THE MICROMECHANICS OF THE
MOVING CONTACT LINE

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ABSTRACT

The proposed research is divided into three components concerned with molecular structure, molecular orientation, and continuum averages of discrete systems. In the experimental program, we propose exploring how changes in interfacial molecular structure generate contact line motion. Rather than rely on the electrostatic and electrokinetic fields arising from the molecules themselves, we augment their interactions by an imposed field at the solid/liquid interface. By controling the field, we can manipulate the molecular structure at the solid/liquid interface. In response to controlled changes in molecular structure, we observe the resultant contact line motion. In the analytical portion of the proposed research we seek to formulate a system of equations governing fluid motion which accounts for the orientation of fluid molecules. In preliminary work, we have focused on describing how molecular orientation affects the forces generated at the moving contact line. Ideally, as assumed above, the discrete behavior of molecules can be averaged into a continuum theory. In the numerical portion of the proposed research, we inquire whether the contact line region is, in fact, large enough to possess a well-defined average. Additionally, we ask what types of behavior distinguish discrete systems from continuum systems. Might the smallness of the contact line region, in itself, lead to behavior different from that in the bulk? Taken together, our proposed research seeks to identify and accurately account for some of the molecular dynamics of the moving contact line, and attempts to formulate a description from which one can compute the forces at the moving contact line.

INTRODUCTION

That fluid in the neighborhood of the contact line does not behave as fluid within the bulk is now supported by direct observation. In general, fluid near the interface with a solid or another liquid is found to possess different material properties from bulk fluid. Liquids in channels of molecular width were shown to possess a layered structure proximal to a solid surface. Liquid molecules are also found to possess a particular orientation at solid interfaces. Numerous other studies established the concept of *vicinal liquid*, in the vicinity of an interface, which has properties different from those within the bulk. Distinctive properties of these interfaces could in some cases be modeled numerically [1, 2].

Note that the experimental evidence cited above was not made on the moving contact line geometry. Most of the observations have been made at the solid/liquid interface which is the most accessible to available experimental techniques. These techniques also require that there is no

fluid motion. It is from these observations that one may infer that the same effects of molecular orientation and structure are present at the contact line.

PROPOSED WORK

The proposed work is divided into three problems: Surface energy of the solid/liquid interface; Continuum model of the contact line region; and, Averaging and energy transport. The first problem addresses molecular structure at the solid/liquid interface. The second problem deals with molecular orientation. The third is concerned with questions arising when discrete (molecular) systems are modeled as continua.

Surface Energy of the Solid/Liquid Interface

Introduction– This part of the proposed work is a look at the factors that give the solid/liquid interface its particular properties and how these factors affect the forces at a moving contact line. In the experiments an electric field is applied at the solid/liquid interface. In response to the field, the solid/liquid surface tension is altered and the contact line moves. Measurements of the position of the contact line[1] then allow us to compute the dynamic contribution of molecular structure to the force on the moving contact line.

Experiment-Concept– Adjacent to a conducting solid, then there will be a organized layer of vicinal liquid. The energy required to organize this layer contributes to the surface tension

$$\gamma_{SL} = \gamma_{SL}^{\circ} - E \tag{1}$$

where γ_{SL}° is the surface tension in the absence of the organized layer and E is the energy per unit area contributed by the organized layer. Equation (1) is often referred to as Lippman's equation. In the case of simple point ions the contribution E to the surface tension can be calculated from double-layer theory

$$E = \frac{C}{2}(V_M - V_S)^2 \tag{2}$$

where V_S is the potential of the bulk liquid and the differential capacity of the double layer C depends on the parameters of the situation including the ionic content of the fluid. Note that by varying the applied potential V_M at the solid/liquid interface the ions in the double layer are reorganized resulting in a change in the energy stored in the double layer and a resultant change in the surface tension Eq. (1). This imbalance in force can be calculated by a form of Young's equation, the static form of which is given by

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta \tag{3}$$

where θ is the contact angle, and the subscripts indicate the surface tension at the solid/vapor (SV) and liquid/vapor (LV) intefaces. The imbalance of force thus created at the contact line will cause it to move. By measuring the motion of the contact line, the contribution to the surface

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[1]For convenience, we often refer to the contact *line*, it being understood that there is actually a small finite *volume* of anomolous behavior.

tension from the organization in the solid/liquid interface E can be parsed out from the total surface tension γ_{SL}.

Experiment-Technique– A CCD camera observes changes in the rise height $h(t)$ and contact angle $\theta(t)$ at the moving contact line. A potentiostat applies and maintains a fixed potential at the surface of a conducting solid which is in contact with the liquid. The surface potential is changed by an step change of potential and the resultant change in contact line position $h(t)$ and $\theta(t)$ are recorded.

