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On Phase Changes of Bose-Einstein Fluid Models

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It is shown that all Bose-Einstein (B.E.) fluid models investigated thus far undergo first-order transformations in phase space. The ideal fluid condenses smoothly, e.g., without any possibility of supersaturation, insofar as its thermodynamic characteristic functions and their first derivatives, with respect to the independent variables, are continuous along the transition or saturation curve. The non-ideal B.E. fluids considered, in which attractive interatomic forces averaged over the volume of the fluid are assumed to operate, undergo sudden condensation strictly similar to that exhibited by ordinary fluids in coordinate space. This process is accompanied by the occurrence of discontinuities of the first derivatives of the characteristic functions. By introducing a suitable repulsive interatomic force, smeared over the volume of the fluid, the smooth condensation of the ideal fluid is changed to a phase transformation of the third order. Here the second derivatives of the characteristic functions exhibit discontinuities along the transformation curve. The same interatomic force lifts the order of the sudden first-order transformation by changing it to a second-order one. This is accompanied by the appearance of the lambda-point type discontinuity of the constant pressure heat capacity along the transition or lambda line. The interplay of forces of parallel and opposing tendencies in modifying the nature of a phase transformation without changing its order and in lifting or lowering their order is thus brought out in these studies over B.E. fluid models. The bearing of these results on the problems connected with the thermal properties of liquid helium is touched upon briefly.

INTRODUCTION

THE possible intervention of the Bose-Einstein (B.E.) condensation phenomenon in the peculiar transition liquid He I→liquid He II, as first suggested by London[1] has led us to investigate different B.E. fluid models. The ideal fluid undergoes what may be called a smooth condensation process in phase space. In this smooth transformation, beside the thermodynamic characteristic functions, their first derivatives with respect to the chosen independent variables remain also continuous at the transition. For instance, the heat capacity at constant volume remains continuous at the transition line but has a break, i.e., its temperature derivative is discontinuous. In the modified B.E. fluid models,[2,3] the phase changes exhibited were strictly of the ordinary first-order type. The condensation process shown by these fluids resembled strictly that undergone by ordinary fluids in coordiate space. Since the transformation undergone by liquid He is of the second order, these models are even formally unsatisfactory for its description. It is intended here to investigate further the B.E. fluid models exhibiting first-order phase changes and to clarify and point out some of their properties which were not considered before. A modification of the assumed properties of these models will then be described. This modification has the effect of lifting the order of the phase change from the first to the second or third order. Apart from the theoretical interest of the B.E. fluid models which allow a complete and rigorous analysis of their phase transformations, the study of lifting or lowering the order of phase changes may also shed some light on some of the more elementary aspects of other cooperative phenomena.

I. THE SMOOTH CONDENSATION PROCESS OF THE IDEAL B.E. FLUID

The proof that the ideal B.E. fluid undergoes a smooth condensation process is already apparent on the thermodynamic diagram of this fluid in the pressure-volume plane.[1,4] For volumes less than the saturation volume, at a given temperature, the pressure becomes independent of the volume, e.g., the isothermals coincide with the isobars in the mixed two-phase or condensation region. The smoothness of the condensation of the ideal B.E. fluid is also apparent on the shape of its isothermals. These reach the saturation or

* Now with the Federal Telecommunication Laboratories, Inc., New York, New York.
[1] F. London, Nature **141**, 643 (1938); Phys. Rev. **54**, 947 (1938).
[2] F. London, J. Phys. Chem. **43**, 49 (1939).
[3] L. Goldstein, J. Chem. Phys. **9**, 472 (1941).
[4] B. Kahn, Dissertation, Utrecht (1938).

