Maxwell Construction and Phase Transitions in Fermi Fluids *, **

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We apply elementary thermodynamics to Fermi fluids with a view to establishing the conditions for liquid-gas phase transitions at absolute zero. Particular attention is paid to the case of single-component nuclear matter (both charge-symmetric and pure neutronic cases).

1. Introduction

The use of the Maxwell construction, in conjunction with the van der Waals equation of state, to represent the liquefaction of gases is familiar to all students of thermodynamics. The present paper is concerned with the application of the Maxwell construction to Fermi fluids, and in particular with the question as to whether or not they can undergo a liquid-gas phase transition at $T=0$. We shall be particularly interested in the case of nuclear matter in the low-energy domain, where there can be no question of any internal degrees of freedom of the nucleon being excited. Some of our considerations will also be relevant to fluid ^{3}He.

Liquid-gas phase transitions of nuclear matter certainly take place in collapsing stars, where nuclei become more and more neutron-rich as they capture high-energy degenerate electrons. Eventually, the neutron-drip line is reached and neutrons leak out, forming a vapour that is in equilibrium with the residual nuclei, which may be regarded as forming liquid droplets. However, this phase transition, which can occur even at absolute zero, $T=0$, is rather difficult to compare with that of a van der Waals gas, since it takes place in what is essentially a two-component system: the neutron/proton ratio is quite different in the gas and liquid phases.

Our considerations of nuclear matter will thus be limited to the single-component situation. Two different cases of this can be envisaged, although neither corresponds exactly to anything that can occur in reality.

The first of these is the pure neutron gas, which would exist in the centre of neutron stars if the weak interaction could be shut off; in fact, neutron-star matter has about 5% protons, neutralized by electrons. Whether or not phase transitions can occur in the system is not clear at the present time: we address this question at the end of Section 3.

The other case is that of symmetric nuclear matter, i.e., nuclear matter having equal densities of neutrons and protons, with the Coulomb interaction switched off. While such a system can clearly exist only in the minds of theoreticians, it nevertheless served as a model of the volume term a_v in the semi-empirical mass formula of von Weizsäcker and Bethe, which expresses the energy per nucleon in a nucleus with Z protons and N neutrons $(A=N+Z)$ as

$$e = a_v + a_{sym} \{(N-Z)/A\}^2 + a_{sf} A^{-1/3}$$
$$+ a_{coul} Z^2 A^{-4/3} + \ldots \qquad (1)$$

Here the second term refers to the symmetry energy, the third to the surface energy, and the fourth to the Coulomb energy (see, for example, [1] for a discussion of this and some elementary aspects of nuclear astrophysics). It is in this way that the properties of this hypothetical system can be determined from those of real nuclei: the energy per nucleon is $e=a_v \cong -16.0$ MeV and the density (inferred from that of real nuclei) is $\rho \cong 0.16$ nucleon fm^{-3}.

Although symmetrical nuclear matter contains both neutrons and protons it can nevertheless be regarded as a single-component system, since it will always be energetically favorable for the neutron/proton ratio to be everywhere equal to unity, if the total numbers allow this. Treated in this way, it is found theoretically that symmetric nuclear matter can indeed undergo a liquid-gas phase transition at finite temperatures, $T>0$ (see Section 3). Experimentally, there is some evidence for such phase tran-

sitions (see, for example, [2]), but the interpretation is complicated by surface and Coulomb effects.

However, our main concern in this paper is with the possibility of phase transitions in Fermi fluids at $T=0$. The elucidation of this question involves an instructive application of elementary thermodynamic principles.

2. Van der Waals Equation of State for Molecular Gases

We recall in this section some of the relevant properties of the van der Waals equation of state for real molecular gases,

$$P = RT/(v-b) - a/v^2. \tag{2}$$

Here P is the pressure, v the molar volume, and a and b are characteristic constants for the gas in question. To be specific, we consider the case of O_2, for which optimal fits to the data are given by $a \cong 1.38 \times 10^5$ J · m^3 · kmole^{-2}, $b \cong 3.18 \times 10^2$ m^3 · kmole^{-1} (see, for example, Sears and Salinger [3]).