Proposed Work– We propose a series of experiments using water as the working fluid. The experimental protocol can be represented as

$$\text{Molecular Structure} \stackrel{Eq.(2)}{\Rightarrow} E(t) \stackrel{Eq.(1)}{\Rightarrow} \gamma_{SL}(t) \stackrel{Eq.(3)}{\Rightarrow} F(t) \stackrel{\text{data}}{\Leftrightarrow} \left\{ \begin{array}{l} h(t) \\ \theta(t) \end{array} \right. \tag{4}$$

which yields a calculation of the force on the moving contact line which can be compared to measurements of its position and geometry. Starting on the left hand side of Eq. (4), double layer theory provides a description of the molecular structure of adsorbed ions in the neighborhood of a solid surface. From the theory one can calculate the energy $E(t)$ stored in the organized ions at the solid/liquid interface. This energy contributes to the total surface tension at the solid/liquid interface γ_{SL}. The force $F(t)$ on the contact line can then be computed by Young's equation. This time varying force can be correlated to the data $h(t)$, $\theta(t)$ measured from the contact line motion. In this manner, contact line postion and geometry is measured coincident with the force generated at the moving contact line by the molecular double layer structure.

Continuum Model of the Contact Line Region

Background– As discussed in the Introduction, there is experimental evidence that molecules at interfaces have preferred orientations. There is also experimental measurements supporting the supposition that accounting for the change of orientation of the liquid molecules at solid surfaces and the point couples induced by them is necessary in order to accurately predict the forces and loads in squeeze films and other flows restricted to thin domains. While the relevance of these measurements to the contact line geometry is not obvious, we consider that due to the large stresses expected near the moving contact line, as well as its restricted geometry, consideration of the scaling suggests that the forces at the contact line may be similarly affected by molecular orientation.

Concept– In this part of the work, effects of molecular orientation, and other molecular properties, will be formulated into a continuum model of the contact line. Preliminary work, described in a Master's Thesis [3], has shown that incorporating finite molecule size and molecular orientation may account for some of the anomalous features of the contact line region. Consider that molecules not only translate but also rotate and change their orientation. The molecular rotation in a Newtonian fluid would occur randomly with a short relaxation time. For example, the characteristic rotational period for a water molecule at room temperature is about 10^{-11} second and is therefore negligible. If, however, the molecule is in a field that does not fluctuate randomly but controls the long-time behavior of the molecule, the contribution of the molecular rotation could be considerable. A polarized or polarizable molecule, for example, would orient itself to an

applied electric field, a field induced at a conducting wall, or due to configurational changes as it leaves one type of interfacial orientation and becomes incorporated into another. While reorienting itself, the fluid molecule would interact with the surrounding molecules. If its action on neighboring molecules is modeled as a couple applied on the fluid, the equation of motion would be

$$\rho\frac{D\vec{u}}{Dt} = -\nabla p + \rho\vec{f} + \mu\nabla^2\vec{u} + \mu'\nabla \times \vec{L} \tag{5}$$

where ρ is the density, $\vec{u}$ is the velocity, t is time, p is pressure, μ is the viscosity, μ' is a constant, and $\vec{L}$ is the couple, respectively. Here, we have assumed that only a dilute population of atoms are stronly oriented; the remaining volume has no particular orientation. So, each oriented molecule influences its immediate neighborhood with no mutual interaction with other oriented molecules.

Proposed Work– The orientation of a molecule (or a cluster of molecules) can be indicated by a director. The director can be of dipole kind, or quadrupole kind, etc. For example, a quadrupole-kind director can be defined such that

$$m_{ij} \equiv \delta_{ij} - \cos\theta_i \cos\theta_j \tag{6}$$

where m_{ij} is the director, δ_{ij} is the Kronecker delta, and θ_i is the angle between the axis of a specified direction of the molecule and the i-th axis, respectively. The m_{ij} gives the degree of alignment of the molecule in the specified directions i, j. The quadrupole-type director can be related to the molecular rotation ω_o [4]

$$\frac{Dm_{ij}}{Dt} = \omega_o \times m_{ij} - m_{ij} \times \omega_o. \tag{7}$$

As an example, if a two-dimensional case (x, y)-domain is considered and θ_o is the angle between the direction of the molecuar orientation and the x-axis, then equation Eq. (7) reduces to

$$\frac{D\theta_o}{Dt} = \frac{\partial\theta_o}{\partial t} + u\frac{\partial\theta_o}{\partial x} + v\frac{\partial\theta_o}{\partial y} = -\omega_{o_z} \tag{8}$$

If now Eq. (5) is also restricted to a two-dimensional domain, the streamfunction ψ can be introduced. If the equation is now nondimensionalized and considered in the limit of low Reynolds number, it can be written as

$$-C_O\nabla^2\omega_{o_z} + \nabla^4\psi = 0 \tag{9}$$

where C_O is a known constant, and ω_{o_z} is the molecular rotation in the z-direction. Equations (8) & (9) should be solved simultaneously. The most difficult part of this work is seen to be that the couple field $\vec{L}$ and the flow field are dependent. If successful, the slip condition could then be specified as a known function of the properties of the liquid, the solid, and the flow parameters.