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transition line with a horizontal slope. The isothermal compressibility of the ideal fluid tends in a continuous way toward infinity as the fluid approaches saturation and remains infinite in the condensation region. It is equally worth noting in this connection that the zero slope of the isothermals of the non-condensed saturated ideal fluid is associated with a maximum of these curves. One has indeed for the isothermal curves of the fluid of spinless atoms:

$$\begin{aligned} p_+ &= NkTG(\alpha)/VF(\alpha), \quad V \geqslant V_0 \\ p_- &= \frac{NkT}{V}\left(\frac{T}{T_0}\right)^{\frac{3}{2}} G(0)/F(0), \quad V \leqslant V_0. \end{aligned} \tag{1}$$

Here V_0 is the condensation volume at temperature T, T_0 is the condensation temperature at volume V defined, respectively, by

$$\begin{aligned} V_0 &= Nh^3/F(0)(2\pi mkT)^{\frac{3}{2}}; \\ T_0 &= \frac{h^2}{2\pi mk}\left(\frac{N}{VF(0)}\right)^{\frac{2}{3}}. \end{aligned} \tag{2}$$

In (1) and (2), α is the negative Gibbs potential per atom of mass m, divided by kT, N is the total number of atoms forming the fluid, and the functions $G(x)$, $F(x)$ are generalized ζ-functions;

$$\begin{aligned} &G(x) = \sum_{n=1}^{\infty} e^{-nx}/n^{5/2}; && F(x) = -dG/dx; \\ &E(x) = -dF/dx; && D(x) = -dE/dx, \text{ etc.} \\ &G(0) = \zeta(5/2) = 1.341; && F(0) = \zeta(3/2) = 2.612; \\ &E(x) \underset{x \ll 1}{\cong} \pi^{\frac{1}{2}}/x^{\frac{1}{2}}; && D(x) \underset{x \ll 1}{\cong} \pi^{\frac{1}{2}}/2x^{\frac{3}{2}}. \end{aligned} \tag{3}$$

One finds then easily

$$\begin{aligned} &\lim_{V \to V_0} (\partial p_+/\partial V)_T = 0; \\ &(\partial p_-/\partial V)_{T \leq T_0} = 0; \\ &\lim_{V \to V_0} (\partial^2 p_+/\partial V^2)_T = \lim_{\alpha \to 0} \left(-\frac{NkT}{V_0^3}\right)\frac{(F(\alpha))^2 D(\alpha)}{(E(\alpha))^3} \\ &\qquad = -1.09NkT/V_0^3, \end{aligned} \tag{4}$$

which shows that the isothermal curves $p_+(V)_T$ have a maximum at the saturation line. In other words, an extrapolation of the isothermal $p_+(V)_T$ of the non-condensed fluid into the condensation region leads to a physically inadmissible portion of the curve along which the pressure decreases with decreasing volume. A physical interpretation of the vanishing slope of the isothermals $p_+(V)_T$ at the saturation line and the impossibility of their continuation into the two-phase region corresponds to the absence of supersaturation in phase space where the condensation of the ideal fluid takes place. In regard to this, the condensation of the ideal B.E. fluid might be compared to what seems to happen with ordinary fluids between the temperatures T_m of disappearance of the meniscus and the critical temperature T_c.[5] The experimental evidence for the existence of a temperature T_m less than T_c is rather scarce.[5] The experimental results favor in the range (T_m, T_c) the same trend of the isothermal curves of ordinary fluids as that shown by the ideal B.E. fluid. The interpretation of the condensation of ordinary fluids in the temperature interval (T_m, T_c) corresponds to the absence of surface tension. Now, in an ideal B.E. fluid where there are no forces acting in coordinate space one would naturally expect that surface forces be absent and that the condensation in phase space should proceed without the intervention of surface tension. It may be recalled in this connection that clusters of 3, 4 or more atoms play but a negligible role in the condensation of the ideal B.E. fluid.[6] It seems, therefore, that there is here an interesting argument favoring the interpretation given by Mayer[5] to the condensation of ordinary fluids in the temperature interval (T_m, T_c) provided that further experimental evidence be accumulated assuring the existence of a temperature T_m less than T_c.

This condensation accompanied by the above-mentioned behavior of the isothermals may be considered as a continuous or smooth first-order phase change, in which only the second derivatives of the characteristic functions of the fluid are discontinuous. One has indeed

$$\Delta(\partial p/\partial V)_{T,V=V_0} = (\partial p_+/dV)_{T,V=V_0} - (\partial p_-/\partial V)_{T,V=V_0} = 0. \tag{5}$$

Similarly, one finds that, C_v denoting the constant volume heat capacity,

$$\Delta C_v = C_{v+}(V_0) - C_{v-}(V_0) = 0. \tag{6}$$

[5] J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley and Sons, Inc., New York, 1940), pp. 295–317.
[6] L. Goldstein, J. Chem. Phys. **10**, 295 (1942).

