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Continuum Fluids with a Discontinuity in the Pressure

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A class of one-dimensional continuum fluid models is defined in which classical particles interact through translationally invariant, strongly tempered many-body potentials meeting conditions sufficient to ensure a proper thermodynamic limit. However, an exact analysis demonstrates that for certain ranges of parameter values the pressure versus density isotherms are *discontinuous*. The basic models also entail discontinuous temperature versus configurational entropy isobars but extended models are described which exhibit either type of anomaly alone and various unobserved but thermodynamically allowed, anomalous types of first-order transitions.

KEY WORDS: Pressure discontinuity; phase transitions; thermodynamic anomalies; one dimensional fluids.

1. INTRODUCTION

Many thermodynamic systems, such as a gas which condenses into a liquid, exhibit a discontinuity in the density, ρ, as a function of pressure, p, at constant temperature, T, i.e., in a (ρ, p) isotherm. Yet, although it is permitted by thermodynamics, no one has experimentally observed the opposite situation, namely, a discontinuity in an isotherm of pressure versus density. Even the most rigid materials have some nonvanishing isothermal compressibility, $\rho^{-1}(\partial\rho/\partial p)T$, under all conditions. Proofs forbidding a discontinuity in the pressure have been established by various authors,[1-6] in particular by Griffiths and Ruelle,[5] but all demand more restrictive conditions on the potentials of interaction than required merely for the existence of a proper, well-behaved thermodynamic limit.[7,8]

An interesting question arises: "Is it possible to construct models with well-defined Hamiltonians, however unrealistic, which exhibit a pressure

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discontinuity?" The answer is "Yes." Indeed, a one-dimensional lattice gas model displaying such a discontinuity was constructed some years ago[9] and its significance in a general statistical mechanical context has been discussed by Israel[10,11] and Wightman.[12] In this lattice model the discontinuity arises, physically, from a "condensation" of the low-density gas into a rigid "crystal" of fixed density, ρ_Δ, which is then crushed to higher densities only when the pressure is raised by a sufficiently large further increment. The fixed density, ρ_Δ, in this model is tied directly to the lattice spacing a_0 via $\rho_\Delta = 1/2a_0$; it might thus be felt that the presence of an underlying periodic lattice structure plays a crucial role in the existence of a pressure discontinuity. In addressing this issue in the discussion of the model it was suggested[7] that it should be possible to construct one-dimensional *continuum* fluid models which would, nevertheless, display similar pressure discontinuities. In this paper we verify this conjecture by exhibiting and analyzing such continuum models. Our results demonstrate that the existence of a pressure discontinuity is *not* dependent on any spatial periodicity in the model.

Our one-dimensional, classical, continuum models are introduced in the following section. They utilize the idea of "cluster interactions" devised originally in discussing the droplet picture of condensation[13] and developed later to exhibit a variety of more-or-less orthodox phase transitions in one-dimensional continuum models[14,15] and to establish a pressure discontinuity in a lattice gas.[9] The phase transitions in these models arise through the presence and character of many-body forces, $\Phi_k(r_1, r_2, \ldots, r_k)$, of indefinitely high order in k. However, the overall forces are of short range in the sense that the total potential energy, U_N, of a system with N particles partitioned into two disjoint intervals does not depend on the distance of separation, R, between the intervals provided R exceeds a finite distance, R_0, i.e., a "strong tempering" condition[7,8] is satisfied. Nevertheless the many-body forces may induce effective interactions of long range *within* a suitably defined *cluster* of particles and these can lead to phase transitions if the "surface tension" becomes unbounded.

In Section 3 we check that the new models satisfy conditions sufficient to ensure the existence of a proper thermodynamic limit. The strong tempering property is invoked here. The analysis of the simple *basic model* is presented in Section 4. Appropriate generating functions provide a complete elucidation of the thermodynamic properties. Section 5 discusses typical phase diagrams realized by the special subclass of *logarithmic models*. The nature of the corresponding pressure versus density isotherms where they display discontinuities is explained in Section 6. Finally, a variety of extended models are described briefly in Section 7. These, together with the basic model, provide examples of systems in which

anomalous isobars with discontinuities in temperature, T, versus configurational entropy, S, are combined in various ways with discontinuous (p, ρ) isotherms and with more orthodox first-order phase transitions with discontinuities in (ρ, p) isotherms and (S, T) isobars.

2. NEW TYPES OF CLUSTER INTERACTION MODELS

Consider a one-dimensional system composed of identical, classical particles. A *cluster* refers to a group of adjacent particles satisfying certain conditions, for example that the nearest-neighbor spacing lies between specified upper and lower limits, say c and c'. By introducing appropriate many-body potentials which energetically favor clusters of very large size, phase transitions may occur, even though the system is one dimensional.[13–15] Roughly speaking, "condensation" corresponds to the formation of clusters of macroscopic size. A pressure discontinuity at condensation may be anticipated if the clusters are defined in such a way that as their size increases, the average density of particles within any cluster tends to a fixed limit.

In the one-dimensional lattice gas models displaying pressure discontinuities[9] clusters were defined to be sequences of particles with a nearest-neighbor spacing exactly twice the lattice spacing, a_0. Thus each cluster was, in essence, a rigid crystallite of fixed density, $\rho = 1/2a_0$. A natural generalization of this model to the continuum case would be to define a cluster to be a set of particles such that the nearest-neighbor spacing falls between specified upper and lower limits, c_l and c_l', which converge as the cluster size, l, increases. However, we have not been successful with this approach since the large clusters, which are almost rigid crystallites, occupy too small a region in phase space for condensation to occur in the thermodynamic limit, no matter how energetically favorable are the clustering energies. To obtain condensation in the continuum case it proves necessary to allow particles in large clusters to have a greater degree of internal freedom.

In the previous one-dimensional continuum cluster interaction models[13–15] a set of particles was defined as a cluster only according to whether the nearest-neighbor separations were *all* between fixed upper and lower limits, c and c'. This definition simplifies the analysis, and phase transitions can occur, but, as mentioned, it seems unsuitable for the construction of a model with a pressure discontinuity. Hence we introduce here a new class of one-dimensional cluster interaction models. In these models, the identification of a set of particles as a cluster depends *also* on the *average* density of particles in the set. To construct a continuum model with a pressure discontinuity it would be natural to specify both upper and

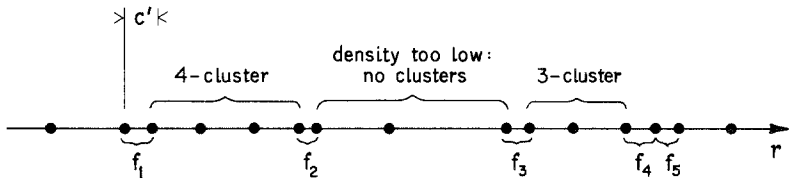

Fig. 1. A configuration of particles in a one-dimensional system showing "flags," f_1, $f_2, \ldots, f_5$, and clusters. The lower clustering distance, c', which determines which adjacent pairs are flags, is indicated.

lower limits on the density of particles in a cluster. As we shall see, however, it is sufficient to set only a lower limit.

To describe the models more precisely let the particles be located on the real line, and suppose they interact with a hard core pair potential,

$$\begin{aligned} \varphi(r) &= +\infty \qquad \text{for} \quad r \leqslant a \\ &= 0 \qquad\quad \text{for} \quad r > a \end{aligned} \tag{2.1}$$

where r is the interparticle distance. Let us call the open interval between each pair of adjacent particles separated by *less* than the *lower clustering distance* $c' > a$ a *flag*. A set of n particles between two neighboring flags is then defined as a *cluster* provided the average density of particles in the set is not too low (see Fig. 1). Specifically the set is an n-cluster, if $n \geqslant 3$ and the following condition is satisfied:

C. Cluster Condition:

$$l_n \leqslant d_m \qquad \text{with} \quad m = n - 1 \geqslant 2 \tag{2.2}$$

where l_n is the distance between the pair of flags bounding the n-cluster while the upper limit d_m takes the form

$$d_m = m(b + c') + v_m > mc' \tag{2.3}$$

in which b is a nonnegative length and

$$v_m^2/m \to 0 \qquad \text{as} \quad m \to \infty \tag{2.4}$$

Note the sign of the inequality in (2.3): the *mean* spacing in a cluster *exceeds* c'. The condition (2.4) is needed to obtain the asymptotic inequalities derived in the appendix, which, in turn, are crucial to the proof of a pressure discontinuity. In the most basic model both b and c' are taken as fixed parameters.

