Dynamic Crossover in Fluids: From Hard Spheres to Molecules

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Abstract

We propose a simple and generic definition of a demarcation reconciling structural and dynamic frameworks when combined with the entropy scaling framework. This crossover line between gas- and liquid-like behaviors is defined as the curve for which an individual property, the contribution to viscosity due to molecules' translation, is exactly equal to a collective property, the contribution to viscosity due to molecular interactions. Such a definition is shown to be consistent with the one based on the minima of the kinematic viscosity. For the hard sphere this is shown to be an exact solution. For Lennard-Jones spheres and dimers and for some simple real fluids this relation holds very well. This crossover line passes nearby the critical point and for all studied fluids is well captured by the critical excess entropy curve for atomic fluids, emphasizing the link between transport properties and local structure.

TOC Graphic



Fluids composed of molecules possessing attractive interactions exhibit a critical point which is a point in the pressure and temperature space beyond which distinct gas and liquid phases do not exist.^{1,2} Above this critical point, i.e in the supercritical state, the density of a fluid continuously increases along an isotherm as the pressure is increased without exhibiting any first order transition (which introduce a discontinuity in thermodynamic properties). Supercritical fluids are naturally present on earth, underground, as in oil and gas reservoirs³ or when considering water issuing from black smokers found on the sea floor.⁴ They are also widely used in a range of industrial processes from fluid extraction² to carbon dioxide geological sequestration⁵ taking advantage of their high compressibility, their relatively low viscosity and their good ability to dissolve materials.

This fascinating possibility of a continuous transformation from gaseous to liquid states of matter has attracted attention since the seminal experiments of Andrews back in 1869.⁶ More recently, the possibility of defining a demarcation between liquid- and gas-like behaviors for the whole supercritical domain has been the subject of numerous investigations.^{1,2,7–20} Determining such a signature of a subcritical behavior, where the gas and liquid phases are distinct, in the supercritical region is of obvious fundamental interest but would also certainly be beneficial for the design of modern equation of states and transport properties models. This topic has led to many debates, which were particularly vivid during the last decade,^{17–19} because of multiple definitions often not compatible which one another, even within the same family, e.g. Widom Lines, inversion lines or Frenkel lines.² Among the main reasons of such incompatibility is that such a crossover can be seen either from a structural point of view Widom lines²), a dynamic perspective (e.g. kinematic viscosity minimum line⁹), or (e.g. from a free energy point of view.^{21,22} However. as pointed out in a previous work,²⁰ there is a possible way to reconcile structural and dynamics points of view by relying on the entropy scaling concept, which was introduced by Rosenfeld with little fanfare in 1977.²³ Still, the entropy

scaling demarcation of gas- and liquid-like fluid behaviors proposed so far,²⁰ despite some interesting features obtained on simple model fluids, is not entirely satisfactory because it does not start at the critical point in model fluids that exhibit one and is difficult to interpret when applied to molecular fluids.

To reconsider the definition of a demarcation line between liquid- and gas-like behaviors, valid for fluids composed of molecules possessing or not attractive interactions and applicable to both atomic and molecular fluids, we propose in this work to go back to the very nature of what differentiates liquid- and gas-like properties from a microscopic perspective. At the molecular scale, gas properties are mostly driven by the individual behaviors whereas liquid properties are mainly controlled by collective behaviors. Such a decomposition is at the very core of the modeling of fluid equilibrium properties which are described by an "ideal" term, related to individual behaviors, and a "residual" contribution, corresponding to collective behaviors.²⁴ From the transport properties point of view, these two behaviors are exemplified by the two corresponding possible modes of heat and momentum propagation in fluids: (i) due to molecules' displacements or (ii) due to molecular interactions, both terms directly emerging from the microscopic formulation of the momentum and heat fluxes.²⁵ Thus, within that simple framework, we propose to define the demarcation line between gas and liquidlike behaviors as the curve for which an individual property, the contribution to viscosity due to molecules' translation, is equal to a collective property, the contribution to viscosity due to molecular interactions. In the following this line is denoted the crossover line. To emphasize its generality, this simple and universal definition is tested in this work on the hard-sphere fluid, i.e. a fluid that does not exhibit a critical point, as well as on the Lennard-Jones and the Lennard-Jones dimers in their supercritical regions. As it will be shown, the crossover line so defined is fully consistent with the recently proposed definition based on the kinematic viscosity minimum^{7,9,26} and can be rationalized in the framework of excess entropy scaling for both

atomic and molecular fluids providing a link between structural and dynamic point of views of such a demarcation.

