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On thermodynamics of fluid interfaces

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ABSTRACT

A recently introduced method for the derivation of thermodynamically consistent boundary conditions will be used in order to study the interaction of two fluids at the common interface and the contact line to a solid body. The calculations allow for temperature dependent surface energy/surface tension and yield thermodynamical conditions on dynamic contact angles. Furthermore, we will show how mean curvature flow and Mullins–Sekerka models fit into this general framework and give a possible explanation for the Dussan and Davis experiment (Dussan and Davis, 1974) compared to the Huh and Scriven paradox (Huh and Scriven, 1971) within the presented theory.

1. Introduction

Moving interfaces and the interaction of moving interfaces with solids and liquids is an important issue in many fields of the applied physics such as engineering or biology. Some of the currently investigated problems include cell membranes in biology (Mercker et al., 2012; Mercker, 2012) or microfluidics (Stone, Stroock, & Ajdari, 2004). Other examples might be found in Bonn, Eggers, Indekeu, Meunier, and Rolley (2009).

There is a huge literature on the subject of fluid–fluid interactions, among the most remarkable seems to us the recent paper by Buscaglia and Ausas (2011), which up to now, to the author's opinion, is the most complete approach from the thermodynamical point of view. Reference to former results can be found therein.

Further interesting summaries on existing models can be found in the book by De Gennes, Brochard-Wyart, and Quéré (2003) and recent reviews by Bonn et al. (2009). Further classical books on the topic of surface processes and surface energy are by Adam (1941) and Oudar (1975) (the latter only for solid surfaces).

Bonn et al. (2009) emphasize the different scales we face when dealing with the contact line: The molecular level, the smooth interface level and the sharp interface level. Depending on the scale, the notion of contact angle has different meaning and we note that the mathematically rigorous transition between these three scales is a challenging topic for future investigations, although this has been studied by simulations (refer to Bonn et al., 2009 and reference therein). In the present approach, we will not focus on the molecular level, but shortly discuss the smooth interface level in the context of moving contact lines. Thus, we assume the choice of the contact angle to be uniquely given by the sharp interface. However, note that we will discover that some macroscopic effects can be described within sharp interface models if we account for macroscopic effects that have their roots on the micro scale.

To the author's knowledge, there is no satisfactory approach to a complete thermodynamical description of moving fluid interfaces within modern thermodynamical approaches, and the closest approach seems to be the aforementioned approach

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by Buscaglia and Ausas (2011). However, they did not include several issues such as temperature dependent surface tension, fluids slipping on top of another, mean curvature flow, Mullins–Sekerka flow and moving contact lines with no slip condition for the bulk. To include all these effects into a unified framework is the main result of this study.

Of course, the major issue in this context are the derivation of boundary conditions for tangential and normal stress on the interface, derivation of thermodynamically consistent formulas for the (dynamic) contact angle and the moving contact line. A particular issue involved with the derivation of contact angles was already outlined by Buscaglia and Ausas (2011): The dynamically varying contact angles as soon as the fluid interface moves along the wall, see Bonn et al. (2009) or De Gennes et al. (2003). While diffuse interface models come up with this feature automatically (see Heida, 2013; Qian, Wang, & Sheng, 2003, 2006) in sharp interface models one might be tempted to introducing a contact line energy or entropy depending on the local contact angle. De Gennes et al. (2003) in their book show that effects of such an energy are negligible, and the calculations below will show that indeed such an assumption would lead to strange effects. However, we cannot circumvent the assumption of a contact line *dissipation*.

Note in this context that the relation between sharp interface models and diffuse interface models has been subject to intensive studies by formal calculations and rigorous asymptotic analysis, refer to Abels and Röger (2009), Abels, Garcke, and Grün (2012), Bonn et al. (2009), Lowengrub and Truskinovsky (1998), Pego (1989) and Qian, Wang, and Sheng (2006) and references therein. However, to the authors knowledge, there is no result taking sufficient care of the limit behavior at the contact line.

Another important issue is the correct choice of the slip condition on the solid surface: While Dussan and Davis (1974) observed that the moving of the contact line is due to a rolling movement with no-slip condition on the velocity field, Huh and Scriven (1971) showed that coupling no-slip Stokes equation with a moving contact line should lead to tremendous thermodynamical problems, as dissipation becomes infinite. In this paper, we show that there is indeed a thermodynamically consistent way to couple a moving contact line with no-slip condition on the bulk (refer to Section 9), by including microscopic effects. This approach will be based on effects at the surface that are sharp interface equivalents of diffusive processes in phase field models.

The modeling technique we use is rather simple and can be considered as a simplified version of a recently developed one by Heida (2013) in order to study the interactions of immiscible liquids at a moving interface within a diffuse interface approach. The derivations are based on functionals for the total energy $\mathcal{E}$ and the total entropy $\mathcal{S}$. From conservation of global energy and nonnegativity of the rate of entropy production (the second law of thermodynamics) we get restrictions on the form of thermodynamically consistent boundary conditions. Note that the calculations can be performed also in the framework of the so called "assumption of maximum rate of entropy production" (Heida, 2013; Rajagopal, 2006) or within an Onsager framework such as usually used by Mielke (2013, 2011). However, we do not focus on theory but on the constitutive equations and their physical implications.

The advantage of our approach is threefold: First, it can be combined with models derived in the context of the maximum rate of entropy production or other thermodynamical methods, second, the derivation is quite easy to understand and does not need mathematical tools beyond calculus on manifolds. This will enable the reader to easily generalize the models to a broad class of applications, deriving suitable models for his own needs. Third, our approach is formulated in an integral/variational formalism that is well suited for numerical simulations as it also provides automatically some apriori estimates.

For the calculations presented below, we focus on the interaction of immiscible Newtonian fluids with a solid boundary. Note that the constitutive equations for the interface and contact line movements are not limited to Newtonian fluids, but may also be generalized to a huge class of non-Newtonian fluids, which are considered in Málek and Rajagopal (2007) and Málek and Rajagopal (2010) (see also references therein).

The structure of the article is as follows: The geometric setting and some fundamental physical assumptions are introduced in Section 2. In Section 3 we introduce some mathematical notations and results which will be used throughout the paper. In Section 4, we derive a model for fluid–fluid interactions based on the assumption that surface tension is independent on temperature. These considerations are useful as they help to better understand the fully thermodynamic calculations in Section 5. The calculations and results from Section 5 are interpreted in Section 6, where we recover (among other results) the classical formula for the contact angle. In Section 7, we recall that the mean curvature flow and Mullins–Sekerka flow can be derived from phase field models and we explain that it might be reasonable to include these effects in sharp interface models if diffusive surface processes or phase transitions are of macroscopic importance. In Section 8, we show that these models may be derived within our framework and in Section 9 we show that these models might explain the Dussan–Davis experiment (Dussan & Davis, 1974) and provide a new view on the Huh and Scriven paradox (Huh & Scriven, 1971).

2. Physical setting

We assume that for both fluids the standard balance laws hold in a way they are introduced in most books on continuum thermodynamics (e.g. Truesdell, 1985). In particular, we assume conservation of mass, momentum and energy.

2.1. Basic assumptions

We assume that the system is limited to a bounded domain Ω in dimension $d = 3$ with boundary $\partial\Omega$. In applications, Ω may vary with time t, but although the method we use could easily cope with such situation, we restrict to time independent