G. D. KAHL
USA Ballistic Research Laboratories, Aberdeen Proving Ground, Maryland

(Received 29 April 1966)

A method is proposed for generalizing the Maxwell equal-area rule for replacing isobaric isotherm segments in the condensing phase for van der Waals equation. The new vapor-pressure isotherm cuts off lobes unequal by an amount depending on the internal energies and differing specific heats of the liquid and vapor phases. Improved predictions of both liquid specific heat and entropy of vaporization for some metals are demonstrated by a simple example.

THE van der Waals equation is often used as a simple model description for a fluid consisting of two phases, such as liquid and vapor. In phase equilibrium, the van der Waals pressure function is replaced by a pressure function of temperature only, independent of volume, by a method due to Maxwell.[1] Despite widespread belief to the contrary, this Maxwell method is not unique, and a generalization of it permits a more realistic description of a two-phase fluid by van der Waals equation. Such a generalization will now be demonstrated for this state equation, while noting that similar arguments apply to other state equations.

In what follows, for unit mass of fluid the state variables P (pressure), E (internal energy), and S (entropy) are required to be continuous functions of the independent variables V (specific volume) and T (temperature). As a consequence, certain linear combinations of the state variables must likewise be continuous in (V,T) as, for example, $E+PV-TS=G$, (Gibbs free energy) and $E-TS=F$, (Helmholtz free energy). The combined thermodynamical law,

$$TdS=dE+PdV\,, \qquad (1)$$

must be satisfied along a reversible path. The van der Waals state equation is $P_W(V,T)$,

$$P_W=\hat{R}T/(V-b)-a/V^2, \quad V\geq b,\ T>0\,, \qquad (2)$$

where $\hat{R}$ is the gas constant per unit mass, and a and b are substantive constants. For $T<T_C$, where subscript C always denotes critical value, Eq. (2) yields physically unrealistic oscillatory pressure isotherm segments for a range of V. In this (V,T) region the functional form of Eq. (2) is discarded, and a new pressure function, $P_A(T)$, independent of V, replaces it so that the over-all pressure state surface is still continuous. The isotherm segments for $P_A(T)$ are isobaric. The (V,T) region of $P_A(T)$ is that of phase equilibrium, bounded on the small-volume side by $V_3(T)$, the "liquidus," and on the large-volume side by $V_1(T)$, the "vaporus"; also, $V_3(T_C)=V_1(T_C)$. The liquidus and vaporus lines separate the coexisting phase equilibrium state from the all-liquid and all-vapor states, respectively. The new continuous $P(V,T)$ surface consists of the van der Waals function $P_W(V,T)$ outside coexistence, and the vapor-pressure function, $P_A(T)$, within coexistence. The isobaric isotherm segments of $P_A(T)$ are reversible paths on which the differentials dP_A and dG are both zero; continuity then prescribes $P_W(V_3,T)=P_W(V_1,T)=P_A(T)$, and $G(V_3,T)=G(V_1,T)$.

The pressure state surface does not give either $E(V,T)$ or the specific heat $C_V=(\partial E/\partial T)_V$. However, requiring that S be an exact differential of V and T within a given (V,T) region leads to

$$(\partial E/\partial V)_T=T(\partial P/\partial T)_V-P \qquad (3)$$

in that region. From (3), the caloric state equation $E=E(V,T)$ can be found in the given region only to within an arbitrary function of temperature, which function cannot be further specified by thermodynamics alone. Nevertheless, some condition on this arbitrary function must be imposed at the region boundary, to insure continuity of E.

We consider three regions, the liquid, vapor, and coexistence regions. The liquid region (V_L,T_L), where the subscript L refers to the liquid phase, is assumed to consist of $\{b\leq V_L\leq V_3(T),T_L\leq T_C\}$. The gaseous region (V_G,T_G), with subscript G denoting gaseous phase, consists of both $(V_G,T_G\geq T_C)$ and $\{V_G>V_1(T),T\leq T_C\}$. Integrating Eq. (3) by using (2) in the liquid and vapor regions, and compacting the notation by letting subscript j be either L or G, results in

$$E_j(V_j,T_j)=-a/V_j+f_j(T_j)\,, \qquad (4)$$

where each $f_j(T_j)$ is some function of temperature only, with f_L and f_G not necessarily identical. Continuity of E requires in particular $f_L(T_C)=f_G(T_C)$ for $V\leq V_C$.