Each $(m + 1)$-cluster is assigned an energy E_m which can be written in the form

$$E_m = W_m - (m + 1)\tilde{E} = W_m - n\tilde{E} \tag{2.5}$$

where $\tilde{E}$ is positive and

$$W_m/m \to 0 \qquad \text{as} \quad m \to \infty \tag{2.6}$$

Thus $-\tilde{E}$ can be regarded as the "bulk" contribution per particle while W_m is the effective "surface" energy of the cluster.[13] To ensure the existence of the thermodynamic limit (see below) we will require the cluster energies to be negative, i.e.,

$$E_m < 0 \qquad \text{for all} \quad m \geqslant 2 \tag{2.7}$$

This basic model can be described alternatively in terms of many-body potentials, without reference to clusters.[7] In addition to the pair potential (2.1) we may define $(m+3)$-body potentials $(m = 2, 3, \ldots)$ which act only if $m+3$ particles are adjacent with sequentially labeled coordinates r_{-1}, $r_0, \ldots, r_{m+1}$ satisfying the conditions

$$\begin{aligned} &\text{(i)} && |r_0 - r_{-1}| < c', \qquad |r_{m+1} - r_m| < c' \\ &\text{(ii)} && |r_j - r_{j-1}| \geqslant c' \qquad \text{for} \quad j = 1, 2, \ldots, m \\ &\text{(iii)} && |r_m - r_0| \equiv l_{m+1} \leqslant d_m \end{aligned} \tag{2.8}$$

These many-body potentials are then given explicitly by

$$\begin{aligned} \tilde{\Phi}_{m+3}(r_{-1}, r_0, \ldots, r_{m+1}) &= E_m \qquad \text{if (i), (ii), and (iii) hold} \\ &= 0 \qquad \text{otherwise} \end{aligned} \tag{2.9}$$

To establish the equivalence of this description of the model with the previous one, note that if conditions (i) and (ii) hold then the open intervals (r_{-1}, r_0) and (r_m, r_{m+1}) constitute neighboring flags. If, additionally, (iii) holds then the set of $(m+1)$ particles at $r_0, r_1, \ldots, r_m$ forms an $(m+1)$-cluster. The potentials $\tilde{\Phi}_k$ defined here are not quite the standard many-body potentials $\Phi_k(r_1, \ldots, r_k)$ defined without regard to linear sequence[7,8]; however, these can easily be derived recursively from the energies of k-particle configurations.

The precise nature of the many-body forces described here depends on the variation of E_m and d_m with m. Note that (iii), or equivalently the condition **C**, places a lower limit

$$\rho_\Delta = (b + c')^{-1} \tag{2.10}$$

on the average density of particles in a macroscopic cluster. To permit the formation of macroscopic clusters, i.e., "condensation," it proves necessary to choose E_m and d_m so that isolated flags entail a high cost in either entropy or energy when embedded in regions of mean density exceeding ρ_Δ. This helps to prevent the break-up of large clusters into smaller ones. For a pressure discontinuity to occur, a sufficiently large value of the bulk energy parameter, $\tilde{E}$ is also necessary so that an increase in the average

spacing of particles within a macroscopic cluster of mean density ρ_Δ, which destroys the cluster, is strongly suppressed. We show (in Section 4) that the density of the system in the condensed phase then remains stuck at $\rho = \rho_\Delta$ as the pressure is decreased from high values, until the macroscopic clusters eventually break up at sufficiently low pressures. Thus the pressure exhibits a discontinuity at $\rho = \rho_\Delta$.

Many variations of the basic model, perhaps more realistic, can be conceived. For example, one could reverse all the inequalities in (2.8) or one could impose an additional condition such as

$$\text{(iv)} \qquad |r_j - r_{j-1}| < c \qquad \text{for} \quad j = 1, 2, \ldots, m \tag{2.11}$$

where $c > c'$. In the latter case by choosing $c < 2a$, the unnatural requirement that the $m + 3$ particles be adjacent is superfluous since (i) and (iv) ensure this. We have no doubt that a pressure discontinuity could still occur; however, we do not investigate such models here, since the basic model is much easier to analyze and suffices to demonstrate the existence of pressure discontinuities.

3. EXISTENCE OF THE THERMODYNAMIC LIMIT

An important question must be addressed: namely, does the basic model outlined in the previous section satisfy the conditions established by Ruelle[1,8] and Fisher,[9] which ensure the existence of the thermodynamic limit? To state these conditions let X denote a finite set of distinct points, $r_1, r_2, \ldots, r_{N(X)}$ on the real line and let $U(X)$ denote the total potential energy of $N(X)$ particles, one located at each point of the set X. For the existence of the thermodynamic limit it suffices[8,9] that the potentials satisfy the following conditions:

T. Translational Invariance: Namely, for all r_T one has

$$U(X + r_T) = U(X) \qquad \text{for all } X \tag{3.1}$$

A. Stability: There is a $Q < \infty$ such that

$$U(X) \geqslant -QN(X) \qquad \text{for all } X \tag{3.2}$$

B*. Strong Tempering: For some $R_0 < \infty$ one has

$$U(X \cup X') \leqslant U(X) + U(X') \qquad \text{whenever} \quad R(X, X') \geqslant R_0 \tag{3.3}$$

where

$$R(X, X') = \min\{|r - r'|;\ r \in X, r' \in X'\} \tag{3.4}$$

denotes the shortest distance between a point in X and a point in X'. This strong-tempering condition can be replaced by less restrictive weak tempering conditions.[7,8]

The potentials in the basic model are clearly translationally invariant since they depend only on the particle separations. Furthermore, each particle can belong to at most one cluster and, by virtue of (2.5) and (2.6), the energy per particle must be bounded below, by some constant Q. Thus the stability requirement **A** is satisfied.

Unfortunately the strong tempering condition **B*** as stated (and even the weak tempering condition[7]) is not necessarily satisfied by the model. For instance X might be a sufficiently large set of particles which constitute a single cluster in which, for any R_0, there is a gap devoid of particles of width at least $2R_0 + c$; the remaining particles in the cluster would have to be bunched together in order to compensate for the gap and meet the cluster condition **C**. The set X' might then consist of an inserted pair of particles forming a flag located close to the middle of the gap. Then $X \cup X'$ could contain two, one, or even no clusters according to the average density of particles between the various flags. Whether (3.3) holds then depends in detail on the variation of E_m and d_m with m.

It may well be possible to define E_m and d_m so that **B*** is always satisfied, while still permitting a pressure discontinuity to be established. However, we can avoid such complications by noting that the proofs of the existence of the thermodynamic limit use the strong tempering condition in a less restrictive form than stated in **B***. In the proofs,[7,8] X and X' are not arbitrary sets of particles but, rather, in the one-dimensional case are subsets of two disjoint intervals, say Γ and Γ', respectively, where the distance between Γ and Γ' is at least R_0. Thus the sets X and X' cannot "intermix." Hence we need check only that the basic model satisfied the following condition:

B†. Modified Strong Tempering Condition: For some $R_0 < \infty$ one has

$$U(X \cup X') \leqslant U(X) + U(X') \qquad \text{whenever} \quad D(X,X') \geqslant R_0 \tag{3.5}$$

where, deleting the modulus bars entering the previous definition of $R(X, X')$, we take

$$D(X,X') = \min\{r - r';\ r \in X,\ r' \in X'\} \tag{3.6}$$

Now any cluster in X or X' will still be a cluster in $X \cup X'$ provided $D(X,X') > 0$; which ensures that X and X' do not intermix. There may, however, still be clusters in $X \cup X'$ not present in either X or X'. Nevertheless since, by (2.7), the cluster energies are always negative, it follows that the modified strong tempering condition holds for any $R_0 > a$.

It would now be appropriate to show that the basic model violates conditions, which if satisfied, forbid a discontinuity in the pressure. Unfortunately the conditions of which we are aware[1-6,10,11] do not apply to continuum models with many-body forces. In the case of lattice gas models with many-body forces it was pointed out[9] that the condition used by Griffiths and Ruelle[5] to prove continuity of the pressure places a bound on the total energy of interaction of one particle with all others. In the cluster models, removing one particle can destroy a cluster of indefinitely large size, and since E_m is unbounded, the total energy of interaction of one particle with all others is likewise unbounded. Therefore, although our present model is not a lattice gas, it also seems a reasonable candidate to have a discontinuity in the pressure.