Averaging and Energy Transport

Concept– In formulating a continuum model from a description of molecular interaction, as outlined above, it is necessary to average over a collection of molecules. Within the bulk this averaging is a standard procedure which relies on the large number of molecules within the volume being averaged. Within the contact line region, however, the volume may not be sufficiently large to justify the use of the averaging procedures which work so well within the bulk. In this part of

the proposed research, we seek to determine 1) the minimum size for which bulk-type averaging is accurate, 2) how to average over small groups of molecules, as in the contact region, which may be smaller than this minimum size, and 3) how energy is transported in small systems.

Preliminary work– In preliminary work the interaction of molecules along an interface has been modeled as a one-dimensional chain of point masses interacting through a power-law potential. It can be shown that such a potential models the nearest-neighbor interactions between polarized molecules [5]. Much is known about systems of this type. However, almost all prior work was concerned with large systems or with the thermodynamic limit of broad-band forcing [6]. However, we have found that small systems do not show the same type of behavior as large systems [7]. The normalized entropy is defined as

$$\eta(t) \equiv \frac{S_{max} - S(t)}{S_{max} - S(0)} \qquad (10)$$

where $S(t)$ is the entropy of the system at time t whose maximum value is given by

$$S_{max} = \ln(N/2) \qquad (11)$$

so that $\eta = 1$ implies that all of the energy is in one mode, and $\eta = 0$ is that the energy is equally shared by all modes. For large systems η decreases to zero or a small value (there are some exceptional cases given by Fermi-Pasta-Ulam recurrence). However, for small systems the entropy shows a cascade of peaks. These peaks appear even at extremely long times. The peaks in normalized entropy indicate organized motion among the masses. From further measurements of the dispersion of waves propagating along the chain we speculate that this organized motion may indicate the presence of solitary waves. In small systems this type of energy transfer appears to be intermittent, and the organized wave motion is disturbed by long intervals of thermal motion. In other preliminary work, contained in a Master's thesis [8], we have identified the frequency content of the organized motion. We have found that the evolution of the normalized entropy is self-similar as the number of masses N increases, at least over a limited range $3 < N < 256$. Within this range the time of occurrence of any particular peak t_{peak} scales with number of masses as $t_{peak} \sim N^2$

Proposed work– In the proposed work, we address the following questions: 1) What is the minimum size such that a chain of masses (molecules) can be treated by the usual types of statistical averages [9]? However, these types of averages may not be valid when applied to the small numbers of atoms which make up the contact line region or the neighborhood of an interface. 2) What are the parameters which determine the continuum limit? The limit is not quite so simple as simply increasing the number of masses N. For example, if excited by a single spatial mode, the energy density–the energy per mass–has to decrease as N increases in order to reach the continuum limit. We here try to delineate how a discrete system approaches the continuum limit. In addition, we try to determine the proper manner to take the limit. 3) What types of behavior are found for small systems? In particular, what types of energy transport are found in small systems? We have already pointed out that in our preliminary work we have found that small systems seem to support intermittent solitary waves. We would like to determine the extent to which energy is transported along the interface (chain) by these types of waves.

SUMMARY

Our overall goal is to accurately describe microgravity fluid motion in the presence of a moving contact line. We seek to identify the molecular dynamics which make the moving contact line a unique region and to then incorporate these dynamics into a continuum model. Part of our proposed research is experimental in which we measure how a vicinal layer affects contact line motion. These measurements relate contact line motion with changes in solid/liquid interfacial structure. Initially we are trying to use double layer theory to relate changes in double layer structure to contact line motion. Other analytical work seeks to formulate the effects of molecular orientation on contact line motion. Implicit in our continuum theory is a means of averaging discrete molecular behavior into continuum equation. We investigate the proper manner of averaging small collections of molecules by simulating the interface numerically and observing the behavior as a function of the parameters of the system including system size. We consider the proper limiting procedure needed in order to extract the continuum limit. However, we recognize also that small systems have behavior which is distinctively different from continuum behavior. We seek to identify the mechanisms of energy transport along the interface and how these mechanisms scale with system size.

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