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But

$$\Delta(\partial^2 p/\partial V^2)_T = \lim_{\alpha\to 0}\left(-\frac{NkT}{V_0^3}\right)\frac{(F(\alpha))^2 D(\alpha)}{(E(\alpha))^3} = -1.09NkT/V_0^3. \quad (7)$$

We recall here that, E being the total energy of the fluid,

$$C_{v+}/Nk = \frac{1}{Nk}\frac{dE_+}{dT} = \frac{15}{4}G(\alpha)/F(\alpha) - \frac{9}{4}F(\alpha)/E(\alpha),$$
$$C_{v-}/Nk = \frac{1}{Nk}\frac{dE_-}{dT} = \frac{15}{4}\left(\frac{T}{T_0}\right)^{\frac{3}{2}} G(0)/F(0), \quad (8)$$

and, consequently,

$$\Delta\left(\frac{dC_v}{dT}\right) = \Delta\left(\frac{d^2E}{dT^2}\right) = -\frac{27}{8}\frac{Nk}{T}\lim_{\alpha\to 0}\left(\frac{(F(\alpha))^2 D(\alpha)}{(E(\alpha))^3}\right) = -3.66Nk/T, \quad (9)$$

using the asymptotic values of $D(x)$ and $E(x)$ as given by (3).

Finally the trend of variation of the constant pressure heat capacity is worth noting. One finds

$$\frac{C_{p+}}{Nk} = \frac{5}{4}\frac{G(\alpha)}{F(\alpha)}5\left[\frac{G(\alpha)E(\alpha)}{(F(\alpha))^2} - 3\right], \quad (10)$$

showing that as the fluid approaches saturation, e.g., as $\alpha\to 0$, $C_{p+}\to\infty$ as $1/\alpha^{\frac{1}{2}}$ according to the asymptotic value of $E(\alpha)$ for $\alpha \ll 1$. Clearly, in the condensation region C_{p-} remains infinite.

2. THE ORDINARY CONDENSATION PROCESS IN PHASE SPACE OF SOME B.E. FLUID MODELS

In contrast with the preceding behavior of an ideal B.E. fluid, the modified fluid models considered thus far undergo condensation in phase space as do ordinary fluids in coordinate space. They exhibit supersaturation in phase space and their heat capacity at constant volume has a lambda point along the saturation or transition curve as is the case with ordinary fluids along their vapor saturation curve, at volumes larger than their critical volume. Of these modified B.E. fluid models the one studied before[3] seems to have the simplest formalism generalizing that of the ideal fluid. It is assumed that the influence of the $(N-1)$ atoms of the system acting on the particular atom in question can be described by a potential energy well independent of the volume and temperature. Any given atom can have one or several discrete levels in this well. The generality of the model is not reduced, however, by assuming that there is but one level $-E_0$ extending the individual free particle level spectrum of the ideal fluid. The correspondingly increased cohesion in coordinate space, as expected, hastens the condensation process in phase space. One finds thus that, at a given volume, the modified fluid starts condensing at a higher temperature, while at a given temperature it starts condensing at a larger volume than the ideal fluid.

The formulas giving the pressure of this fluid above and below the transition temperature, denoted here by T_f, are the following:

$$p_+ = \frac{NkT}{V}\frac{G\left(\alpha' + \frac{E_0}{kT}\right)}{F\left(\alpha' + \frac{E_0}{kT}\right)}, \quad T \geqslant T_f$$
$$p_- = \frac{NkT}{V}\left(\frac{T}{T_f}\right)^{\frac{3}{2}}\frac{G(E_0/kT)}{F(E_0/kT_f)}, \quad T \leqslant T_f \quad (11)$$

since now the statistical parameter α has to satisfy the inequality

$$\alpha \geqslant E_0/kT \quad \text{or} \quad \alpha' = \alpha - \frac{E_0}{kT} \geqslant 0.$$

For $T \geqslant T_f \geqslant T_0$ the family of isothermals of the ideal and modified fluids are identical.

