

SUPERCRITICAL FLUIDS: DEVIATIONS OF TRANSPORT PROPERTIES FROM A FUNDAMENTAL APPROACH

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Abstract. *This work presents a method to predict transport properties of supercritical and near critical fluids using a microscopical approach by molecular dynamics with Green-Kubo method. The first results were obtained for argon. The fluid was modeled by spherical Lennard-Jones pair-potentials with parameters adjusted to experimental vapor liquid equilibrium. Good agreement between predictions from simulation and experimental data from NIST is found for shear viscosity and thermal conductivity. The method can be extended for other fluids and mixtures and can be an useful tool to predict properties when experimental data is not available.*

Keywords: *bulk viscosity, shear viscosity, thermal conductivity, molecular dynamics, Green-Kubo*

1. INTRODUCTION

An important class of fluids is the supercritical fluids. They are not gases. They are not liquids. The easiest way to explain what they are can be found in the pVT phase diagram. Supercritical fluid is the thermodynamic state above the critical point (critical temperature, T_c , and critical pressure, p_c) on a pT diagram (Arai et al., 2002).

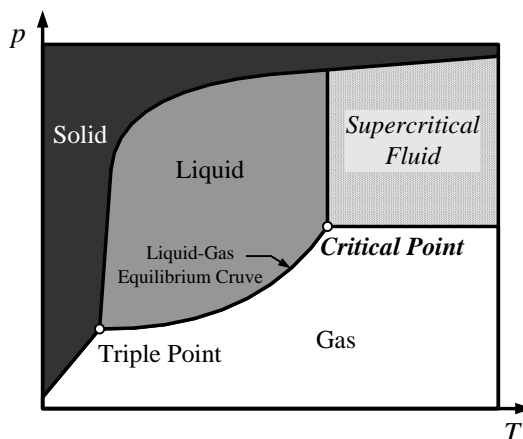


Figure 1. pT diagram showing supercritical state.

This state can be found in numerous industrial applications such as extractions, media for chemical reactions, high efficiency cleaning, nanoparticles production and it is the state of oil in the Pre-salt layer. In the defense field one can find rocket motors, gas turbines, and many projected advanced combustor designs operating supercritically or near supercritical conditions (Kubota, 2007). Table 1 below shows us how accessible is the supercritical region due to the magnitude of critical constants.

Table 1. Critical point of some substances.

Substance	T_c (K)	p_c (MPa)	Substance	T_c (K)	p_c (MPa)
N ₂	672,50	3,39	NH ₃	951,95	11,30
O ₂	700,88	5,02	H ₂ O	1193,43	21,94
CO ₂	850,51	7,39	NO	726,45	6,52
Ar	697,16	4,90	CO	679,22	3,49
SO ₃	1037,15	8,19	HCl	870,95	8,36

Some properties diverge near critical point. While shear and bulk viscosities, thermal conductivity, heat capacities tends to infinite, sound speed and thermal diffusivity tends to zero (Carlès, 2010). It occurs because near critical point the correlation length becomes macroscopic (Huang, 1987). Microscopically, this makes supercritical fluids to be

inhomogeneous media with high and low-density regions. Macroscopically, one can notice that these fluids are compressible and dense at the same time. This makes them very versatile. They can dissolve a solid like liquids, diffuse through a solid like gases, and are considered adjustable fluids by small variations of temperature and pressure.

As it is difficult to determinate rheological properties near critical point and there are not many data about supercritical fluids in literature, this work aims to show that a microscopical approach is a good strategy to obtain transport properties of this kind of fluid. We use here molecular dynamics which is introduced in the following section.