4. ANALYSIS OF THE BASIC MODEL

Having checked the existence of a proper thermodynamic limit for our models, we proceed to examine the thermodynamics of the basic model. The analysis closely parallels that developed previously.[13-15]

It is helpful to introduce the notions of *strings* and *endstrings* as illustrated in Fig. 2. Consider particles in an interval Λ of length L on the real line. The $n = 1, 2, \ldots$ particles lying between two neighboring flags are defined as an n-string. Similarly we denote the $n = 0, 1, 2, \ldots$ particles between one end of Λ and the nearest flag (or the other end of Λ if no flags exist) as a n-endstring. With these definitions any configuration of particles on Λ can be partitioned uniquely into a set of strings and at most two endstrings. The length l_n of a string or endstring is taken as the length of the interval between the neighboring flags, between the end of Λ and the nearest flag, or between both ends of Λ, as appropriate. Strings, but not endstrings, of length satisfying condition **C** will be clusters, provided $n \geqslant 3$.

The grand canonical partition function, for the interval Λ of length L,

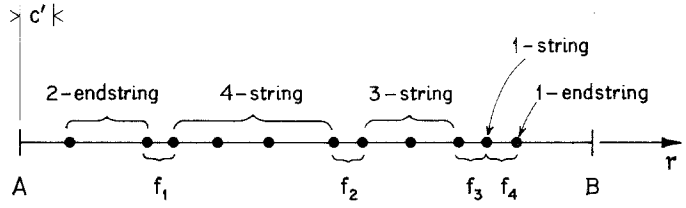

Fig. 2. An interval Λ, bounded by the end points A and B, containing a configuration of particles partitioned into "strings" and "endstrings." As in Fig. 1, the flags are labeled $f_1, f_2, \ldots$.

is given by

$$\Xi(z, \beta, L) = \sum_{N=0}^{\infty} z^N \int dr_1 \cdots \int dr_N \exp\left[-\beta U(\{r_1, \ldots, r_N\}) \right] \quad (4.1)$$

where

$$\beta = 1/k_B T \quad (4.2)$$

is the inverse temperature and

$$z = e^{\beta\mu}/\lambda(T), \qquad \lambda(T) = \left(h^2/2\pi m k_B T\right)^{1/2} \quad (4.3)$$

is the activity, $\lambda(T)$ being the thermal de Broglie wavelength. A standard approach[16] for solving one-dimensional models is to introduce the Laplace transform

$$\Psi(z, \beta, s) = \int_0^{\infty} e^{-sL} \Xi(z, \beta, L)\, dL \quad (4.4)$$

which, in our case, can be considered as a generating function for all possible sets of strings separated by flags of all possible sizes and bounded by all possible endgroups. Following the previous methods[14,15] we introduce the following:

(i) The *flag-generating function*:

$$J(s) = \int_0^{c'} e^{-sr} e^{-\beta\varphi(r)}\, dr = (e^{-sa} - e^{-sc'})/s \quad (4.5)$$

which accounts for all possible sizes of a single flag.

(ii) The *endstring-generating function*

$$G(z, s) = \sum_{m=0}^{\infty} z^{m+1} \left[K(s) \right]^m \quad (4.6)$$

which accounts for all possible configurations of a single endstring, where

$$K(s) = \int_{c'}^{\infty} e^{-sr} e^{-\beta\varphi(r)}\, dr = e^{-sc'}/s \quad (4.7)$$

accounts for all possible interparticle spacings within the endstring.

(iii) The *string-generating function*, $H(z, \beta, s)$. To obtain an explicit expression for $H(z, \beta, s)$ recall that strings fall into two categories: clusters, and strings that are not clusters. Hence we can write

$$H(z, \beta, s) = C(z, \beta, s) + H'(z, s) \quad (4.8)$$

where $C(z, \beta, s)$ is the cluster-generating function and $H'(z, s)$ is the generating function for strings which are not clusters.

In an $(m+1)$-cluster, all interparticle distances exceed the flag distance c' and the cluster length, l_n, satisfies the condition **C**. Thus the

cluster-generating function is

$$C(z,\beta,s) = \sum_{m=2}^{\infty} z^{m+1} \int_{mc'}^{d_m} dl\, e^{-sl} \int_{(m-1)c'}^{l-c'} dr_{m-1} \int_{(m-2)c'}^{r_{m-1}-c'} dr_{m-2} \cdots \times \int_{c'}^{r_2-c'} dr_1\, e^{-\beta E_m} \tag{4.9}$$

which accounts for all possible single clusters with their associated Boltzmann factors. Upon integrating we obtain

$$C(z,\beta,s) = \sum_{m=2}^{\infty} z^{m+1} e^{-\beta E_m} I(s,m) \tag{4.10}$$

where

$$I(s,m) = \int_{mc'}^{d_m} dl\, e^{-sl} \big[l - mc' \big]^{m-1}/(m-1)! \tag{4.11}$$

As might have been expected, $I(s,m)$ is, in fact, the incomplete Laplace transform of the canonical partition function of a pure hard-core ("hard-rod") gas,[16] consisting of $m-1$ particles located on an open interval of length $l < d_m$, bounded by two other particles and with all interparticle spacings exceeding the flag distance c'. Such a configuration of particles, with adjacent flags, forms an $(m+1)$-cluster.

The distinction between the string-generating function $H(z,\beta,s)$ and the endstring-generating function $G(z,s)$ must disappear when all the cluster energies E_m are zero. Hence from (4.8) and (4.10) we deduce that

$$H'(z,s) = G(z,s) - \sum_{m=2}^{\infty} z^{m+1} I(s,m) \tag{4.12}$$

and so, finally, we obtain

$$H(z,\beta,s) = \sum_{m=0}^{\infty} z^{m+1} \big[K(s) \big]^m + \sum_{m=2}^{\infty} z^{m+1} (e^{-\beta E_m} - 1) I(s,m) \tag{4.13}$$

Since the total energy of the system is just the sum of energies of the individual strings, the integral in (4.1) can be expressed as the sum of iterated Laplace convolutions. Consequently the overall generating function, $\Psi(z,\beta,s)$, can be written as the sum of products of flag-, endgroup-, and group-generating functions as

$$\Psi(z,\beta,s) = s^{-1} + s^{-2} G(z,s) + s^{-2} \big[G(z,s) \big]^2 \sum_{k=1}^{\infty} \big[J(s) \big]^k \big[H(z,\beta,s) \big]^{k-1} \tag{4.14}$$

Here the first term accounts for all lengths of line with no strings, the second term for all single endstrings, and each successive term for all sets of

$k-1$ strings located between two endstrings and separated by k flags. Any possible configuration of particles is included in one, and only one, of the terms in (4.14).

The value of the abscissa of convergence, $s_0(\beta, z)$, of the Laplace transform (4.4) is directly related to the pressure, p, of the system in the thermodynamic limit, since from (4.4) and the definition of p in the grand canonical ensemble we have

$$s_0(\beta, z) = \lim_{L\to\infty} L^{-1} \ln \Xi(z, \beta, L) = \beta p(T, \mu) \tag{4.15}$$

From (4.14), the abscissa of convergence of the series for $\Psi(s)$, at $s = s_0$, for fixed values of β and z is determined *either* by the

Exterior Condition:

$$H(z, \beta, s)J(s) = 1 \tag{4.16}$$

or using (4.13), (2.5), and (2.6), by the

Interior Condition:

$$u(s, \beta) \equiv zI_\infty(s)/y = 1 \tag{4.17}$$

where

$$I_\infty(s) = \lim_{m\to\infty} \left[I(s, m) \right]^{1/m} \tag{4.18}$$

and

$$y = e^{-\beta \tilde{E}} \tag{4.19}$$

Although the series for $\Psi(s)$ will also diverge under other conditions, either (4.16) or (4.17) must be satisfied on the abscissa of convergence. For example, on recalling the condition $E_m > 0$ we deduce that

$$H(z, \beta, s) > G(z, s) \tag{4.20}$$

thus the exterior condition is always met before one realizes the condition $zK(s) = 1$ [which gives $G(z, s) = \infty$].

The possibility of a phase transition is now evident. If $s_0 = \beta p$ is determined by the interior condition over a region Ω in (β, z) or (T, μ) space and by the exterior condition for values of β and z outside Ω, then there will be a nonanalytic change in the thermodynamic behavior across the boundary of Ω. This corresponds to a phase transition.[13–18] Let us tentatively suppose such a region Ω exists.