We now consider two reversible paths from the critical point (V_C,T_C). One path stays in the liquid region leading to a point (V_L,T_L); the other path stays in the vapor region and leads to the point (V_G,T_G). The entropy function on either of these paths is

$$S_j(V_j,T_j)=S_C+\hat{R}\left\{\ln\left[\frac{V_j-b}{V_C-b}\right]\right\} +\int_{T_C}^{T_j}\frac{1}{T}\frac{df_j}{dT}dT\,, \quad (T_j>0). \qquad (5)$$

This entropy function can be seen to satisfy the differential Eq. (1) by using Eqs. (2)–(4). For some

---

[1] E. Fermi, *Thermodynamics* (Dover Publications, Inc., New York, 1956), p. 71.

fixed $T<T_C$, the difference of the Gibbs free energy functions of the gas and liquid is

$$G_G(V_G,T)-G_L(V_L,T)=V_GP_W(V_G,T)-V_LP_W(V_L,T)$$
$$+f_G(T)-f_L(T)-[(a/V_G)-(a/V_L)]$$
$$-\hat{R}T[\ln(V_G-b)-\ln(V_L-b)]$$
$$-T\int_{T_C}^{T}\left\{\frac{df_G}{dT}-\frac{df_L}{dT}\right\}\frac{dT}{T}. \quad (6)$$

Both $P_W(V_G,T)$ and $P_W(V_L,T)$ are defined by the van der Waals function, Eq. (2). At the coexistence boundary, where $V_L=V_3(T)$ and $V_G=V_1(T)$, continuity requires $P_W(V_3,T)=P_W(V_1,T)=P_A(T)$ and $G_L(V_3,T)-G_G(V_1,T)=0$. Then from Eq. (6) we get, for fixed T,

$$\int_{V_3}^{V_1}P_WdV=P_A\{V_1-V_3\}+\phi(T),$$
$$P_W(V_1)=P_W(V_3)=P_A(T), \quad (7)$$
$$\phi(T)=f_G(T)-f_L(T)$$
$$+T\int_{T}^{T_C}\left\{\frac{df_G}{dT}-\frac{df_L}{dT}\right\}\frac{dT}{T}. \quad (8)$$

Reversibility was not required along any of the unstable oscillatory van der Waals isotherm segments, $P_W(V,T)$ for $\{V_3(T)<V(T)<V_1(T),T<T_C\}$, contrary to a widespread unacceptable justification for the Maxwell recipe, where $\phi(T)=0$.[1,2]

With $\phi(T)$ given, one can now find $P_A(T)$, $V_1(T)$, $V_3(T)$ and their temperature derivatives by satisfying Eq. (7); a numerical method must be used since (7) is transcendental. Values obtained can be used to determine all the thermodynamic properties of the equilibrium coexistence state. The magnitude of $\phi(T)$ must not be allowed so large that Eq. (7) cannot be satisfied; such a violation might appear likely for T near T_C, since the oscillatory van der Waals isotherm segments have decreasing oscillatory amplitudes as T approaches T_C. However, Eq. (8) forces $\phi(T)$ also to be smaller for these T, since the difference $f_G(T)-f_L(T)$ must be continuous for all T and is zero at T_C, as is $\phi(T_C)$.

When $\phi(T)$ is identically zero, Eq. (7) reduces to the well-known Maxwell criterion; then $f_L(T)=f_G(T)$, with the restrictive consequence that $C_V(\text{liq})=C_V(\text{vap})$.