The saturation curve whose equation is

$$p_+(V)_{T_f} = p_-(V)_{T_f} = \frac{NkT}{V}G(E_0/kT_f)/F(E_0/kT_f), \quad (12)$$

is now displaced to larger volumes. The combined thermodynamic diagrams of the ideal and modified B.E. fluid models, in the $p-v$ representation, are given in Fig. 1. The energy of the system is given by

$$E_+ = \frac{3}{2}\frac{V}{h^3}(2\pi mkT)^{\frac{3}{2}}kTG\left(\alpha' + \frac{E_0}{kT}\right), \quad T \geqslant T_f$$
$$E_- = -N_0E_0 + \frac{3}{2}\frac{V}{h^3}(2\pi mkT)^{\frac{3}{2}}kTG(E_0/kT), \quad T \leqslant T_f \quad (13)$$

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where N_0 is the number of condensed particles, or

$$N_0 = 1/(e^{\alpha'}-1)$$
$$= N\left[1-\left(\frac{T}{T_f}\right)^{\frac{3}{2}}\frac{F(E_0/kT)}{F(E_0/kT_f)}\right]; \qquad (14)$$

and $\alpha' \sim 0$ for $T \leqslant T_f$.*

The constant volume heat capacities are, as a simple calculation shows,

$$\frac{C_{v+}}{Nk} = \frac{15}{4}\frac{G\left(\alpha'+\frac{E_0}{kT}\right)}{F\left(\alpha'+\frac{E_0}{kT}\right)} - \frac{9}{4}\frac{F\left(\alpha'+\frac{E_0}{kT}\right)}{E\left(\alpha'+\frac{E_0}{kT}\right)}, \qquad (15)$$

$$\frac{C_{v-}}{Nk} = \frac{15}{4}\frac{G(E_0/kT)}{F(E_0/kT_f)} + 3\left(\frac{E_0}{kT}\right)\left(\frac{T}{T_f}\right)^{\frac{3}{2}}\frac{F(E_0/kT)}{F(E_0/kT_f)} + \left(\frac{E_0}{kT}\right)^2\left(\frac{T}{T_f}\right)^{\frac{3}{2}}\frac{E(E_0/kT)}{F(E_0/kT_f)}.$$

Therefore,

$$\frac{\Delta C_v}{Nk} = \frac{(C_{v+}-C_{v-})_{T_f}}{Nk}$$
$$= -\frac{9}{4}\frac{F(E_0/kT_f)}{E(E_0/kT_f)} - 3\left(\frac{E_0}{kT_f}\right) - \left(\frac{E_0}{kT_f}\right)^2\frac{E(E_0/kT_f)}{F(E_0/kT_f)}, \qquad (16)$$

which is negative and indicates that the constant volume heat capacity has a lambda point along the transition line.

The constant pressure heat capacity is also discontinuous but its discontinuity is negatively infinite. One finds, indeed, that

$$\frac{C_{p+}}{Nk} = \frac{C_{v+}}{Nk} + \frac{25}{4}\frac{(G(x))^2E(x)}{(F(x))^3} - \frac{15}{2}\frac{G(x)}{F(x)} + \frac{9}{4}\frac{F(x)}{E(x)};$$
$$x = \alpha' + \frac{E_0}{kT}. \qquad (17)$$

C_{p+} is thus finite at the saturation line, for $T = T_f$, but jumps to infinity in the condensation region.

* In reference 3, the energy E_+ included also the energy of the very few atoms which were in the discrete level $-E_0$. However, in order to obtain heat capacities with the discontinuities predicted by thermodynamics it is necessary to omit this energy term in (13). The ΔC_v given in reference 3 is thus incomplete.

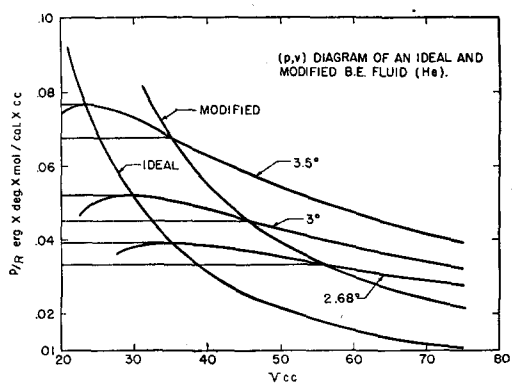

FIG. 1.

