Fully Atomistic Molecular Dynamics Simulations of the Behavior of a Simple Model of Crude Oil Confined between Graphene Planes

E. Maldonado,[†] M. W. Roth,[†,*] and Paul A. Gray[‡]

Departments of Physics and of Computer Science, University of Northern Iowa, Cedar Falls, Iowa 50614

ABSTRACT We present and discuss the results of molecular dynamics computer simulations of crude oil confined between graphene planes. The crude oil is represented as a mixture of alkanes having $6 \leq n \leq 30$ carbons that contain explicit hydrogen atoms; the confining structure is a floor and ceiling, each comprised of graphene sheets. At low temperature, the system adsorbs completely onto the confining layers, showing an interesting domain structure in its own right. As the temperature increases, various species desorb in order of increasing molecular mass and enter the vapor phase between the confining sheets. Desorption proceeds through a roughening of the adsorbed layers but does not appear to couple to any inter- or intramolecular phase transition on the surfaces for any given species. Allowing the graphene sheets to be flexible affects the rate of adsorption as well as the in-plane order and molecular confirmations of the adsorbate. Cursory simulations with more than one layer show droplet-like adsorption at low temperatures and complicated dynamics, which shift the initial desorption temperatures to lower values than those for the monolayer and cause the desorption temperature and process to be much less defined. The results presented here are suggestive of a method of separating alkane mixtures at temperatures significantly different from those of conventional refining processes.

KEYWORDS: petroleum • confinement • adsorption • graphene • alkanes

I. INTRODUCTION

Crude oil and its derivatives are compounds that have deep practical and industrial significance. Although of varying composition, even from the same source, crude oils have distribution spectra of predominantly *n*-alkanes (abbreviated C_n), which are straight-chained hydrocarbons having the general formula C_nH_{2n+2}. Natural gas is comprised of C_1-C_5 molecules in varying ratios (1) and crude oil is generally from C_6-C_{30} (2−7). Some basic practical information about alkanes can be found in Table 1.

Because alkanes comprise a family of compounds, they lend themselves quite nicely to comparative studies in theoretical, computational, and experimental arenas. Because of the wide distribution of alkane chain lengths in crude oils, they make ideal systems for the study of comparisons and contrasts within the alkane family. Computer simulations can give much insight into the behavior of physical systems from both supplementary and predictive standpoints and can shed light on system dynamics not readily accessible in experiments. The studies that exist involving natural gas and crude oil are macroscopic in nature and, although very useful, do not address nanoscale dynamics and processes inside transport pipes and on surfaces. Such an understanding could prove very useful in helping delineate the effects and possible repair of pipe breaks, in facilitating an understanding of new methods of fractionating crude oil and in characterizing the alkane layers adsorbed onto transport pipes that need remediation. In many cases, it then becomes relevant to study the *atomistic* behavior of alkane mixtures in confined geometries.

Table 1. Basic Information about Various Alkanes

compound range	mixture(s) contained in	use
C1−C4	natural gas	cooking, heating
C5−C10	naptha and gasoline	solvent chemicals, car fuel
C10−C16	kerosene	heating, jet fuel, lighting
C14−C20	diesel fuels	fuel for trucks/trains
C20−C70	lubricating and fuel oils	machinery, ships, oils, waxes, polishes
>C70	residue/asphaltines	pavement, roofing

The behavior of atomic and molecular systems in confined geometries has been widely studied (8). Generally, a confined liquid tends to organize into lamellae, or layers. Moreover, there are density and solvation force oscillations perpendicular to the boundary whose wavelength is on the order of the dynamic radius of the confined molecule. Such effects have been studied in confined alkanes (8−16). For organic molecules, branching can disrupt the spatial periodicity of density and solvation force oscillations (17). Another intriguing result is that a confined liquid system can possess a distinctly solidlike character: sheer stress (18). Confinement can also slow down the dynamics of a system and, in particular, longer molecules of a given family can be affected more than shorter ones (18, 19). In addition to the wealth of studies on confined organic systems, computer

* To whom correspondence should be addressed. E-mail: rothm@uni.edu.
Received for review February 10, 2009 and accepted May 14, 2009
† Department of Physics.
‡ Department of Computer Science.
DOI: 10.1021/am900086u