In the appendix we prove on the basis of (2.3), (2.4), and (4.11), that given any $\delta > 0$, $\epsilon > 0$, and sufficiently large $m > M(\delta, \epsilon)$, one has the bounds

$$(1 + \delta)B(s, m) > I(s, m) > (1 - \delta)B(s, m) \qquad \text{for} \quad s < b^{-1} - \epsilon \tag{4.21}$$

and

$$\left[K(s)\right]^m + (1-\delta)B(s,m) > I(s,m) > \left[K(s)\right]^m + (1+\delta)B(s,m) \quad \text{for} \quad s > b^{-1} + \epsilon \tag{4.22}$$

where

$$B(s,m) = \frac{(eb)^m e^{-s(b+c')m}}{(2\pi m)^{1/2}(1-bs)} e^{-v_m(s-1/b)} \tag{4.23}$$

Thus we obtain the limiting value

$$\begin{aligned} I_\infty(s) &= be^{1-s(b+c')} \qquad \text{for} \quad s < b^{-1} \\ &= K(s) \equiv e^{-sc'}/s \qquad \text{for} \quad s > b^{-1} \end{aligned} \tag{4.24}$$

Hence if $[s_0(\beta,z) - b^{-1}]$ changes sign within Ω, there will be another phase transition.

The thermodynamic behavior of the system in any subregion Δ of Ω in which $s_0(\beta,z) < b^{-1}$ follows from (4.17) and (4.24) and is given simply by

$$\mu = (c'+b)p - \tilde{E} - k_B T\left\{1 + \ln\left[b/\lambda(T)\right]\right\} \tag{4.25}$$

Therefore within Δ, which we assume to exist, the density of the system remains *fixed* at

$$\rho_\Delta = \left(\frac{\partial p}{\partial \mu}\right)_T = (c'+b)^{-1} \tag{4.26}$$

Thus the ρ versus p isotherms will contain level sections. Recalling the necessary monotonicity of these isotherms[1,7,8] and noting that, in principle, ρ can take values both smaller and larger than ρ_Δ we may presume there will be a corresponding discontinuity in pressure versus density at constant temperature. It remains to show that a region Δ, where the interior condition determines s_0, with $s_0 < b^{-1}$, can exist and that for sufficiently low p the density is less than ρ_Δ while for p sufficiently great the density exceeds ρ_Δ.

An alternative expression for the exterior condition, (4.16), obtained by using (4.17) to eliminate z from (4.13) in favor of $u(\beta,z)$, is the following:

Exterior Condition:

$$\begin{aligned} 1 = \gamma(u,\beta,s) \equiv J(s) \sum_{m=0}^{\infty} \frac{\left[K(s)\right]^m}{\left[I_\infty(s)\right]^{m+1}} (uy)^{m+1} \\ + J(s) \sum_{m=2}^{\infty} \frac{I(s,m)}{\left[I_\infty(s)\right]^{m+1}} u^{m+1}\left[e^{-\beta W_m} - y^{m+1}\right] \end{aligned} \tag{4.27}$$

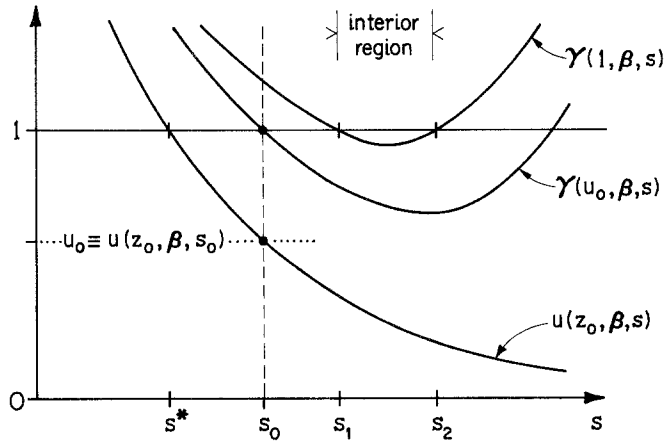

Fig. 3. Sketch illustrating the fact that if s_0 satisfies $\gamma(1, \beta, s_0) > 1$, then the exterior condition determines the thermodynamics when $s = s_0$. Here u_0 and z_0 are defined through the relations $\gamma(u_0, \beta, s_0) \equiv 1$ and $u(z_0, \beta, s_0) \equiv u_0$. As s is decreased, the exterior condition, $\gamma(u_0, \beta, s) = 1$, is encountered at $s = s_0$ before the interior condition, $u(z_0, \beta, s_0) = 1$, is met at $s = s^*$. The interior condition, $u(z_0, \beta, s_0) = 1$, determines the thermodynamics when s_0 lies in the interior region between s_1 and s_2 in which $\gamma(1, \beta, s_0) < 1$.

Since $[K(s)]^m$ exceeds $I(s, m)$ we infer that $\gamma(u, \beta, s)$ is a strictly monotonic increasing function of u for fixed β and s. So if $\gamma(1, \beta, s_0) > 1$ for given β and s_0 then we have $\gamma(u_0, \beta, s_0) \equiv 1$ for some $u_0 < 1$ corresponding to say $z = z_0$. Now it follows from (4.11), (4.17), and (4.18) that u is a monotonic decreasing function of s at fixed β and z. Hence, as illustrated in Fig. 3, when s is decreased from ∞ with β fixed and $z = z_0$, the condition $u = u_0$ will be encountered at $s = s_0$ before the condition $u = 1$ is met. Therefore the abscissa of convergence, $s_0(\beta, z)$, will be determined by the exterior condition whenever $\gamma(1, \beta, s_0) > 1$. Conversely $s_0(\beta, z)$ is determined by the interior condition if $\gamma(1, \beta, s_0) < 1$.

The next step is to establish that we can choose v_m, W_m and $\tilde{E}$ in (2.3)–(2.5) so as to obtain $\gamma(1, \beta, s_0) < 1$ over a range of pressures and temperatures. Let us consider, for simplicity, the following model:

Logarithmic Model:

$$W_m = \tilde{W} + w \ln m \tag{4.28}$$

$$v_m = -\tilde{v} \ln m \tag{4.29}$$

where $\tilde{W}$ is positive. To satisfy (2.3) and (2.7), i.e., to ensure $E_m < 0$ and $d_m > mc'$, for all $m \geqslant 2$, it is sufficient to require

$$\tilde{W} < \tfrac{1}{2}\tilde{E}, \qquad w < 2\tilde{E} \tag{4.30}$$

$$\tilde{v} < 2b \tag{4.31}$$

Substituting (4.28) in (4.27) we deduce that one can achieve $\gamma(1, \beta, s_0) < 1$ (for sufficiently large positive values of $\beta\tilde{E}$ and $\beta\tilde{W}$) if and only if the series

$$\mathscr{S}(1) = \sum_{m=2}^{\infty} I(s_0, m) m^{-\beta w} \left[I_\infty(s_0) \right]^{-m} \tag{4.32}$$

converges. The bounds (4.21) and (4.22) on $I(s_0, m)$ imply convergence of the series $\mathscr{S}(1)$ provided that b does not vanish and that

$$\begin{aligned} \sigma(s_0, \beta) &\equiv \beta w + \tilde{v}(b^{-1} - s_0) - \tfrac{1}{2} \qquad \text{for} \quad s_0 < b^{-1} \\ &\equiv \beta w - 1 \qquad\qquad\qquad\quad \text{for} \quad s_0 > b^{-1} \end{aligned} \tag{4.33}$$

is *positive*. Conversely, if $\sigma(s_0, \beta)$ is negative than $\mathscr{S}(1)$ diverges and hence $\gamma(1, \beta, s_0)$ likewise exceeds unity and the exterior condition always applies.

Now, if either w is positive or $\tilde{v} > \frac{1}{2}b$, it follows from (4.33) that there is a region, say $\hat{\Upsilon}$, of the phase diagram, i.e., the (p, T) plane, in which $\sigma(s_0, \beta)$ is positive *and* one has $s_0 \equiv \beta p < 1/b$. Two typical cases illustrating the disposition of the region $\hat{\Upsilon}$ are shown in Fig. 4. The figure also embodies the fact that for sufficiently large $\tilde{E}$ and $\tilde{W}$ with $b \neq 0$, this region must contain a subregion, $\hat{\Delta}$, of the (p, T) plane, corresponding to the region Δ in the (T, μ) plane, within which the interior condition is satisfied. Indeed since $\mathscr{S}(1)$ converges throughout $\hat{\Upsilon}$ the region $\hat{\Delta}$ must expand to fill $\hat{\Upsilon}$ as $\tilde{E}$ and $\tilde{W}$ approach infinity.