This behavior is characteristic to ordinary fluids undergoing condensation or, in general, a regular first-order phase change. One finds, indeed, that in this case and along the transition line

$$\Delta C_v = -T\frac{dV}{dT}\Delta\left(\frac{\partial p}{\partial T}\right)_V, \qquad (18)$$

in which C_{v-} is the constant volume heat capacity of the mixed phase, dV/dT is a derivative taken along the transition line, and $(\partial p/\partial T)_V$ is to be obtained from the equation of state of the fluid. This general thermodynamic relationship, of the Ehrenfest type, is indeed satisfied when ordinary condensation takes place. Using numerical data available for water[7] we have computed and constructed c_v curves around the vapor saturation curve, i.e., for volumes larger than the critical volume. Figure 2 gives typical Δc_v discontinuities for water. It is seen that Δc_v decreases with increasing temperature.

It is worth noting here that the modified B.E. fluids are the only fluids whose formalism allows a rigorous computation of the ΔC_v discontinuity and provides thus the only known case where a direct statistical checking of the thermodynamic formula (18) is at hand.

It will be shown in the next section that by introducing interatomic forces of the repulsive type, it is possible to lift the order of the phase change of such B.E. fluid models.

[7] Cf. N. E. Dorsey, *Properties of Ordinary Water Substance* (Reinhold Publishing Corporation, New York, 1940).

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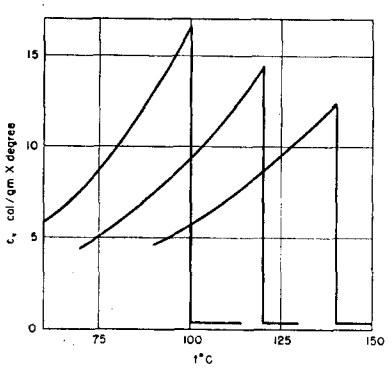

FIG. 2.

3. SECOND- AND THIRD-ORDER TRANSFORMATIONS IN PHASE SPACE

Consider a B.E. fluid model in which the total potential energy due to repulsion in coordinate space can be represented by a term of the type*

$$U(V)=a/V,$$

V being the total volume at the disposal of the fluid. The constant a will be considered independent of the temperature in a first approximation. In this model, the number of individual energy levels of spinless atoms associated with the momentum range $(p, p+dp)$ is, at temperature T,

$$dn(p)=\frac{4\pi V}{h^3}\frac{p^2dp}{\exp\left[\alpha+\left(U+\frac{p^2}{2m}\right)\Big/kT\right]-1}. \quad (19)$$

With

$$\alpha'=\alpha+\frac{U}{kT},$$

one finds again that at volume V the fluid begins to undergo a phase change at temperature T_0 given by Eq. (2). Similarly, at any given temperature T, the fluid undergoes a phase change at a volume V_0 given also by (2). It can also be shown without difficulty that

$$\begin{aligned} p_+&=p_{id+}-N\frac{\partial U}{\partial V},\\ p_-&=p_{id-}-N\frac{\partial U}{\partial V}, \end{aligned} \quad (20)$$

* It can be seen without difficulty that the results of this section are quite general insofar as the potential energy function $U(V)$ may contain both attractive and repulsive temperature independent terms. The choice of $U(V)$ is restricted by the trivial condition that the model so constructed behave in a physically admissible way, i.e., its compressibility has to be normal.

where p_{id} is the pressure of the ideal fluid. Since $U(V)$ is assumed to be independent of the temperature, the constant volume heat capacity of this non-ideal B.E. fluid is the same as that of the ideal fluid. The pressure, however, is still increasing with decreasing volume at temperatures and volumes less than their transition values, in the transition region. The introduction of a volume dependent repulsive force field of the atoms changes completely the nature of the phase transition of the originally ideal fluid. The modified fluid does not undergo a first-order phase change. This is already visible on the trend of variation of the isothermal curves in the transition region. In order to establish the nature of the phase change it is convenient to study the constant pressure heat capacity of the model.