To quantitatively revisit the definition of the demarcation line between liquid- and gas-like behaviors, we start from the microscopic definition of the shear viscosity, η , which characterizes the transverse momentum transfer in the linear response regime. From a molecular point of view, such momentum transfer can occur by displacement of individual molecules from one point in space to another point and/or by collective interaction with other molecules.²⁷ It is thus possible to define the shear viscosity of any type of fluid as the sum of two terms named hereafter the kinetic contribution to viscosity, η_{kk} , and the configurational contribution to viscosity, η_{cc} .²⁸ The former is dominant in low density fluids (gas like) while the latter term prevails in dense fluids (liquid like). Such a shear viscosity decomposition into two additive contributions naturally emerges when performing reverse Non-Equilibrium Molecular Dynamics (NEMD) simulations.²⁹ In these nonequilibrium simulations, shear viscosity is deduced from the ratio between the imposed shear stress,³⁰ i.e. the transverse momentum flux which is composed of a kinetic term and a configurational term, and the measured shear rate²⁹ as described in detail in the SI. In equilibrium molecular dynamics simulations (EMD), shear viscosity can be computed from the autocorrelation of the shear stress through a Green-Kubo relation²⁷ and a similar decomposition can be done into kinetic η_{kk} and configurational η_{cc} contributions, but an additional crossterm $\eta_{\rm kc}$ is generated.³¹ These differing notions of the various contributions to shear viscosity can be reconciled by pragmatically splitting the cross-term from EMD simulations in half, and distributing half to each of the kinetic and configurational contributions, i.e. $\eta_{\rm kk, NEMD} =$ $\eta_{\rm kk,EMD} + \eta_{\rm kc,EMD}/2$ as demonstrated to hold in the SI on the Lennard-Jones fluid.

As it will be shown later, the above definition of the crossover line is closely related to a recently suggested one based on a specific signature of the kinematic viscosity, ν , in the supercritical region.^{7,9,26} Indeed, kinematic

viscosity, i.e. shear viscosity divided by mass density, is known to exhibit a minimum along an isotherm in supercritical conditions, a result already known in the 1960s (see section 16.5 of Ref. 32). Interestingly, it has been shown recently that the loci of the local minimum of the kinematic viscosity is a promising definition of the demarcation between gasand liquid-like behaviors in supercritical fluids, that is also applicable to fluids without attractive interaction.²⁶ In simple model atomic fluids, it has been shown that such a definition is consistent with the Widom line defined by the loci of the local maxima of the isobaric specific heat, even if not perfectly correlated.²⁰ Furthermore, the demarcation so defined is also tightly correlated to the dynamic crossover exhibited by sound propagation, related to the positive sound dispersion, in the Terahertz frequency regimes.⁹ Application of the phonon theory^{33–37} also demonstrates qualitatively different behaviors passing through this crossover region, both experimentally and in simulations.

To connect our shear viscosity based definition of the crossover line to the more classical structural point of view, we will take advantage of the excess entropy scaling framework in the following. The core idea introduced by entropy scaling is that the transport properties are connected with the excess entropy, making a link between structural and dynamic properties.²³ Yoon et al. further demonstrate how the entropy scaling approach is connected to the Shannon entropy.³⁸ The reduced excess entropy is defined by $s^+ \equiv -s^{\text{ex}}/k_{\text{B}}, k_{\text{B}}$ being the Boltzman constant, where s^{ex} is the entropy per particle minus that of the ideal gas at the same temperature, T, and number density, $\rho_{\rm N}$; i.e. $s^{\text{ex}} = s(T, \rho_{\text{N}}) - s^{(\text{ig})}(T, \rho_{\text{N}})$. Much of the modern understanding of excess entropy scaling comes from isomorph theory.^{39–43} A significant body of theoretical and practical work now exists on excess entropy scaling which shows a promising means of modeling and understanding transport properties of both atomic and molecular fluids. $^{20,44-50}$