Figure 1 (a–c), respectively, show isotherms for three distinct situations, according to the temperature: a) $T > 8a/(27 R b) \equiv T_c$, the critical temperature b) $T_c > T > a/(4 R b)$, c) $T < a/(4 R b)$. In the first case the isotherm is monotonic and no phase transition is possible, while in each of the last two cases the isotherm is non-monotonic, and a phase transition occurs along the straight lines ABC. These lines are constructed according to the well known rule of Maxwell: the areas above and below the line, bounded by the van der Waals isotherm, are equal. (The validity of this construction follows from the condition that for equilib-

rium between the two phases their respective pressures and chemical potentials must be equal: see, for example, Callen [4] for the complete proof.) The straight lines ABC, along which the phase transition normally occurs, are not, of course, represented by the van der Waals equation (2), while the curves ABC (broken), which are represented by this equation, do not correspond to stable states of the fluid: the portions with negative slope are realisable as metastable states, while whose with positive slope cannot be realized at all.

The distinction between cases (b) and (c) is that in the latter the pressure can become negative. This can be physically interpreted in terms of the tensile strength of the liquid, but the associated phenomena are clearly metastable. In any case, for the Maxwell construction to be meaningful the corresponding pressure for equilibrium between the two phases must be positive; this condition will obviously hold in both cases (b) and (c).

Thus according to the van der Waals equation, liquid-gas phase transitions are possible at all finite temperatures, $T > 0$. (An obvious limitation of this equation of state, insofar as it is applied to molecular gases, is that it fails to recognize the existence of the solid phase and triple point.) If our van der Waals fluid is placed in a container fitted with a piston, then no matter what the volume of the container the fluid will always fill it, either as liquid, or gas, or both.

On the other hand, at $T=0$ negative pressures are predicted by (2) for all values of v, except $v=b$, where the pressure is indeterminate. Thus in the absence of an applied tension, i.e., with $P \gtrless 0$, the gas will collapse down to $v-b$. This means that, as the piston is withdrawn in our container of fluid at $T=0$, the fluid will not expand to fill the container but rather will remain completely condensed as a liquid. In other words, at $T=0$ there is no evaporation.

In the rest of this paper we discuss to what extent comparable properties hold for Fermi fluids at $T=0$.

Fig. 1. $P-v$ isotherms for van der Waals gas, with parameters as given in Section 2.

3. Fermi Fluids

Following, for example [5] and [6], we adopt a mean-field model of the fluid and write the Helmholtz free energy per unit volume of our Fermi fluid at temperature T as

$$\mathscr{F} = \mathscr{T} + \mathscr{V} - T \mathscr{S}, \tag{3}$$

where $\mathscr{T}$, $\mathscr{V}$, and $\mathscr{S}$ represent the densities of kinetic energy, potential energy, and entropy, respectively. Fermi-
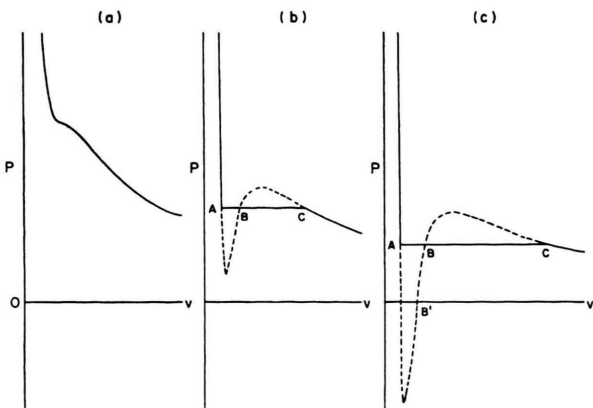
Dirac statistics give

$$\mathcal{T} = (2\pi^2)^{-1} (2M/\hbar^2)^{3/2} (kT)^{5/2} I_{3/2}(\nu), \qquad (4a)$$