When $f_L(T)\not\equiv f_G(T)$, a variety of realistic improvements in the model description occurs. The constant volume specific heats $C_V(\text{liq})$ and $C_V(\text{vap})$ can now differ; the particular specific heat, C_{SL}, along the saturated liquid line can assume more realistic values. The "equal-area lobe" rule must be abandoned, and the liquidus and vaporus lines take on different loci than for $\phi(T)$ identically zero. The thermodynamic properties such as heat and entropy of vaporization are thereby changed. The limiting values of various properties of the coexistence phase at the critical point will be altered.[3] If $\phi(T/T_C)$ is not the same function for different substances, then properties of phase equilibrium for different materials cannot be correlated completely by the reduced variables P/P_C, V/V_C, and T/T_C.

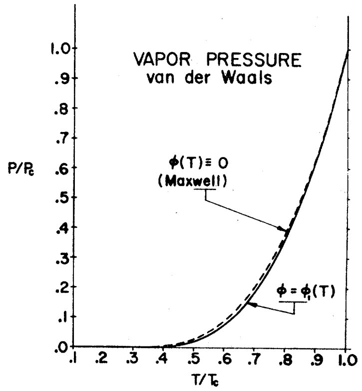

FIG. 1. Vapor pressure using the Maxwell criterion ($\phi=0$) and the example $\phi_1(T)\neq0$ $\{C_V(\text{liq})=\frac{5}{2}R,$ $C_V(\text{vap})=\frac{3}{2}R\}$.

As a simple illustrative example, we choose $f_G(T)=\frac{3}{2}\hat{R}T$, and $f_L(T)=\hat{R}\{\frac{5}{2}T-T_C\}$, thus assuming both $f_L(T)$ and $f_G(T)$ to be linear in T and coinciding at T_C. This choice might be realistic for T not too near T_C, but it admittedly leads to a possibly unrealistic discontinuity in C_V at T_C for $V<V_C$; other choices for $f_L(T)$ can easily be made which avoid the C_V discontinuity. Nevertheless, for this example, $\phi(T)=\phi_1(T)=\hat{R}\{T\ln(T/T_C)+T_C-T\}$, and these values were used in (7) to compute thermodynamic properties. Figures 1 and 2 show comparisons of the reduced vapor pressure and entropy of vaporization for both this $\phi_1(T)$ and for the Maxwell construction where $\phi(T)\equiv0$. The predicted vapor pressures are seen to be little affected, and either curve gives a fair description of the vapor

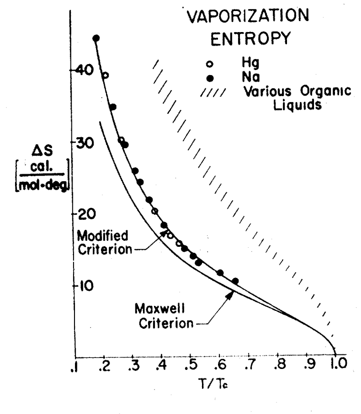

FIG. 2. Vaporization entropy (in cal/mole deg) for same criteria as in Fig. 1. Solid lines are theoretical prediction. Experimental data are those shown in Ref. 4.

---

[2] For a discussion, see H. N. V. Temperley, *Changes of State* (Cleaver-Hume Press, Ltd., London, 1956), p. 62.

[3] Limiting values for the example $\phi(T)\equiv0$ (Maxwell method) are given by R. E. Barieau, Phys. Rev. Letters, **16**, 297 (1966). It appears that a negative sign was omitted from Eq. (27) of this reference.

pressure for the metal Hg, as quoted in Ref. 4. However, as shown in Fig. 2, a much better prediction for vaporization entropy with this nonzero $\phi_1(T)$ is noted for the metals than for $\phi(T)\equiv 0$.

In conclusion, it should be noted that recent statistical mechanical treatments for a condensing fluid derive not only the van der Waals state equation, but also the Maxwell equal-area rule.[5–7] Thus, there seems to be some difference between these statistical treatments and the thermodynamic arguments given here. A resolution of this difference appears desirable.