2. MOLECULAR DYNAMICS

The first molecular dynamics simulation was performed in 1959 (Alder and Wainwright, 1959) and since then this method is increasingly used in science and engineering to predict thermophysical properties of materials, allowing a deeper understanding of macroscopic properties from microscopic structure. In this method, the Newtonian equations of motion of a set of N interacting particles (atoms and/or molecules) in a defined volume V are solved numerically (Rapaport, 2004). The basic equation for each particle i is

$$\mathbf{F}_i = m_i \frac{d^2 \mathbf{r}_i}{dt^2} \quad (1)$$

where \mathbf{F}_i is the resulting force acting over particle i , m_i is the mass of the particle and \mathbf{r}_i its position. The forces are obtained from the interaction potential U_{ij} between any two particles i and j as

$$\mathbf{F}_i = \sum_{i,j,i \neq j} \mathbf{f}_{ij} = - \sum_{i,j,i \neq j} \nabla U_{ij} \quad (2)$$

Generally for simple no-charged systems the Lennard-Jones (LJ) 12-6 pairwise spherically symmetric potential U_{ij}^{LJ} is used (Allen & Tildesley, 1987). It is a two parameters potential in the form

$$U_{ij}^{\text{LJ}} = \begin{cases} 4\epsilon\{(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^6\}, & r_{ij} \leq r_c \\ 0, & r_{ij} > r_c \end{cases} \quad (3)$$

where ϵ is the modulus of the lowest energy value and σ is the distance where potential goes to zero. r_{ij} is the intermolecular distance between any particles i and j , and r_c is the cutoff radius that is used to improve computational efficiency as U_{ij}^{LJ} tends to zero for large r_{ij} . It is well known that the LJ potential gives a reasonable description of the behavior of noble gases dense systems. Other potentials can be used to model more complex chemical systems.

Integration of Eq. (1) considering Eq. (2) and Eq. (3) let us determinate explicitly positions, velocities and acceleration of all particles at each instant. The numerical method used is Velocity-Verlet algorithm (Swope et al., 1982) that is obtained by a Taylor series expansion

$$\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \Delta t \mathbf{v}_i(t) + \frac{1}{2} \Delta t^2 \mathbf{a}_i(t) + O(\Delta t^3) \quad (4)$$

$$\mathbf{v}_i(t + \Delta t) = \mathbf{v}_i(t) + \frac{1}{2} \Delta t [\mathbf{a}_i(t + \Delta t) + \mathbf{a}_i(t)] + O(\Delta t^2) \quad (5)$$

where Δt is the time step, and \mathbf{v}_i and \mathbf{a}_i velocity and acceleration of particle i . To represent a bulk system, periodic boundary conditions can be used.

2.1 Transport Coefficients from Molecular Dynamics

Transport coefficients are associated to irreversible processes and entropy production (Green, 1969). Using fluctuation-dissipation theorem it is possible to describe irreversible phenomena in terms of reversible microscopic fluctuations (Nyquist, 1928). It can be shown that transport coefficients can be calculated as specific integrals of time-correlation functions (Green, 1954), (Kubo, 1957) and (Mori, 1958).

2.1.1 Shear and bulk viscosity

From a microscopic point of view, shear viscosities η_s can be calculated by integration of the time-autocorrelation function of the off diagonal elements of the stress tensor \mathbf{S} .

$$\eta_s = \frac{1}{Vk_B T} \int_0^\infty \langle S^{x_1 x_2}(t_0) S^{x_1 x_2}(t_0 + t) \rangle dt \quad (6)$$

where V is the volume, k_B is the Boltzmann Constant, T the temperature, and $\langle \dots \rangle$ is the ensemble average. Each element of the off diagonal of the stress tensor is given by

$$S^{x_1 x_2} = \sum_{i=1}^N m_i v_i^{x_1} v_i^{x_2} - \sum_{i=1}^N \sum_{j>i}^N r_{ij}^{x_1} \frac{\partial U_{ij}}{\partial r_{ij}^{x_2}} \quad (7)$$

Here, i and j are the indices of the particles and x_1 and x_2 are different vector components of the particle velocity v_i

Bulk viscosities η_b can be calculated by integration of the time-autocorrelation function of the diagonal elements of the stress tensor and an additional term that involves the product of pressure p and volume V . The adiabatic formulation allows us to write

$$\eta_b = \frac{1}{Vk_B T} \int_0^\infty \langle (S^{x_1 x_1}(t_0) - pV(t_0))(S^{x_1 x_1}(t_0 + t) - pV(t_0 + t)) \rangle dt \quad (8)$$

where

$$S^{x_1 x_1} = \sum_{i=1}^N m_i v_i^{x_1} v_i^{x_1} - \sum_{i=1}^N \sum_{j>i}^N r_{ij}^{x_1} \frac{\partial U_{ij}}{\partial r_{ij}^{x_1}} \quad (9)$$