where M is the fermion mass, k the Boltzmann constant, and ν is determined from the density ρ by

$$\rho = (2\pi^2)^{-1} (2M/\hbar^2)^{3/2} (kT)^{3/2} I_{1/2}(\nu). \qquad (5a)$$

Here we are using the Fermi integrals

$$I_\sigma(\nu) = \int_0^\infty x^\sigma [1 + \exp(x - \nu)]^{-1} \, dx, \qquad (6)$$

the following asymptotic expansions of which are to be noted:

$$I_\sigma(\nu \gg 1) = \nu^{\sigma+1} \qquad (7a)$$
$$\cdot \{1 + \sigma(\sigma+1) \pi^2 \nu^{-2}/6 + \ldots\}/(\sigma+1)$$

and

$$I_\sigma(\nu \ll -1) = e^\nu \Gamma(\sigma+1) \{1 - (1/2)^{\sigma+1} e^\nu + \ldots\} \qquad (7b)$$

(see, for example, [7]). Also

$$T\mathcal{S} = 5 \mathcal{T}/3 - k\nu T\rho. \qquad (8)$$

From (4a), (5a), and (7b) we find for $T > 0$ and low density the classical expression

$$\mathcal{T} \cong 3 kT\rho/2. \qquad (9)$$

On the other hand, using (4a), (5a), and (7a), we find that at $T = 0$ we have for all densities

$$\mathcal{T} = (3\hbar^2/10M) (3\pi^2)^{2/3} \rho^{5/3}. \qquad (10a)$$

For symmetric nuclear matter, where the total density is shared equally by neutrons and protons, (4a), (5a), and (10a) are modified as follows:

$$\mathcal{T} = (\pi^2)^{-1} (2M/\hbar^2)^{3/2} (kT)^{5/2} I_{3/2}(\nu), \qquad (4b)$$

$$\rho = (\pi^2)^{-1} (2M/\hbar^2)^{3/2} (kT)^{3/2} I_{1/2}(\nu), \qquad (5b)$$

and

$$\mathcal{T} = (3\hbar^2/10M) (3\pi^2/2)^{2/3} \rho^{5/3}, \qquad (10b)$$

respectively.

In all cases the parameter ν is related to the chemical potential μ by

$$\nu T = \mu - U, \qquad (11)$$

where U represents the mean field, assumed to be momentum-independent, in which the fermions are supposed to move.

As for the potential-energy density, we note first that this will depend on what we assume for the interactions

between the fermions. We shall make the simplest possible choice that is consistent with the main qualitative properties of the fermion system in question. The simple fact that ^{3}He and symmetric nuclear matter are bound means that in both cases the interaction must have a long-range attraction and a short-range repulsion, the latter because neither system collapses to infinite density. An example of such an interaction, frequently used for studies of ^{3}He, is the Lennard-Jones potential

$$v(r_{ij}) = v_0 \{(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^6\}, \qquad (12)$$

where r_{ij} is the distance between fermions i and j.

In this paper, which concentrates on the case of nuclear matter, we shall turn to the much simpler Skyrme-type forces, which are widely used in nuclear physics (see, for example, the review article of Brack et al. [8]). It will be sufficient for our purposes to take the highly simplified form

$$v(r_{ij}) = \{t_0 + (1/6) t_3 \rho^{1/3}\} \delta(r_{ij}). \qquad (13)$$

Although both terms are of zero range, the density dependence of the second term means that it will become increasingly significant as the density increases. Thus, with t_0 negative and t_3 positive the necessary features of the force can be reproduced.

For this force, the potential-energy density of symmetric nuclear matter is

$$\mathcal{V} = (3/8) t_0 \rho^2 + (1/16) t_3 \rho^{7/3}. \qquad (14a)$$

Then, combining this with (10b) to get the energy per nucleon at $T = 0$, we find that with $t_0 = -1804$ MeV·fm^3 and $t_3 = 12930$ MeV·fm^4 we reproduce the experimental saturation point of symmetric nuclear matter at $a_v = -16.0$ MeV, $\rho = 0.16$ fm^{-3}; the corresponding incompressibility is $K = 237$ MeV. (It should be realized that if our Skyrme-type force had included the usual momentum-dependent terms in t_1 and t_2, then (4), (5), and (8) would have been complicated by the appearance of an effective nucleon mass. Also, the mean field U would have been momentum-dependent.

