Integrable extended van der Waals model

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HIGHLIGHTS

- C-integrable extension of the van der Waals model.
- Integrable viscous conservation laws and thermodynamic equations of state.
- Integrability criterion and thermodynamics of multicomponent systems.
- Equations of state in the critical region.

ARTICLE INFO

ABSTRACT

Inspired by the recent developments in the study of the thermodynamics of van der Waals fluids via the theory of nonlinear conservation laws and the description of phase transitions in terms of classical (dissipative) shock waves, we propose a novel approach to the construction of multi-parameter generalisations of the van der Waals model. The theory of integrable nonlinear conservation laws still represents the inspiring framework. Starting from a macroscopic approach, a four parameter family of integrable extended van der Waals models is indeed constructed in such a way that the equation of state is a solution to an integrable nonlinear conservation law linearisable by a Cole–Hopf transformation. This family is further specified by the request that, in regime of high temperature, far from the critical region, the extended model reproduces asymptotically the standard van der Waals equation of state. We provide a detailed comparison of our extended model with two notable empirical models such as Peng–Robinson and Soave's modification of the Redlich–Kwong equations of state. We show that our extended van der Waals equation of state is compatible with both empirical models for a suitable choice of the free parameters and can be viewed as a *master* interpolating equation. The present approach also suggests that further generalisations can be obtained by including the class of dispersive and viscous-dispersive nonlinear conservation laws and could lead to a new type of thermodynamic phase transitions associated to nonclassical and dispersive shock waves.

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1. Introduction

The van der Waals model first introduced to describe liquid–vapour coexistence in simple fluids [1] is now considered a classical paradigm for the description of phase transitions for a large family of physical systems (see e.g. [2,3].) In fact, the celebrated van der Waals equation of state

$$\left(P + \frac{a}{v^2}\right)(v - b) = RT \tag{1}$$

can be both obtained from first principles as a mean field approximation for a system of hard core particles with electrostatic interaction and also via a simple and intuitive heuristic derivation (see e.g. [3]). An alternative mean field approach has been recently introduced in [4] that allows to rigorously establish a formal analogy between the van der Waals model and magnetic mean field models such as the Curie–Weiss model and its multi-component extensions [5–8]. Interestingly, the phenomenological approach has played a key role over the decades, in particular for chemical engineering applications [9–13] aimed at providing a more accurate description of composite systems, such as solutions and multi-phase systems, for which a statistical physics approach and a mean field theory is not currently available. It should also be mentioned that although the van der Waals models catches many fundamental

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qualitative features of phase transitions in fluids, a quantitative improvement demands for more accurate, though empirical, equations of state.

Hence, a number of alternative and/or generalised approaches to the van der Waals theory have been introduced based on both mean field theory or phenomenological approaches (see e.g. [14–20,9–11]).

More recently, in a series of papers [4,21,22] it was observed that the van der Waals equation of state can be interpreted as a particular solution to an integrable nonlinear partial differential equation (PDE), that is equivalent to the first law of thermodynamics, specified by assigning a particular isothermal/isobaric curve, possibly far from the critical region. The choice of such particular isothermal/isobaric curves is equivalent to the choice of an initial datum for the PDE and it is sufficient to fix uniquely the solution. Therefore, initial data can be used to parametrise a large family of integrable models of which the van der Waals equation is one example. Moreover, as shown in [21,4] this approach formulated through integrable nonlinear conservation laws can be extended to the critical region relying on an asymptotic procedure that automatically encodes Maxwell's equal areas rule and provides an asymptotic analytic description of phase transitions in terms of shock wave solutions to hyperbolic nonlinear conservation laws [23].

We note that the correspondence between phase transitions and shock solutions of nonlinear PDEs has been also observed and studied in depth in the context of mean field spin models [24–26, 5–8], chemical kinetics and cybernetics [27], neural networks [28] and their statistical mechanical description.

In the present work we propose a new method to extend a thermodynamic model by the request that the equation of state remains a solution to a suitable extended nonlinear conservation law. Although the approach can be easily formulated for any model within the general class studied in [22], for the sake of simplicity we will focus on the construction of the extension to the van der Waals model only. Our fundamental assumptions are:

(i) the van der Waals model is assumed to be accurate in regime of high temperature and low density, so that the proposed extension must asymptotically reproduce the van der Waals equation of state;

(ii) the nonlinear conservation law is required to be *C-integrable* [29], that is linearisable via a Cole–Hopf transformation.