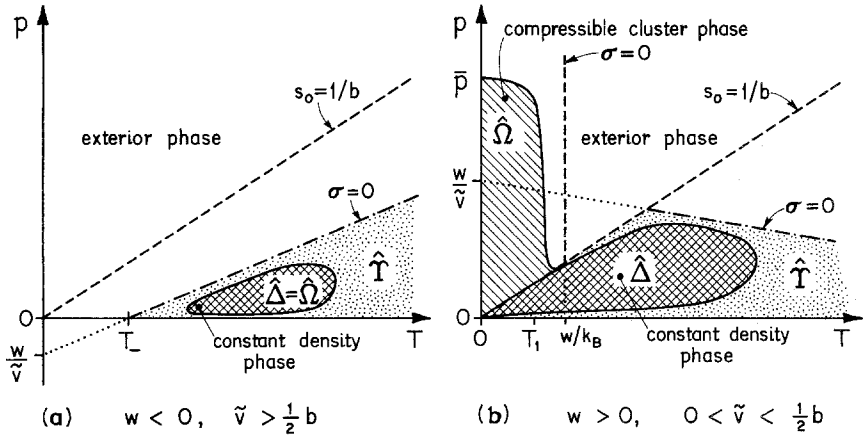

Fig. 4. Schematic phase diagrams in the (p, T) plane for the logarithmic model for two ranges of the parameters w and $\tilde{v}$. The constant density region, $\hat{\Delta}$, is a subset of both $\hat{\Omega}$ and $\hat{\Upsilon}$. As $\tilde{E}$ and $\tilde{W}$ approach infinity, $\hat{\Delta}$ fills $\hat{\Upsilon}$ and $\hat{\Omega}$ fills all the region $\sigma > 0$. Three phases are possible: the *exterior* or *disordered phase* outside $\hat{\Omega}$; the *constant density phase* within $\hat{\Delta}$; and the *compressible cluster phase*, which is within $\hat{\Omega}$ but outside $\hat{\Delta}$. [Note that the region $\hat{\Upsilon}$ does not represent a phase and that the compressible cluster phase occurs only in case (b).] A sketch of the (p, ρ) isotherm for case (b) at temperature T_1 is presented in Fig. 5.

Now note from (4.27) that we have

$$\gamma(1, \beta, s_0) > \frac{J(s_0)}{K(s_0)} \sum_{m=0}^{\infty} y^{m+1} = \frac{(e^{s_0(c'-a)} - 1)}{(e^{\beta\tilde{E}} - 1)} \tag{4.34}$$

and hence

$$\gamma(1, \beta, s_0) > 1 \qquad \text{for} \quad p \equiv s_0/\beta > p_+ \equiv \tilde{E}/(c' - a) \tag{4.35}$$

Thus the exterior condition must determine the thermodynamics whenever the pressure exceeds p_+. From (4.27) one also finds

$$\gamma(1, \beta, s_0) > y^2 J(s_0) K(s_0) / \left[I_\infty(s_0) \right]^2 \tag{4.36}$$

Upon substituting the expressions (4.5), (4.7), and (4.24) for $J(s_0)$, $K(s_0)$, and $I_\infty(s_0)$ into (4.36) and using the inequality

$$e^x - 1 > x \tag{4.37}$$

we conclude

$$\gamma(1, \beta, s_0) > y^2(c' - a)/b^2 e^2 s_0 \qquad \text{for} \quad s_0 < b^{-1} \tag{4.38}$$

This in turn implies

$$\gamma(1, \beta, s_0) > 1 \qquad \text{for} \quad p \equiv s_0/\beta < p_- \equiv \min\left\{ 1/\beta b, y^2(c' - a)/\beta b^2 e^2 \right\} \tag{4.39}$$

and, consequently, at $T \neq 0$, the exterior condition must also dictate the thermodynamics whenever the pressure falls below p_-. Therefore the level sections of the ρ versus p isotherms (for $T \neq 0$) associated with $\hat{\Delta}$ (or Δ) cannot extend to either zero or infinite pressures. Owing to the monotonicity of these isotherms[1,7,8] the density must exceed ρ_Δ for sufficiently large p and must be less than ρ_Δ when p is small enough. Thus a bounded discontinuity, Δp, in the (p, ρ) isotherm must exist.

In the special model with $b = 0$ one has $I_\infty(s_0) = 0$ and consequently by (4.17) the interior condition can never be satisfied, irrespective of the values of $\tilde{E}$, W_m, and v_m. Thus a discontinuity in the (p, ρ) isotherms cannot occur. This substantiates the comment made in Section 2, namely, that to permit condensation it is necessary for the particles within the large clusters to have sufficient internal freedom.

5. PHASE DIAGRAMS

By an appropriate choice of many-body interaction potentials we have constructed a model with discontinuous pressure versus density isotherms. We have also established that three distinct phases are possible within the model, namely:

The exterior or disordered phase, arising when

$$\gamma(1, \beta, s_0) > 1$$

The constant density phase with $\rho \equiv \rho_\Delta$, occurring when

$$\gamma(1, \beta, s_0) < 1 \quad \text{and} \quad s_0 < b^{-1}$$

The compressible cluster phase, which occurs when

$$\gamma(1, \beta, s_0) < 1 \qquad \text{with} \quad s_0 > b^{-1}$$

Let us investigate the qualitative features of the phase diagram and give a physical interpretation of the existence of pressure discontinuities.

Two typical phase diagrams are illustrated, somewhat schematically, in Fig. 4. To justify their form note that, in addition to the pressure conditions (4.35) and (4.39), regions of temperature where the exterior condition must apply can also be found. Thus the condition $\beta\tilde{E} < 1$ implies, via (4.19), $y > e^{-1}$. The further condition

$$s_0 < \min\{b^{-1}, (c' - a)/b^2e^4\} \tag{5.1}$$

then implies, through (4.39), that $\gamma(1, \beta, s_0)$ exceeds unity. Hence the exterior condition must also apply when

$$T > T_+ \equiv (\tilde{E}/k_B)\max\{1, b/(c' - a), b^2e^4/(c' - a)^2\} \tag{5.2}$$

which supplements the previous condition (4.35), namely, $p > p_+ = \tilde{E}/(c' - a)$. Consequently neither the constant density phase nor the compressible cluster phase can exist at temperatures exceeding T_+ or at pressures exceeding p_+. The region $\hat{\Omega}$ in the (p, T) plane, corresponding to Ω in the (T, μ) plane, encompasses both cluster phases, and must likewise be *bounded*, as illustrated in Fig. 4. In the previous section we deduced from (4.39) that the exterior condition holds at fixed $T \neq 0$ if the pressure is sufficiently small. Hence the region $\hat{\Omega}$ cannot extend to the $p = 0$ axis, except, possibly, at $T = 0$.

To analyze further details of the phase diagram it is helpful to distinguish the three cases

$$\begin{aligned} &\text{(i)} && w \leqslant 0, && \tilde{v} \leqslant \tfrac{1}{2}b \\ &\text{(ii)} && w \leqslant 0, && \tilde{v} > \tfrac{1}{2}b \\ &\text{(iii)} && w > 0 \end{aligned} \tag{5.3}$$

In the first case the convergence condition (4.33) implies that $\sigma(s_0, \beta)$ is always negative and so only the disordered, exterior phase can exist.

At larger values of $\tilde{v}$, such that condition (ii) is satisfied, $\sigma(s_0, \beta)$ does take positive values within the sector $\hat{\Upsilon}$ of the (p, T) plane, as illustrated in Fig. 4a. Note that, by definition, $\hat{\Upsilon}$ does not overlap the region where

$s_0 > b^{-1}$ holds when $w \leqslant 0$; nor does it extend below temperatures less than

$$T_- \equiv 1/k_B\beta_+ = w/k_B(\tfrac{1}{2} - \tilde{v}/b) \tag{5.4}$$

(see Fig. 4a). Hence the compressible cluster phase cannot exist in case (ii) and the constant density phase, which must exist if $\beta_+ \tilde{E}$ and $\beta_+ \tilde{W}$ are sufficiently large, cannot extend to temperatures below T_-. Physically, when w is negative, as here, the surface energy term, W_m, favors the break up of large clusters into smaller ones. When $T > T_-$, however, this tendency can be overcome *provided* the average density is precisely equal to ρ_Δ because the cost in entropy entailed in breaking large clusters into smaller ones then becomes prohibitive owing to the v_m dependence in the cluster condition **C**.