For the Helmholtz free energy per nucleon in symmetric nuclear matter we now have

$$f = kT \{\nu - (2/3) I_{3/2}(\nu)/I_{1/2}(\nu)\}$$
$$+ (3/8) t_0 \rho + (1/16) t_3 \rho^{4/3}. \qquad (15)$$

We plot this in Fig. 2 as a function of the volume, $v = 1/\rho$, for a number of temperatures T (we express temperature here in the usual nuclear-physics manner as kT, measured in MeV). The minimum of the $T = 0$ curve, the so-called
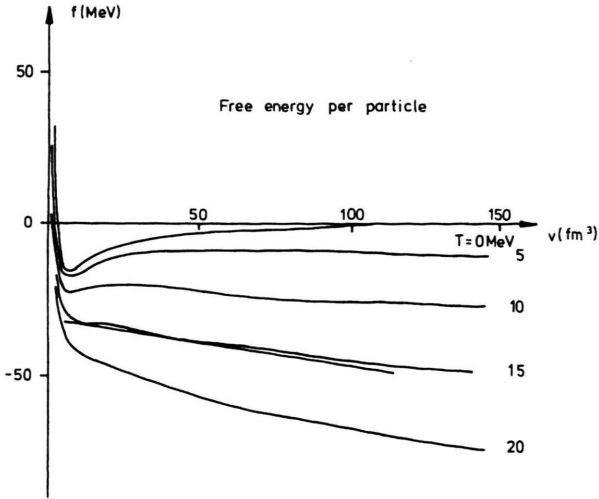
Fig. 2. $f-v$ isotherms for symmetric nuclear matter, according to (15), with parameters given in Section 3. The minimum for $T=0$ corresponds to the saturation point of nuclear matter. For $0<T<Tc\approx17$ MeV the curves exhibit two bulges permitting a common-tangent construction, equivalent to Maxwell's equal-area rule in the $P-v$ diagram.

saturation curve for symmetric nuclear matter, corresponds to the above saturation point.

The equation of state follows from (15) and the thermodynamic identity

$$P=\rho^2(\partial f/\partial\rho)_T. \qquad (16)$$

We find

$$P=(2/3)\,\rho kT\,I_{3/2}(v)/I_{1/2}(v)+(3/8)\,t_0\,\rho^2$$
$$+(1/12)\,t_3\,\rho^{7/3}, \qquad (17)$$

where we have used the relation

$$I'_{3/2}(v)=(3/2)\,I_{1/2}(v). \qquad (18)$$

(This follows from the definition (6) on integrating by parts.) The asymptotic expansion (7b) then leads to the classical perfect-gas equation of state in the low-density limit

$$P\sim\rho kT, \qquad (19)$$

provided $T>0$. On the other hand, the asymptotic expansion (7a) shows that at $T=0$ we have for all densities

$$P=(\hbar^2/5\,M)\,(3\,\pi^2/2)^{2/3}\,\rho^{5/3}+(3/8)\,t_0\,\rho^2$$
$$+(1/12)\,t_3\,\rho^{7/3}. \qquad (20)$$

Figure 3 shows the $P-v$ isotherms corresponding to (20) for a number of temperatures, including $T=0$. A

qualitative resemblance to the van der Waals isotherms will be perceived, with the existence of a critical temperature T_c (around 17 MeV in the present case). The inset in Fig. 3 shows what happens at very low densities, which is not always apparent in the main figure: at all temperatures, including $T=0$, the pressure always becomes positive for large enough v, and then falls off to zero.

Now for $T>0$ we see from (19) that this low-density fall-off in P goes as v^{-1}, as for the van der Waals gas. Thus, using the same argument as in Sect. 2, we see that the Maxwell construction and hence a liquid-gas phase transition are possible in our nuclear matter for all temperatures $T_c>T>0$.