One obtains after a simple calculation, $C_{v,id}$ denoting the constant volume heat capacity of the ideal fluid,

$$\begin{aligned} \frac{C_{p+}}{Nk}&=\frac{C_{v,id}}{Nk}+\frac{1}{4}\frac{\left[5\frac{G(\alpha')}{F(\alpha')}-3\frac{F(\alpha')}{E(\alpha')}\right]^2}{\frac{F(\alpha')}{E(\alpha')}+\frac{2a}{kTV}}, \quad T\geqslant T_0\\ \frac{C_{p-}}{Nk}&=\frac{C_{v,id-}}{Nk}+\frac{25}{8}\left(\frac{T}{T_0}\right)^3\frac{(G(0)/F(0))^2}{a/kTV}. \quad T\leqslant T_0 \end{aligned} \quad (21)$$

It is seen now that, in the first place, the constant pressure heat capacity is always finite and continuous along the transition line, with a break, since $(dC_p/dT)_{T_0}$ is discontinuous. One has, indeed,

$$\left(\frac{C_{p+}}{Nk}\right)_{T_0}=\left(\frac{C_{v,id+}}{Nk}\right)_{T_0}+\frac{25}{8}\frac{(G(0)/F(0))^2}{a/kT_0V},$$

$$\left(\frac{C_{p-}}{Nk}\right)_{T_0}=\left(\frac{C_{v,id-}}{Nk}\right)_{T_0}+\frac{25}{8}\frac{(G(0)/F(0))^2}{a/kT_0V},$$

and

$$\begin{aligned} \Delta C_p&=(C_{p+}-C_{p-})_{T_0}\\ &=(C_{v,id+}-C_{v,id-})_{T_0}=0. \end{aligned} \quad (22)$$

In this model, therefore, both the constant volume and constant pressure heat capacities are continuous with a break, e.g., their temperature derivatives are discontinuous along the transition line. The smooth condensation process undergone by the ideal B.E. fluid is changed by the re-

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pulsive interatomic potential energy smeared over the whole volume of the fluid. The transition, in phase space, of the modified fluid is of the third order.

The question arises now under what conditions will a second-order phase change occur, e.g., a transition which is accompanied by a lambda-point type discontinuity of the constant pressure heat capacity of the fluid along the transition line. The answer to this question can be given at once using fluid models in which the forces between atoms are represented by the potential energy terms involved in the above discussed models. Suppose, indeed, that in a B.E. fluid model there is an attractive force field represented by the individual negative energy level $-E_0$ and a repulsive force field represented by a term a/V considered above. One then finds that such a B.E. fluid model has a constant volume heat capacity given by Eq. (15), as if the repulsive force field were absent. However, the work function of the fluid is now increased by the total potential energy term Na/V and the pressure is

$$\begin{aligned} p_+ &= p_{no+} + Na/V^2, \\ p_- &= p_{no-} + Na/V^2, \end{aligned} \tag{23}$$

where p_{no+} and p_{no-} are the pressures above and below the transition temperature of that fluid in which there are no repulsive forces. The pressures p_{no+} and p_{no-} are given by Eq. (11). It is clear from Eq. (23) that this fluid model has no coincident isobars and isothermals in the transition region. The repulsive forces giving rise to the pressure Na/V^2 have prevented the fluid from undergoing a first-order condensation as was the case above.

A long but straightforward calculation leads to the following expressions of the constant pressure heat capacity of this model:

$$\begin{aligned} \frac{C_{p+}}{Nk} &= \frac{C_{v+}}{Nk} + \Phi(x) \Big/ \left[\frac{F(x)}{E(x)} + \frac{2a}{kTV}\right]; \\ & \qquad x = \alpha' + \frac{E_0}{kT}; \quad T \geqslant T_f \\ \frac{C_{p-}}{Nk} &= \frac{C_{v-}}{Nk} + \left(\frac{T}{T_f}\right)^3 \Psi\left(\frac{E_0}{kT}, \frac{E_0}{kT_f}\right) \Big/ \frac{2a}{kTV}. \quad T \leqslant T_f \end{aligned} \tag{24}$$

The functions Φ and Ψ are given by the following expressions:

$$\begin{aligned} \Phi(x) &= \frac{25}{4}\left(\frac{G(x)}{F(x)}\right)^2 + \frac{9}{4}\left(\frac{F(x)}{E(x)}\right)^2 - \frac{15}{2}\frac{G(x)}{E(x)}; \\ & \qquad x = \alpha' + \frac{E_0}{kT}, \\ \Psi(y, z) &= \frac{25}{4}\left(\frac{G(y)}{F(z)}\right)^2 + 2y\frac{G(y)}{F(z)} + y^2\left(\frac{F(y)}{F(z)}\right)^2; \\ & \qquad y = \frac{E_0}{kT}; \quad z = \frac{E_0}{kT_f}. \end{aligned} \tag{25}$$

The constant volume heat capacity C_{v+} and C_{v-} are given by Eqs. (15).

