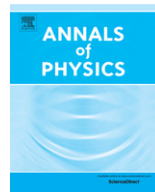




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Shock dynamics of phase diagrams



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HIGHLIGHTS

- A new generalisation of van der Waals equation of state.
- Description of phase transitions in terms of shock dynamics of state curves.
- Proof of the universality of equations of state for a general class of models.
- Interpretation of triple points as confluence of classical shock waves.
- Correspondence table between thermodynamics and nonlinear conservation laws.

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ABSTRACT

A thermodynamic phase transition denotes a drastic change of state of a physical system due to a continuous change of thermodynamic variables, as for instance pressure and temperature. The classical van der Waals equation of state is the simplest model that predicts the occurrence of a critical point associated with the gas–liquid phase transition. Nevertheless, below the critical temperature theoretical predictions of the van der Waals theory significantly depart from the observed physical behaviour. We develop a novel approach to classical thermodynamics based on the solution of Maxwell relations for a generalised family of nonlocal entropy functions. This theory provides an exact mathematical description of discontinuities of the order parameter within the phase transition region, it explains the universal form of the equations of state and the occurrence of triple points in terms of the dynamics of nonlinear shock wave fronts.

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1. Introduction

A phase transition is a general concept denoting a drastic change of physical properties of a system from one state to another. Everyday experience as well as sophisticated physical experiments provides

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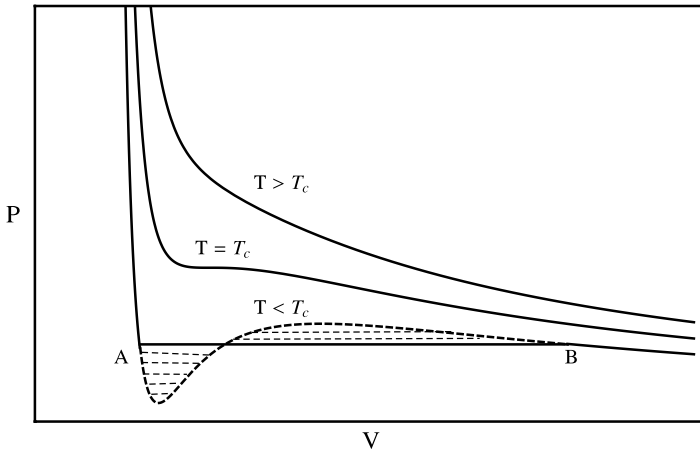


Fig. 1. Isothermal curves for a van der Waals fluid. The dashed line corresponding to the theoretical behaviour as predicted by the classical van der Waals equation is replaced by a constant pressure line according to the Maxwell equal areas rule.

numerous examples of processes where a certain physical system undergoes a thermodynamic phase transition, e.g. boiling water, melting ice, magnetic transitions, phase separation of mixtures, superfluid He, superconductors (see e.g. [1–6]). More specifically, a thermodynamic phase transition is a change of state of a physical system in thermodynamic equilibrium induced by a continuous change of thermodynamic variables as, for instance, pressure, temperature, volume. The celebrated van der Waals model provides the first simple example of equation of state that predicts the occurrence of a critical point associated with a gas–liquid phase transition.

Fig. 1 shows the behaviour of three isothermal curves as predicted by the van der Waals equation of state. Above a certain critical temperature T_c , the curves show a smooth monotonic decrease of pressure as a function of volume. At the critical temperature the isothermal curve develops an inflection at the point (V_c, P_c) . The critical point (V_c, P_c, T_c) detects the occurrence of a phase transition in the system. Below the critical temperature the van der Waals model predicts an oscillating behaviour, the dashed curve in Fig. 1, associated to a metastable state that is usually not observed. Typical experimental isothermal curves show that within the oscillating region the pressure remains constant as long as the fluid is compressed from the volume V_B to the volume V_A . Hence, the volume, as a function of pressure, experiences a jump that is associated with the coexistence of both gas and liquid phases. The classical criterion to resolve the discrepancy between theoretical and experimental results within the phase transition region AB is known in thermodynamics as the Maxwell principle. Maxwell's criterion allows to recover the physical isotherm from the theoretical one by requesting that the intersection of the constant pressure line with the van der Waals isotherm detects two regions of equal areas as shown in Fig. 1. The theoretical justification of the Maxwell principle relies on the observation that the equal areas condition is equivalent to the fact that the Gibbs potential admits two equal valued minima across the phase transition (see e.g. [1]).

The approach to classical thermodynamics recently introduced in [7] shows how van der Waals type equations of state can be constructed as solutions to nonlinear hyperbolic conservation laws. Under suitable general assumptions on the functional form of the entropy, the first law of thermodynamics can be equivalently formulated in terms of a Riemann–Hopf type partial differential equation. Such equations are well known to be integrable and exactly solvable by the method of characteristics.

As a specific example, let us consider a macroscopic physical system, as for instance a fluid characterised by its Gibbs potential Φ , entropy function S , pressure P , volume V and temperature T . The first law of thermodynamics in differential form reads as follows

$$d\Phi(P, T) = -S(P, T)dT + V(P, T)dP. \quad (1.1)$$

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