As for $T=0$, we see form the inset of Fig. 3 that there is still a positive-pressure bump in the isotherm at very large volume. Although the fall-off goes now as $v^{-5/3}$, rather than as v^{-1}, according to (20), the qualitative resemblance to the $T>0$ van der Waals case prompts us to ask whether or not the Maxwell construction and hence a phase change are still possible at $T=0$. Of course there is a discontinuity in the behaviour of the area of the isotherms with the v-axis when going from a $T>0$-value to $T=0$: the positive pressure bump has an infinite area with the v-axis in the $T>0$-case, whereas it becomes finite for $T=0$. The area under the bump is now finite, so that in the case we have illustrated here no Maxwell construction can be made. Nevertheless, one might think that if the force parameters were chosen appropriately, the Maxwell construction might still be possible at $T=0$. Addressing this question is the principle objective of this paper.

To be more specific, we refer to the schematic isotherm ($P-v$) of Fig. 4a and ask whether there is any choice of force parameters for which the negative-pressure area A_1 is smaller than the positive-area A_2 at $T=0$. If so, then it will be possible to make the equal-areas construction for some positive pressure and we shall have a phase transition at $T=0$.

To proceed, we note that (16) reduces for $T=0$ to

$$P=-(\partial e/\partial v)_{T=0}, \qquad (21)$$

where

$$e=(\mathcal{T}+\mathcal{V})/\rho \qquad (22)$$

is the total energy per fermion. Then, with Fig. 4b showing the saturation curve ($e-v$) that corresponds to Fig. 4a, we have for the area A_1 in the latter figure
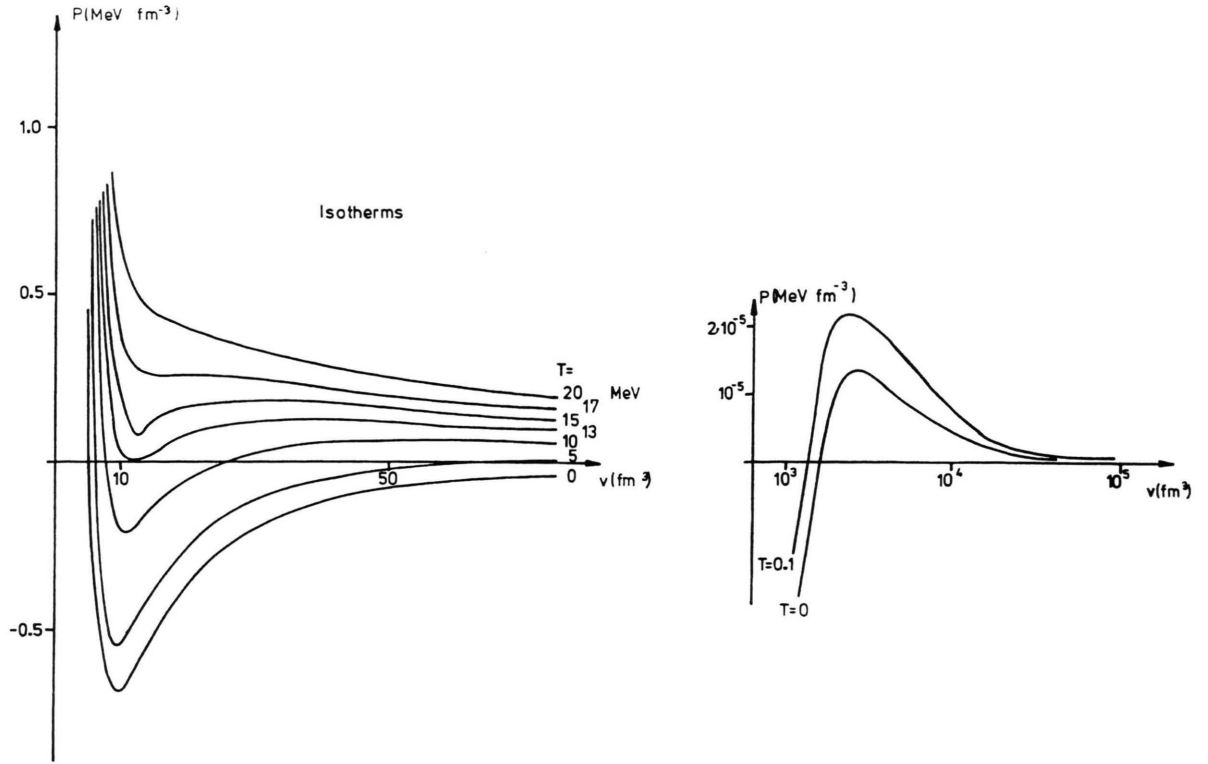
$$A_1=-\int_a^b P\,\mathrm{d}v=e_b-e_a, \qquad (23)$$