The third case, w positive, is more complicated. Note, first, that $w > 0$ implies $W_m > 0$; it then follows from the definition (4.27) that $\gamma(1, \beta, s_0)$ at fixed $s_0 \neq 0$ is a monotonic decreasing function of β which approaches zero when $\beta \to \infty$. Thus we have $\gamma(1, \beta, s_0) < 1$ for sufficiently small T (at fixed $s_0 \neq 0$) and consequently both the compressible cluster phase and the constant density phase must exist. Moreover, any line through the origin in the (p, T) plane of nonzero slope (and hence corresponding to fixed $s_0 \neq 0$) must intersect the boundary of $\hat{\Omega}$ once and only once at a point away from the origin; this feature is embodied in Fig. 4b. In the low-temperature limit, $T \to 0$, at fixed pressure, we find from (4.11) and (4.27) the asymptotic result

$$\gamma(1, \beta, s_0) \approx e^{s_0(c'-a)}\left[e^{-\beta\tilde{E}} + e^{-\beta W_2}\right] \tag{5.5}$$

The boundary of $\hat{\Omega}$, which corresponds to $\gamma(1, \beta, s_0) = 1$, must thus be almost temperature independent at low temperatures and must intersect the $T = 0$ axis at a pressure

$$p = \bar{p} \equiv \min\{\tilde{E}, W_2\}/(c' - a) \tag{5.6}$$

The region $\hat{\Omega}$ must, of course, also be confined to the domain $\sigma(s_0, \beta) > 0$.

We have now accounted for the major features of the possible phase diagrams of the logarithmic model. Figure 5 displays a variety of phase transitions that may be observed on an isotherm such as $T = T_1$ in the phase diagram of Fig. 4b. At intermediate pressures (i.e., $p_2 < p < p_3$ in Fig. 5) the compressible cluster phase occurs and the particles in a macroscopic cluster tend to be sufficiently close together, on average, that the lower bound, ρ_Δ, on the density of particles within any macroscopic cluster is statistically unimportant. Indeed, the thermodynamics of the system in the condensed state, which according to (4.17) and (4.24) is governed simply by

$$\mu = pc' - \tilde{E} + k_B T \ln\left[p\lambda(T)/k_B T\right] \tag{5.7}$$

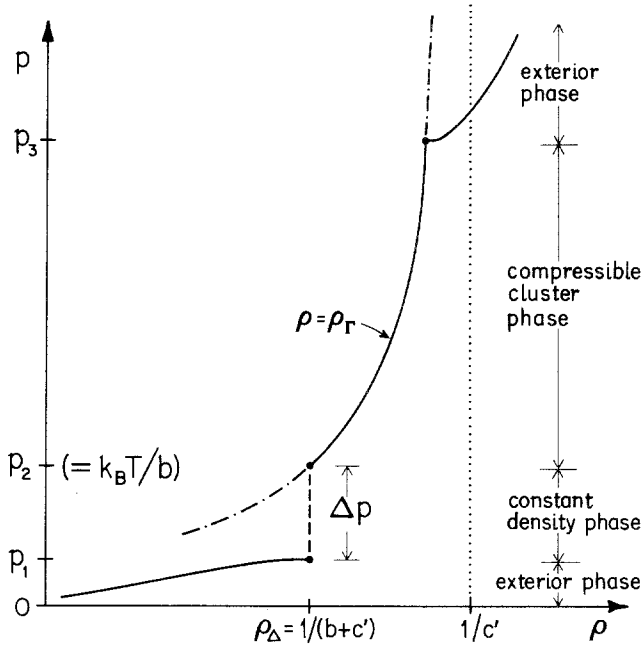

Fig. 5. Sketch of a pressure–density isotherm showing a discontinuity Δp, which may, for example, arise in model (b) of Fig. 4 at temperatures like T_1. The precise nature of the isotherm in the transition regions near p_1 and p_3 depends on the value of σ at these points (see Section 6): here the condition $\frac{1}{2} < \sigma < 1$ has been assumed valid at both points.

is quite independent of ρ_Δ. By (5.7) the "natural" density, of particles within the large clusters is

$$\rho_\Gamma(p, T) = \left(\frac{\partial p}{\partial \mu}\right)_T = p/(k_B T + pc') \tag{5.8}$$

At lower pressures such that $s_0 < b^{-1}$ (which corresponds to $p < p_2$ in Fig. 5) ρ_Γ falls below ρ_Δ. Since ρ_Δ is the minimum allowable density of particles within a macroscopic cluster, the density of the system remains stuck at ρ_Δ until the pressure is lowered further (to $p < p_1$ in Fig. 5) so that the macroscopic cluster or "condensed" state breaks up into a disordered gas of smaller clusters. This accounts for the discontinuity in the pressure at $\rho = \rho_\Delta$. Once macroscopically large clusters have broken up, the thermodynamics of the system is fully determined by the exterior condition which involves only finite clusters. At the opposite extreme of high pressures ($p > p_3$ in Fig. 5) the macroscopic clusters are crushed, forming many flags, and the thermodynamics is again dictated by the exterior condition.

6. ISOTHERM SHAPES IN THE TRANSITION REGION

In order to investigate the possible nature of the pressure–density isotherms in the transition region where macroscopic clusters start to form, i.e., when $u \to 1-$, note from the definition (4.17) of $u(s, \beta)$ that

$$\mu = -\tilde{E} + k_B T \ln\{u(s_0, \beta)\lambda(T)/I_\infty(s_0)\} \tag{6.1}$$

so that the density is given by

$$\rho^{-1} = \beta\left(\frac{\partial \mu}{\partial s_0}\right)_\beta = \frac{1}{u}\left(\frac{\partial u}{\partial s_0}\right)_\beta + \min\{\rho_\Delta^{-1}, \rho_\Gamma^{-1}\} \tag{6.2}$$

Thus we need to understand the variation of $u(s_0, \beta)$: for $u \neq 1$, this is obtained from the exterior condition $\gamma(u, \beta, s_0) = 1$. In the logarithmic model the singular behavior of $\gamma(u, \beta, s_0)$ as $u \to 1-$ arises from the contribution of the series

$$\mathscr{S}(u) = \sum_{m=2}^{\infty} I(s_0, m) m^{-\beta w}\left[I_\infty(s_0)\right] u^{m+1} \tag{6.3}$$

To approximate the singular part of $\mathscr{S}(u)$ differentiate this series j times with respect to u to form a new series $\mathscr{S}^{(j)}(u)$ such that $\mathscr{S}^{(j)}(1)$ is divergent. Then the dominant contribution to $\mathscr{S}_u^{(j)}$ as $u \to 1-$ comes from the terms of high order. A valid asymptotic expression for $\mathscr{S}^{(j)}(u)$ is obtained by replacing the series by an integral which, with the help of (4.21) and (4.22), can be evaluated for $s_0 \neq 1/b$ to yield

$$\mathscr{S}^{(j)}(u) \approx A(\beta, s_0)(1-u)^{\sigma(s_0,\beta)-j} \qquad \text{as} \quad u \to 1- \tag{6.4}$$

where $A(\beta, s_0)$ is an analytic function of β and s_0, except at $s_0 = 1/b$, and $j > \sigma(s_0, \beta)$. The exponent $\sigma(s_0, \beta)$ is given by (4.33) and for simplicity we have assumed it is nonintegral. The marginal case in which $\sigma(s_0, \beta)$ is integral yields logarithmic factors. Upon integrating j times with respect to u and substituting in (4.27) we obtain

$$\gamma(u, \beta, s_0) \approx B_0(u, \beta, s_0) + B_1(\beta, s_0)(1-u)^{\sigma(s_0,\beta)} \tag{6.5}$$

as $u \to 1-$, where $B_0(u, \beta, s_0)$ and $B_1(\beta, s_0)$ are analytic functions of u, β, and s_0, except if $s_0 = b^{-1}$ or if $\sigma(s_0, \beta)$ is integral, which cases we exclude.