Property (i) relies on the idea that if the gas is in thermodynamic equilibrium and sufficiently rarified, particles can be modelled as rigid spheres interacting by a Coulomb potential. In this regime, the van der Waals model is expected to be sufficiently accurate. Property (ii) is based on the result obtained in [4] where it was shown that the van der Waals mean field model is completely integrable by linearisation. In fact, it was proven that volume density fulfils a nonlinear PDE, in the class of conservation laws, that is linearisable to the Klein–Gordon equation via a Cole–Hopf transformation. Hence, we require that the extended model preserves this property. The family of models so obtained is parametrised by four arbitrary constants and contains the van der Waals model as a particular case. These models can be viewed as a two parameter deformation of the van der Waals model. The thermodynamic limit is then calculated via a standard asymptotic expansion in the small expansion parameter $\eta = 1/N_A$, where N_A is Avogadro's number. The associated phase diagrams are then evaluated. We also observe that the Cole–Hopf transformation provides the natural extension of the mean field van der Waals partition function derived in [4].

We finally compare our model with two well-known phenomenological extensions of the van der Waals model: the Soave's modification of the Redlich–Kwong (SRK) equation of state [9,10] and the Peng and Robinson (PR) equation of state [11]. We show

that our model exactly reproduces both Soave–Redlich–Kwong and Peng–Robinson critical points for a suitable choice of the parameters and can be proposed as the interpolating model. Our analysis suggests that the proposed model is suitable for describing a wide class of real systems such as solutions and multi-component thermodynamic systems, within the range of applications of both SRK and PR equations of state.

The paper is organised as follows: In Section 2 we introduce the general macroscopic model and formulate the first principle of thermodynamics in terms of a nonlinear PDE. The integrability condition by linearisation via a Cole–Hopf transformation, given a suitable expansion in the order parameter, allows us to specify the class of models such that the equation of state is obtained as a solution to an integrable nonlinear PDE. In Section 3 we focus on the sub-family of models that can be viewed as an extension of the van der Waals model, provide their full characterisation and construct a natural extension of the mean field partition function. We evaluate the critical asymptotics and phase diagrams in Section 4. Section 5 is devoted to a detailed comparison of our model with PR and SRK models. Final remarks and an outlook on future works is included in Section 6 where we also argue that the present method can be applied to construct a wider class of models where the equation of state is obtained as a solution to a dissipative and dispersive equation implying a richer critical phenomenology.

2. General model equations

Let us consider n moles of a gas whose physical state is determined by its volume V, pressure P and temperature T. The number of particles is $N = nN_A$ where N_A is Avogadro's number. Introducing the Gibbs thermodynamic potential $G = E - TS + PV$ where E is the internal energy, the first principle of thermodynamic reads as

$$dG = -SdT + VdP, \tag{2}$$

where the S is the entropy of the system. Introducing the variables

$$x = \frac{P}{T} \qquad t = \frac{1}{T} \tag{3}$$

and the molar volume density

$$v = \frac{V}{n}$$

the balance equation (2) is written as follows

$$d\psi = \varepsilon dt + v dx \tag{4}$$

where $\psi := tG/n$ and $\varepsilon := E/n$ is the internal energy per mole unit. We also observe that Eq. (4) is locally equivalent to the closure condition

$$\frac{\partial v}{\partial t} = \frac{\partial \varepsilon}{\partial x}, \tag{5}$$

also known as Maxwell relation [2]. In the present paper, we focus on the class of models such that the internal energy function admits the following expansion in terms of the small parameter $\eta = 1/N_A$

$$\varepsilon = \varepsilon_0(v) + \eta \varepsilon_1(v) \frac{\partial v}{\partial x} + \eta \varepsilon_2(v) \frac{\partial v}{\partial t} + O(\eta^2) + g(t) \tag{6}$$

where $\varepsilon_i(v)$, $i = 0, 1, 2$ are functions of the one single variable v and $g(t)$ is an arbitrary function of its argument t. A similar expansion has been considered for the entropy function in [21]. We point out that the internal energy for the van der Waals model is a separable function of volume and temperature (see e.g. [14])

$$E_{vdW} = \frac{Na^2}{V} + g(T).$$