Fig. 3. $P-v$ isotherms corresponding to Figure 2. The right hand side enlargement shows the form of the low-temperature isotherms for large v.
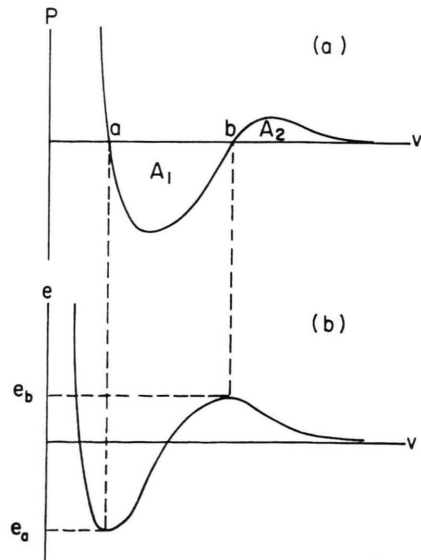

Fig. 4. $P-v$ isotherm (a) and saturation curve (b) for bound nuclear matter at $T = 0$.

while for the area A_2 we have

$$A_2 = \int_b^\infty P \, \mathrm{d}v = e_b - e_\infty = e_b , \qquad (24)$$

where e_a and e_b denote the minimum and maximum values of e, respectively. Then, provided e_a is negative, i.e., if the system can have a negative total energy, we shall have $A_1 > A_2$, and no Maxwell construction will be possible for $T = 0$.

The resulting absence of a phase transition in this $T = 0$ case might suggest a similarity with the $T > T_c$ case. However, there is a very important difference, seen by considering unit mass of our Fermi fluid at $T = 0$ in a container of variable volume v. We begin with the Fermi fluid highly compressed, $v < v_a$ (Figure 4). As the piston of the container is withdrawn, the Fermi fluid will continue to fill the entire container as long as $v \lesssim v_a$, and the pressure will fall, vanishing when $v = v_a$, the volume of the Fermi fluid cannot change any further, and the remaining space in the container will stay empty, rather than fill

with vapour. This is to be contrasted with the $T > T_c$ case, where the single-phase system invariably fills all of the available space, essentially because of the positive pressure. We can thus unhesitatingly identify our Fermi fluid at $T=0$ as being in the liquid phase, and assert that evaporation is impossible.

However, this conclusion is valid only for e_a negative, i.e., it depends on our Fermi fluid having negative energy e over some range of densities. If on the other hand the energy per fermion e is everywhere positive two situations may be discerned. i) The $e-v$ saturation curve is non-monotonic, as in Figure 5a. In this case if follows from (23) and (24) that the Maxwell construction can be made (Fig. 5b), and a phase transition will be possible, even at $T=0$. ii) The $e-v$ saturation curve is monotonic, as in Figure 6. In this case the $P-v$ isotherm will also be monotonic and the Maxwell construction is clearly impossible.