A study of the functions Φ and Ψ shows that

$$(C_{p-})_{T_f} > (C_{p+})_{T_f}$$

or

$$\Delta C_p = (C_{p+} - C_{p-})_{T_0} < 0, \tag{26}$$

ΔC_p is always finite but negative.

One has thus the following result. Consider any B.E. fluid composed of atoms whose interaction in coordinate space can be represented by an average constant attractive potential energy term $-E_0$ and an average repulsive potential energy term a/V, smeared over the whole volume V of the fluid, and independent of the temperature. Such fluid models exhibit a second-order phase change in which the constant pressure heat capacity has a lambda-point discontinuity along the transition line of the fluid. The repulsive force field, averaged over the whole volume of the fluid, has lifted the order of the phase change. If in the absence of this repulsive field the B.E. fluid is ideal and exhibits a smooth first-order condensation in phase space, the switching on of the repulsive forces causes the fluid to undergo instead a third-order transition in phase space. This means continuity of the energy, entropy, or any other characteristic function, with their first derivatives along the transition line. The introduction of the repulsive force field in a B.E. fluid model undergoing in its absence a sudden first-order transformation in phase space, similar to that exhibited by ordinary fluids in coordinate space, leads to a second-order transformation in phase space. This is characterized by the continuity of the characteristic functions, which have discontinuous first derivatives along the transition line.

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The only actual liquid exhibiting a peculiar second-order phase change is liquid helium. And a possible explanation of the thermal properties of this liquid assimilating it to a kind of B.E. fluid has been repeatedly suggested by London.[1,2] The formalism necessary to describe the thermal properties of a B.E. fluid undergoing a second-order phase change in phase space would have to be somewhat similar to the formalism of the just discussed B.E. fluid model. However, as pointed out already,[3] the preceding models behave rather in a normal way below their transition line. Their expansion and pressure coefficients, $(\partial V/\partial T)_p$ and $(\partial p/\partial T)_V$, are positive in contrast with those of liquid He II. It is interesting to recall in this connection that in a recent investigation London[8] was lead to a qualitative argument accounting for this anomalous behavior of liquid He II on the very basis of a B.E. fluid model.

The difficulties inherent in the theoretical treatment of liquids are still further increased for a quantum liquid like He II. Here, the wave-length associated with the average thermal motion of the atoms may become of the same order of magnitude as the macroscopic dimensions of the vessel containing the liquid. This led Landau[9] to build up a continuum type or hydrodynamic model for this liquid. It is as yet not clear whether the anomalous thermal properties of liquid He II in bulk are correctly accounted for by this hydrodynamic model.

We should like finally to add here that a closer analysis of phase changes of higher order observed in cooperative phenomena might disclose also the interplay of forces of opposing tendencies as those existing in the B.E. fluid models studied here. In particular, the raising or lowering of the order of a phase change might be attributed to the intervention of forces of opposing nature.

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The Non-Planar Vibrations of Benzene

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A thorough normal coordinate treatment has been carried out for the non-planar vibrations of benzene and its deuterium derivatives. The analysis has led to a critical survey of the assignments, and has furnished strong independent support for those advanced by Pitzer and Scott. It has also furnished values for all eight force constants of the complete harmonic potential function. For four of the constants two sets of values were obtained, both of which are physically reasonable and which reproduce the frequencies equally well. It was not possible to decide between them. The force constants were then used to calculate frequencies for the various deuterobenzenes. Nearly sixty such frequencies were evaluated, of which about forty could be checked against experiment. With four exceptions the errors are less than 1.5 percent. Lastly, certain valence-force constants pertaining to hydrogen vibrations have been determined.

INTRODUCTION

BENZENE has been the subject of several normal coordinate treatments.[1–9] The first was carried out by Wilson,[1] who suggested a simplified potential function with six force con-

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