Continuum Fluids with a Discontinuity in the Pressure

G. W. Milton\(^1\) and Michael E. Fisher\(^1\)

Received March 18, 1983

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, \(\rho\), as a function of pressure, \(p\), at constant temperature, \(T\), i.e., in a \((\rho, p)\) 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
discontinuity?" The answer is "Yes." Indeed, a one-dimensional lattice gas model displaying such a discontinuity was constructed some years ago and its significance in a general statistical mechanical context has been discussed by Israel and Wightman. In this lattice model the discontinuity arises, physically, from a "condensation" of the low-density gas into a rigid "crystal" of fixed density, \( \rho_0 \), which is then crushed to higher densities only when the pressure is raised by a sufficiently large further increment. The fixed density, \( \rho_0 \), in this model is tied directly to the lattice spacing \( a_0 \) via \( \rho_0 = \frac{1}{2a_0} \); 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 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 and developed later to exhibit a variety of more-or-less orthodox phase transitions in one-dimensional continuum models and to establish a pressure discontinuity in a lattice gas. 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 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