2.1.2 Thermal conductivity

Thermal conductivities κ can be calculated by integration of the time-autocorrelation function of the elements of the microscopic heat flow

$$\kappa = \frac{1}{Vk_B T^2} \int_0^\infty \langle J^{x_1}(t_0) J^{x_1}(t_0 + t) \rangle dt \quad (10)$$

where J^{x_1} is for a pure fluid

$$J^{x_1} = \sum_i^N v_i^{x_1} E_i + \sum_i^N \sum_{j>i}^N r_{ij}^{x_1} \frac{dE_{ij}}{dt} \quad (11)$$

In this expression, E_i is the energy of i molecule (potential, translational, vibrational) and dE_{ij}/dt the temporal rate of energy variation for a molecule i interacting with a molecule j . Evans and Morriss (2008) states that this property is the most difficult to be calculated because Green-Kubo formulation presents difficulties do converge the heat flux \mathbf{J} and its autocorrelation function.

3. SOME RESULTS

We have performed simulations for supercritical argon ($T_c = 150.9$ K, $p_c = 4,86$ MPa), that is simplest fluid (noble gas) to be studied, using LAMMPS. Systems of 1000 and 10000 particles were constructed. r_c was chosen to be 5σ . $\sigma = 3.3952$ Å and $\varepsilon/k_B = 116.79$ K were collected from vapor-liquid equilibrium data. 500k time steps were used to equilibrate the system to the specified temperature and pressure, 1000k time steps were used to evaluate time-autocorrelation functions for shear viscosity and thermal conductivity. Results are presented in graphs below. Predicted shear viscosity are in good agreement to literature data. Predicted thermal conductivity are a constant below experimental data. This constant was not determined yet.

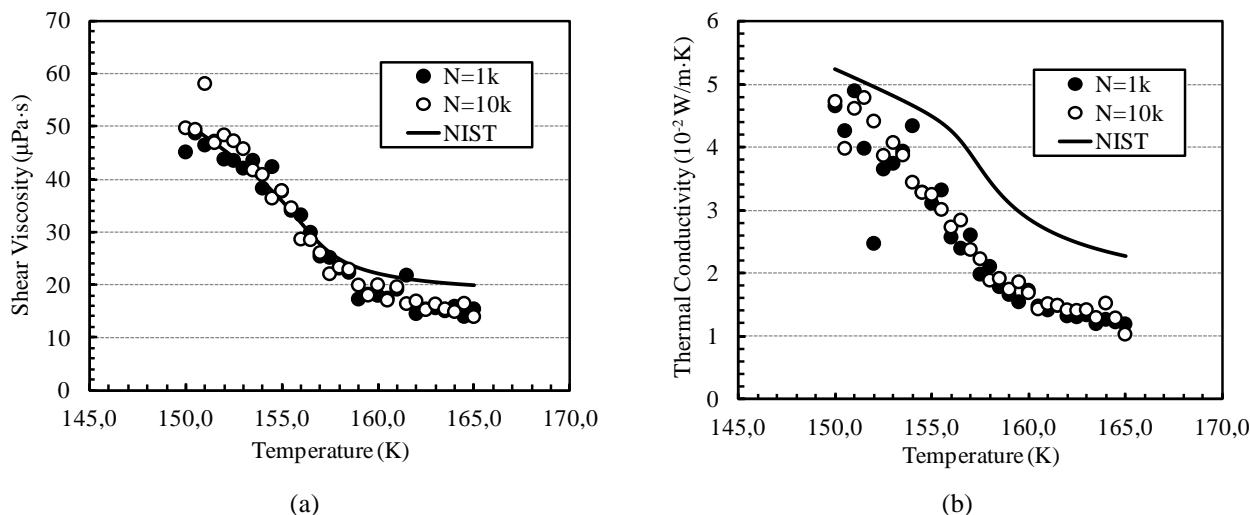


Figure 2. Shear viscosity η_s (a) and thermal conductivity κ (b) of supercritical argon predicted by molecular simulations compared to experimental data from NIST. $p = 1,25 p_c$.

The authors are the only responsible for the printed material included in this paper.

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