Following the approach of Ref. 9 we use this result to solve for $u(s_0, \beta)$ with s_0 close to a transition point, s_t, such as s_1 or s_2 in Fig. 3, where $u = 1$ is just attained. Provided $s_t \neq b^{-1}$ and

$$\left.\frac{\partial B_0}{\partial u}\right|_{u=1} \neq 0 \qquad \text{when} \quad \sigma(s_0, \beta) > 1 \tag{6.6}$$

one finds

$$1 - u \approx C_0 \Delta s + C_1 |\Delta s|^{\tau+1} \quad \text{as} \quad \Delta s = s_t - s_0 \to 0 \tag{6.7}$$

where C_0 and C_1 are independent of s_0, but may depend on s_t and β, and

$$C_0 = 0 \quad \text{for} \quad 1 > \sigma > 0 \tag{6.8}$$

while the exponent is given by

$$\begin{aligned} \tau &= 1/\sigma_t - 1 \quad && \text{for} \quad 1 > \sigma_t > 0 \\ &= \min\{1, \sigma_t - 1\} \quad && \text{for} \quad \sigma_t > 1 \end{aligned} \tag{6.9}$$

where $\sigma_t = \sigma(s_t, \beta)$ is again supposed nonintegral. By (4.27) the derivative of $\gamma(u, \beta, s_0)$ with respect to u is always strictly positive: it follows from (6.5) that (6.6) must always hold. Putting $p_t \equiv s_t/\beta$ and assuming $s_t \neq 1/b$ we find from (6.7) and (6.2) that

$$\rho \approx \rho_0 + \max\{\rho_\Delta, \rho_\Gamma\} + D|p - p_t|^\tau \quad \text{as} \quad p \to p_t \tag{6.10}$$

where ρ_0 and D are related to C_0 and C_1 and

$$\rho_0 = 0 \quad \text{for} \quad 1 > \sigma > 0 \tag{6.11}$$

and $\rho_\Gamma(p, T)$ is given in (5.8).

The possible shapes of the pressure isotherm in the transition region following from this analysis are sketched in Fig. 6. They are basically the same as found in the original lattice gas model.[9] However, in the present

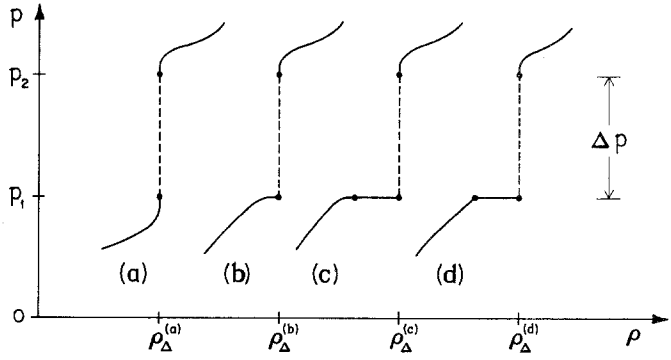

Fig. 6. Schematic pressure–density isotherms illustrating discontinuities which can occur in the logarithmic model with $w < 0$ and $\tilde{v} > \frac{1}{2}b$. The various types of behavior as p approaches the lower transition point, p_1, correspond to (a) $0 < \sigma < \frac{1}{2}$, (b) $\frac{1}{2} < \sigma < 1$, (c) $1 < \sigma < 2$, and (d) $\sigma > 2$, where $\sigma(p_1, T)$ is given by (4.32) with $s_0 = \beta p_1$. Note the horizontal two-phase regions in (c) and (d). Near the upper transition pressure, p_2, the shape of the isotherm is similarly determined by $\sigma(p_2, T)$: here the relation $0 < \sigma(p_2, T) < \frac{1}{2}$ has been assumed although other values of $\sigma(p_2, T)$, giving other shapes, are possible.

model the exponent σ_t, given by (4.33) with $s_0 = s_t$, and thence the exponent τ depend both on the transition temperature and on the transition pressure. Hence, in contrast to the lattice gas model, for which the analogous exponents are independent of pressure, the shape of a given isotherm is not necessarily similar in the two different transition regions on either side of the discontinuity (such as $p \to p_1-$ and $p \to p_3+$ in Fig. 5 or $p \to p_1-$ and $p \to p_2+$ in Fig. 6). As shown in Fig. 6, the pressure isotherm remains constant over a finite density interval when $\sigma > 1$. Thus, as in the lattice gas model, it is possible for a single isotherm to exhibit both a discontinuity in pressure and a discontinuity in density.

7. MODELS DISPLAYING OTHER THERMODYNAMIC ANOMALIES

In a normal first-order, liquid-to-gas transition there is a level section in the pressure-versus-density isotherm *and* in the isobar of temperature versus the entropy per particle, S. Now that we have constructed a model with a discontinuity in the (p, ρ) isotherm it seems natural to ask if the complementary (T, S) isobar can be discontinuous. In any classical one-dimensional system with velocity-independent potentials the total entropy per particle

$$S(T, \mu) = -\left(\frac{\partial \mu}{\partial T}\right)_p \tag{7.1}$$

can be split, uniquely up to a constant term, into a kinetic part

$$S_{\text{kin}}(T) = -\frac{d}{dT} k_B T \ln \lambda(T) = k_B\left[\tfrac{1}{2} - \ln \lambda(T)\right] \tag{7.2}$$

and the configurational part

$$S_{\text{con}}(T, \mu) = S - S_{\text{kin}} = -\left(\frac{\partial \mu}{\partial T}\right)_p - k_B\left[\tfrac{1}{2} - \ln \lambda(T)\right] \tag{7.3}$$

[The chemical potential, $\mu(p, T)$ can likewise be decomposed into a sum of $\mu_{\text{kin}}(T)$ and $\mu_{\text{con}}(p, T)$.] Both S_{kin} and S_{con} must be monotonic increasing functions of T at constant p.[1,7,8] In fact, it follows from (7.2) that S_{kin} is a *strictly* monotonic function of the temperature and hence neither S nor S_{kin} can be independent of T at constant p. Thus the remaining question is whether a discontinuity in the T versus S_{con} isobar can exist. We need not search far for an answer! By (4.25) and (7.3) the configurational entropy in the constant density phase of the basic model remains fixed at

$$S_{\text{con}} = S_\Delta \equiv k_B \ln b \tag{7.4}$$

Furthermore, as shown in Section 5, the constant density phase in the logarithmic model for fixed $p \neq 0$ cannot extend to zero or infinite tempera-

tures. Hence for any $p \neq 0$, such that the constant density phase occurs over a range of temperatures, the T versus S_{con} isobar must be discontinuous at S_Δ. In the one-dimensional lattice gas model with a pressure discontinuity[9] the constant density phase also has constant configurational entropy, but, at fixed p, this phase always extends down to zero temperature. Thus, in the lattice gas model the (T, S_{con}) isobars are not really "discontinuous" in the strict sense.

Since the basic model displays a phase corresponding *both* to discontinuous (p, ρ) isotherms and to discontinuous (T, S_{con}) isobars, it is now natural to ask if these two unphysical anomalies can be obtained separately. The answer is "Yes" but an extension of the basic model is required. Thus consider a class of *extended models* in which the clusters are defined so that the minimum spacing allowed between particles in a cluster depends on the length of the flag immediately to the left of the cluster. More specifically an "n-string" of particles (as defined in Section 4), with sequentially labeled coordinates $r_0, r_1, \ldots, r_{n-1}$, and with adjacent particles at r_{-1}, r_n is an n-cluster for $n \geqslant 3$ if both the condition

$$\tilde{\mathbf{C}}_1: \quad |r_j - r_{j-1}| \geqslant \tilde{c}(r_0 - r_{-1}) \qquad \text{for} \quad j = 1, 2, \ldots, n-1 \tag{7.5}$$

and the generalized cluster condition

$$\tilde{\mathbf{C}}_0: \quad |r_{n-1} - r_0| \equiv l_n \leqslant d_{n-1}(r_0 - r_{-1}) \equiv (n-1)\left[b + \tilde{c}(r_0 - r_{-1})\right] \tag{7.6}$$

are satisfied. The function, $\tilde{c}(r)$, which sets the minimum spacing, may, for our present purposes, be chosen as

$$\begin{aligned} \tilde{c}(r) &= 3\tfrac{3}{4}a - r \qquad \text{for} \quad r < \tfrac{3}{2}a \\ &= 4a - r \qquad \text{for} \quad r > \tfrac{3}{2}a \end{aligned} \tag{7.7}$$

so that it has a discontinuity at $r = \frac{3}{2}a$. For simplicity we suppose that the length c', which serves to define the flags, satisfies

$$c' = 2a \tag{7.8}$$

Finally, an $(m+1)$ cluster is now assigned a negative energy

$$\begin{aligned} E_m &= W_m - (m+1)\left[\tilde{E} - V_-(r_0 - r_{-1})^2\right] \qquad \text{for} \quad r < \tfrac{3}{2}a \\ &= W_m - (m+1)\left[\tilde{E} - V_+(r_0 - r_{-1})^2\right] \qquad \text{for} \quad r > \tfrac{3}{2}a \end{aligned} \tag{7.9}$$

which depends quadratically on the length of the left flag with amplitudes V_+ and V_-.