But in both these cases for which the energy e is always positive, even though there is a phase change in the one case but not in the other, the Fermi fluid will always fill the available space at $T=0$, essentially because the pressure is always positive along the realistic parts of the isotherm (solid portions of Figure 5b). This is to be contrasted with the situation prevailing in the case where the energy e is negative for some densities. That is why we say that a Fermi fluid is unbound if e is positive for all densities, and bound if e is negative for some densities. (But note that this distinction vanishes for $T>0$: as soon as the temperature of a bound Fermi fluid is raised above absolute zero, evaporation begins and all the available space will be filled in all cases.)

While ^{3}He and symmetric nuclear matter both constitute examples of bound Fermi fluids at $T=0$, pure neutron matter is certainly unbound at $T=0$ (the binding of neutron stars is gravitational). This is the case even with the same force (13) that binds symmetric nuclear matter: the difference arises from the fact that the kinetic-energy density is given by (10a) rather than (10b), and the potential-energy density is given by

$$\mathcal{V} = (1/4)\, t_0\, \rho^2 + (1/96)\, t_3 (2\rho)^{7/3} \tag{14b}$$

rather than by (14a). With this force, the saturation curve of neutron matter at $T=0$ is monotonic, as in Fig. 6, but this is by no means conclusive, since this force is highly schematic, and with a different force the curve could be non-monotonic (see, for example, p. 47 of [9]); experimentally the situation is far from clear. If, in fact, the saturation curve is non-monotonic, as in Fig. 5a, then a phase transition is possible, and it will be inappropri-
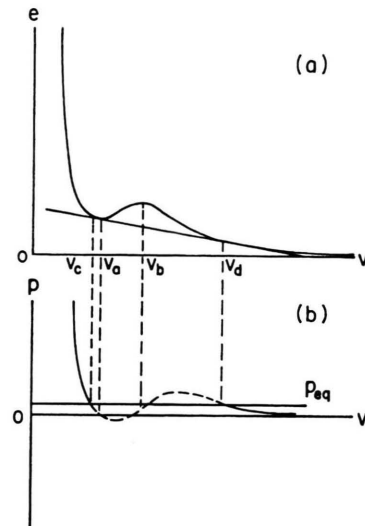

Fig. 5. Saturation curve (a) and $P-v$ isotherm (b) for unbound nuclear matter at $T=0$, with Maxwell construction possible.
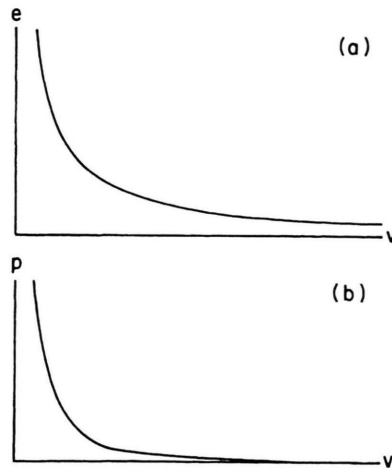

Fig. 6. As for Fig. 5, but no Maxwell construction possible.

ate always to speak of neutron matter as being a neutron gas.

There are other ways for describing stable equilibrium between two phases besides Maxwell's equal-area construction. For instance, using (16) and some elementary calculus, it can be shown (see, for example, Huang [10], or Chandler [11]) that Maxwell's rule, which leads to a pressure horizontal in the $P-v$ diagram, is equivalent to the construction of a common tangent to two points of the corresponding $f-v$ isotherm, as shown in Figs. 2

and 5a. The negative slope of such a tangent is the equilibrium pressure for the two phases. Maxwell's rule says that equilibrium between two phases is possible if, and only if two bulges of the $f-v$ isotherm exist such that a unique common-tangent construction can be made. It is easy to see that such a construction is possible only when $e_a > 0$, as in Fig. 5, but not in Figs. 4 and 6. Thus, we recover the conclusions already drawn from (23) and (24).

4. Conclusion

We have used thermodynamical reasoning to establish some properties of Fermi fluids concerning phase changes at $T=0$, with particular reference to nuclear matter. While these results are intuitively plausible and often tacitly assumed in the literature, we are not aware of their having been proven before, and believe that this would in fact be difficult without thermodynamics.

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