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Exact solution of the van der Waals model in the critical region

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ABSTRACT

The celebrated van der Waals model describes simple fluids in the thermodynamic limit and predicts the existence of a critical point associated to the gas–liquid phase transition. However the behavior of critical isotherms according to the equation of state, where a gas–liquid phase transition occurs, significantly departs from experimental observations. The correct critical isotherms are heuristically re-established via the Maxwell equal areas rule. A long standing open problem in mean field theory is concerned with the analytic description of van der Waals isotherms for a finite size system that is consistent, in the thermodynamic limit, with the Maxwell prescription. Inspired by the theory of nonlinear conservation laws, we propose a novel mean field approach, based on statistical mechanics, that allows to calculate the van der Waals partition function for a system of large but finite number of particles N. Our partition function naturally extends to the whole space of thermodynamic variables, reproduces, in the thermodynamic limit $N \to \infty$, the classical results outside the critical region and automatically encodes Maxwell's prescription. We show that isothermal curves evolve in the space of thermodynamic variables like nonlinear breaking waves and the criticality is explained as the mechanism of formation of a classical hydrodynamic shock.

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1. Introduction

In late 19th century, due to the outstanding contribution of its founding fathers, Boltzmann, Maxwell and Gibbs, Statistical Thermodynamics has been successfully introduced as the general conceptual framework for understanding equilibrium thermodynamic phenomena by means of statistical mechanics [1,2].

The early success of the kinetic theory of gases and the discovery of the mean field approach for the derivation of the classical van der Waals equation [3] nurtured the hope that an equally neat and clear description of critical phenomena would be as effective as it was away from the critical region. Although second order phase transitions, as for example the ergodicity breakdown of real gases at the triple point, have nowadays been completely framed into a rigorous scaffold [4] – also partially guided by techniques from the near field theory [5,6] – first order phase transitions, such as gas–liquid phase transitions, turned out to be more elusive.

Indeed, in spite of the accuracy of the celebrated van der Waals equation for the description of real gases, the behavior predicted within the critical region, where a real gas turns into a liquid, significantly departs from the experimental observations. Fig. 1 shows the typical isothermal curves of a real gas: above the critical temperature (for $T > T_c$) the pressure decreases as a strictly monotonic function of the volume; the critical point corresponds to the temperature $T = T_c$ where the critical isotherm develops an inflection point; below the critical temperature (at $T < T_c$) real isotherms are constant within a certain volume interval in spite of the oscillating behavior predicted by the classical van der Waals equation. Interestingly, the behavior of real isothermal curves within the critical region turns out to be intimately connected to the theoretical one via the celebrated Maxwell rule stating that the constant pressure plateau is placed in such a way it cuts lobes of equal areas on the associated van der Waals isotherm. As it is well known, the Maxwell rule corresponds to the condition of thermodynamic equilibrium such that, below the critical temperature, the Gibbs free energy develops two minima of equal value [7].

The remarkable validity, although heuristic, of Maxwell's approach stimulated countless studies aimed at a rigorous statistical mechanical description of first order phase transitions as for instance in the works of Lebowitz and Penrose [8] and van Kampen [9], where large classes of pairwise interaction potentials for particles (continuous and hard-sphere-like respectively) are considered or the work by Griffiths [10] that focuses on the study of analyticity properties of thermodynamic functions.

Alternative methods to analyze phase transitions have also been developed based on macroscopic approaches to thermodynamics. For instance, the Landau theory allows to construct suitable asymptotic expansions of the free energy in the order parameters to obtain information of the critical exponents in the vicinity of the critical point (see e.g. [11]); the Widom approach relies on the construction of effective free energy functions based on the analysis of their scaling properties [12]. Further recent developments in this direction led to the formulation of the thermodynamic limit as the semiclassical limit of nonlinear conservation laws where phase transitions are associated to shock solutions of a hyperbolic nonlinear PDE in the class of conservation laws [13–16]. Such nonlinear PDEs can be also derived in mean field theories from the analysis of differential identities of the free energy as showed in [13,14,17–19] for the Curie–Weiss and the Sherrington–Kirkpatrick models, or from the analysis of thermodynamic Maxwell relations as showed in [20,15] for the van der Waals model. Both the microscopic statistical mechanical approach, via the study of correlation functions asymptotics, and the macroscopic thermodynamic approach, based on the expansion of the free energy in the vicinity of the critical point, show the intimate connection with the singularity and catastrophe theory – since the very first pioneering contributions by Arnold – and the Hopf bifurcation theory (see e.g. [21]).

Despite the numerous progresses made in understanding phase transitions in a variety of contexts, from thermodynamics to classical and quantum field theory [22,23], or complex and biological systems [24,25], and the discovery of their intrinsic universality, a global analytical description of phase transitions for the van der Waals gas is still missing. In this work, inspired by the theory of nonlinear PDEs, in the class of nonlinear conservation laws, we propose a novel method such that given an equation of state assumed to be accurate outside the critical region allows to construct a partition function