This extended model has a less-than-pleasing left–right asymmetry which could, however, be removed at the cost of further complexity in the exact solution which still follows by application of the methods of Section 4. For suitable choices of the parameter values, including the restriction

$9V_+ > 6V_- > 8V_+$, the chemical potential of the extended model over a limited range of p and T is found to be

$$\mu(p,T) = (b + 3\tfrac{3}{4}a)p - p^2/4V_- - \tilde{E} - k_B T\{1 + \ln[b/\lambda(T)]\} \quad \text{for } p < p^\dagger$$

$$= (b + 4a)p - p^2/4V_+ - \tilde{E} - k_B T\{1 + \ln[b/\lambda(T)]\} \quad \text{for } p > p^\dagger \quad (7.10)$$

where the special pressure is given by

$$p^\dagger = aV_+ V_-/(V_- - V_+) \quad (7.11)$$

Note that the chemical potential is continuous through $p = p^\dagger$ as required thermodynamically. It is now evident that the configurational entropy, S_{con}, is independent of the temperature over a range of fixed pressures while the density varies with pressure over the same range. Furthermore, over a range of temperatures, the model displays a first-order phase transition at the constant pressure, $p = p^\dagger$, which is anomalous in that the configurational entropy is fixed independent of both density and temperature. (This is a stronger but similar anomaly to that observed in a ferromagnet where, as a result of symmetry under reversal of the magnetic field, the magnetic entropy, is independent of the magnetization M through the two-phase (or domain) region at fixed $H = 0$; in that case, however, the magnetic entropy *does* depend on T.)

A second extension of the basic model is to allow the distance b in (7.6) to depend on the flag length, $r_0 - r_{-1}$. A particularly simple situation is obtained by choosing $b \equiv \tilde{b}(r_0 - r_{-1})$ so that the maximum length, d_{n-1}, of an n-cluster is actually independent of $(r_0 - r_{-1})$. One can then find parameters so that the density of the system is, over some region, independent of pressure while the configurational entropy varies with temperature. Associated with this can be a two-phase region with, as normal, T constant over a range of (configurational) entropy (i.e., S discontinuous in T) but with the density fixed with respect to variations of both entropy and pressure. It might be mentioned here that the convexity of the thermodynamic potentials, required thermodynamically or implied by statistical mechanics, yields a series of restrictions on the types of thermodynamic discontinuities that can conceivably be observed. Some of these restrictions are by no means obvious: they will be described in detail elsewhere.[18]

In the previous study[15] of the cluster interaction models it was demonstrated that a locus, say $\mathscr{L}(p,T)$, of normal first-order transitions in the (p,T) plane could exhibit smooth extrema both in pressure, corresponding to *maxibaric* or *minibaric points*, and in temperature, correspond-

ing to *maxithermal* or *minithermal points*. (Of course some examples of these phenomena are known in real systems.) In the models with both the distance b and the minimum cluster spacing depending on the flag length, the analogous maxentropic, minentropic, maxichoric, and minichoric points can be exhibited by a locus, $\mathscr{L}_\Delta(\rho, S_{\text{con}})$, in the (ρ, S_{con}) plane of anomalous transitions in which p and T are discontinuous at fixed ρ and S_{con}.

Finally, on extending the model a step further by introducing the first cluster spacing, $(r_1 - r_0)$, as a second variable in the minimum spacing function, $\tilde{c}$, one is in a position to produce models which display essentially all possible types of discontinuity conceivable in the thermodynamics of a single-component fluid.[18] Explicitly we then have exactly soluble models exhibiting any one of the following features over a region of the (p, T) plane:

(i) The configurational part of the chemical potential, μ_{con}, is linear in *both* p *and* in T;

(ii) μ_{con} is linear in p but nonlinear in T;

(iii) μ_{con} is linear in T but nonlinear in p;

(iv) μ_{con} has the form $\mu_a(p) + \mu_b(T)$, so that $(\partial^2 \mu_{\text{con}}/\partial p\, \partial T) \equiv 0$, with both μ_a and μ_b nonlinear.

In summary, any discontinuous "phase transitions," however peculiar or unobservable in reality, can be found in a suitable one-dimensional, continuum cluster-interaction model provided only that it is not forbidden by thermodynamic convexity.[18]

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APPENDIX: BOUNDS FOR $I(s, m)$

We want to study the integral

$$I(s, m) = \int_{mc'}^{d_m} dl\, e^{-sl} \left[l - mc' \right]^{m-1} / (m-1)! \tag{A.1}$$

for $s > 0$, when m becomes large. The upper limit of integration is given by

$$d_m = m(b + c') + v_m \tag{A.2}$$

where b and c' are positive and independent of m while $(v_m)^2/m \to 0$ as

$m \to \infty$. Now by change of variable we have

$$I(s,m) = \frac{(mb)^{m-1} e^{-sd_m}}{(m-1)!} \int_{-mb-v_m}^{0} dy\, e^{-sy} \left[1 + (v_m + y)/mb\right]^{m-1} \tag{A.3}$$

To obtain an upper bound for the integral here, consider the inequality

$$1 + x \leqslant e^{x} \tag{A.4}$$

On putting $x = (v_m + y)/mb$ this yields

$$\left[1 + (v_m + y)/mb\right]^{m-1} \leqslant e^{(m-1)(v_m+y)/mb} \tag{A.5}$$

and so one has

$$I(s,m) \leqslant \frac{-(mb)^m}{m!\left[bs - (m-1)/m\right]} \exp\left[-sd_m + (m-1)v_m/mb\right] \tag{A.6}$$

for all $s < (m-1)/mb$. A lower bound is found by noting

$$1 + x > e^{x - x^2} \tag{A.7}$$

for sufficiently small x, in particular for $|x| < \frac{1}{2}$. On recalling the condition $v_m^2/m \to 0$ as $m \to \infty$, it follows that for given $\delta' > 0$ and $y_0 < 0$, there exists an $M_0(y_0, \delta')$ such that for $m > M_0(y_0, \delta')$ and $|y| < |y_0|$,

$$\left[1 + (v_m + y)/mb\right]^{m-1} > (1 - \delta') e^{(v_m+y)/b} \tag{A.8}$$

Substituting this in (A.3) and integrating from y_0 to zero we deduce that

$$I(s,m) > \frac{(1-\delta')(mb)^m}{m!(1-bs)} e^{-sd_m + v_m/b}\left[1 - e^{-y_0(s-1/b)}\right] \tag{A.9}$$

for all $m > M_0(y_0, \delta')$, for all $s < 1/b$. From Stirling's formula[17] we have

$$(1 + \delta')(2\pi m)^{1/2}(m/e)^m > m! > (2\pi m)^{1/2}(m/e)^m \tag{A.10}$$

for $m \gg 1/\delta'$. Hence given any $\delta > 0$ and $\epsilon > 0$ we can choose y_0 and δ' so that for sufficiently large $m > M(\delta, \epsilon)$ the inequalities (A.6), (A.9), and (A.10) imply

$$(1 + \delta) B(s,m) > I(s,m) > (1 - \delta) B(s,m) \tag{A.11}$$

for all $s < 1/b - \epsilon$, where

$$B(s,m) = \frac{(eb)^m e^{-s(b+c')m}}{(2\pi m)^{1/2}(1-bs)} e^{v_m(1/b - s)} \tag{A.12}$$

For $s > 1/b$, consider the integral

$$I^{\dagger}(s,m) = \int_{d_m}^{\infty} dl\, e^{-sl}\left[l - mc'\right]^{m-1}/(m-1)! \tag{A.13}$$

which is easily related to $I(s,m)$ via

$$I(s,m) + I^{\dagger}(s,m) = \left[K(s)\right]^m \equiv e^{-mc's}/s^m \tag{A.14}$$

Proceeding as in (A.3)–(A.12) we find that given any $\delta > 0$ and $\epsilon > 0$ there is an $M'(\delta,\epsilon)$ such that for $m > M'(\delta,\epsilon)$ we have

$$-(1+\delta)B(s,m) > I^{\dagger}(s,m) > -(1-\delta)B(s,m) \tag{A.15}$$

and hence

$$\left[K(s)\right]^m + (1-\delta)B(s,m) > I(s,m) > \left[K(s)\right]^m + (1+\delta)B(s,m) \tag{A.16}$$

for all $s > 1/b + \epsilon$. This proves the results (4.21) and (4.22) used in the text.

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