These efforts are motivated by the need for a simple yet fairly accurate model for describing the state and dynamical behavior of superheated liquid metals over large temperature ranges, such as are encountered in exploding wire experiments.[8]

The assistance of D. C. Mylin and F. H. McIntosh in providing the numerical analysis is gratefully acknowledged.

---

[4] A. V. Grosse, J. Inorg. Nucl. Chem. **22**, 23 (1961).

[5] M. Kac, G. E. Uhlenbeck, and P. C. Hemmer, J. Math. Phys. 4, 216 (1963); 4, 229 (1963).

[6] N. G. van Kampen, Phys. Rev. **135**, A362 (1964).

[7] J. L. Lebowitz and O. Penrose, J. Math. Phys. **7**, 98 (1966).

[8] F. D. Bennett, G. D. Kahl, and E. H. Wedemeyer, in *Exploding Wires*, edited by W. G. Chace and H. K. Moore (Plenum Press, Inc., New York, 1964), Vol. 3, p. 65.

PHYSICAL REVIEW VOLUME 155, NUMBER 1 5 MARCH 1967

Long-Range Order in Superfluid Helium[*]

J. W. Kane[†]
Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York

AND

L. P. Kadanoff[‡]
Department of Physics, University of Illinois, Urbana, Illinois

(Received 16 September 1966)

Fluctuations in the phase of the condensate wave function appearing in the single-particle Green's function for a condensed Bose system are examined in one, two, and three dimensions. The results indicate that at nonzero temperatures, long-range order will appear only in three dimensions.

I. INTRODUCTION

THE appearance of a condensate in He^4 is accompanied by coherent, large-scale fluctuations in the phase of the condensate wave function. This phase coherence is responsible for the long-range order in the system. Physically this means that particles, far apart in space, are intimately correlated. Yang[1] has shown that these long-range correlations are manifest in the asymptotic behavior (for large spacial separations) of appropriate correlation functions of the system. In particular, these correlation functions, instead of vanishing as in a normal system, approach a nonzero constant. In He^4 the correlation function of interest is the single-particle Green's function, while in a superconductor it is the two-particle Green's function describing paired states. Rice[2] has argued that a superconducting transition will not occur in one or two dimensions. It is the purpose of this work to show that similar conclusions may apply to the He^4 system.

The behavior of the equilibrium, single-particle Green's function, $G(\mathbf{r},t;\mathbf{r}',t)$, as $|\mathbf{r}-\mathbf{r}'|\rightarrow\infty$, is determined entirely by the long-wavelength correlations. Information about these long-wavelength correlations is the content of the hydrodynamic equations. Kadanoff and Martin[3] have shown that one may obtain the long-wavelength, low-frequency correlation functions, which describe the linear response of a system to a disturbance, from the hydrodynamic equations. These response functions contain all of the information inherent in the linearized hydrodynamic equations.

The hydyrodynamic equations for superfluid helium are well known, they are just the two-fluid equations of Tisza[4] and Landau.[5] The corresponding response functions have been obtained by Hohenberg and Martin.[6]

---

[*] Work supported by the National Science Foundation under Contract Nos. GP-5517 and GP-4937.

[†] Parts of this paper are based on a thesis submitted to the University of Illinois in partial fulfillment of the requirements of the Ph.D. degree.

[‡] A. P. Sloan Foundation Fellow.

[1] C. N. Yang, Rev. Mod. Phys. **34**, 694 (1962).

[2] T. M. Rice [Phys. Rev. **140**, A1889 (1965)] reached these conclusions by using the Landau-Ginzburg molecular-field approximation for the free energy.

[3] L. P. Kadanoff and P. C. Martin, Ann. Phys. (N. Y.) **24**, 419 (1963).

[4] L. Tisza, Nature **141**, 913 (1938).

[5] L. Landau, J. Phys. USSR **5**, 71 (1941). A translation may be found in I. M. Khalatnikov, *Introduction to the Theory of Superfluidity* (W. A. Benjamin, Inc., New York, 1965).

[6] P. C. Hohenberg and P. C. Martin, Phys. Rev. Letters **12**, 69 (1964); Ann. Phys. (N. Y.) 34, 291 (1965).