The first test of our definition of the crossover line concerns its application to the simplest fluid model, the Hard-Sphere (HS). Such a fluid model, which is widely used in fluid physics, is interesting as it does not exhibit any distinct gas and liquid phases in its whole fluid domain because it lacks attractive interactions. To do so, we use the Enskog theory which gives the expressions for the shear viscosity by:

$$\eta_{\rm En} = \eta_{\rho_{\rm N}\to 0} b \rho_{\rm N} \left[\frac{1}{\widetilde{w}} + \frac{4}{5} + \left(\frac{4}{25} + \frac{48}{f_{\eta} \cdot 25\pi} \right) \widetilde{w} \right]$$
(1)

where $\eta_{\rho_{\rm N}\to 0}$ is the dilute-gas contribution, $b = 2\pi\sigma^3/3$ is the hard sphere virial coefficient (σ being the HS diameter), $\rho_{\rm N}$ is the number density, and $\tilde{w} = p/(\rho_{\rm N}k_{\rm B}T) - 1$ is the reduced virial, p being the pressure. The fourth-ordercorrected dilute-gas viscosity of hard spheres is $\eta_{\rho_{\rm N}\to 0} = f_{\eta} \times \frac{5\pi}{16} \frac{\sqrt{mk_{\rm B}T}}{\pi^{3/2}\sigma^2}$, with $f_{\eta} = 1.01600$ and m the mass of a particle. Even if not accurate at very high densities, ⁵¹ Enskog theory provides a reasonable estimation of shear viscosities of the HS fluid up to liquid-like densities.⁵²

Enskog theory gave a decomposition into kk, kc, and cc contributions, indicated by the first, second, and third contributions inside the brackets of eq. (1). By pragmatically splitting the cross-term in half, as shown to be a valid option for the Lennard-Jones fluid in the SI, one can readily obtain from equating η_{kk} and η_{cc} , that $\widetilde{w} = (4/25 + 48/(f_n \cdot 25\pi))^{-1/2}$. Interestingly, as detailed in the SI, the same analytical result is recovered when evaluating the location of the minimum of the kinematic viscosity. Thus, the exact solution from Enskog theory is that the minimum of ν occurs when the translational and configurational contributions to viscosity are equal. This means that our definition of the crossover line and the one based on the kinematic viscosity minimum are strictly equivalent for the HS fluid. Figure 1 shows the curves from Enskog theory, indicating that the minima of kinematic viscosity and crossing of contributions to viscosity occur at the same density for all temperatures.

It is illuminating to define this crossover line within the excess entropy framework, as shown in Fig. 1. To do so, the excess entropy for hard spheres is obtained from the integral $s^+ = \int_0^{\zeta} \frac{Z(a)-1}{a} da$ where $Z(\zeta)$ is the equation of state



Figure 1: Kinematic viscosity and contributions to viscosity. Top: density as independent variable; Bottom: excess entropy as independent variable. In each pane, curves and markers use the same color scale, the upper filled part of pane is values of $\nu^* = \eta^*/\rho^*$, and lower part of pane is the fractional contributions $\eta_{\rm kk}/\eta$ and $\eta_{\rm cc}/\eta$. Markers are for LJ monomer (circle: complete contribution, triangle: fractional translational contribution, square: fractional configurational contribution), smooth curves (both solid and dash-dotted) for HS are from Enskog theory. Values of s^+ for LJ monomer from Ref. 53.

(EOS) for the hard sphere, in terms of the packing fraction $\zeta = \pi \rho_{\rm N} \sigma^3/6$ (or the volume of spheres per total volume). The EOS of Ref. 51 is used, and the integral is evaluated with adaptive quadrature, yielding a value for s^+ on the order of numerical precision. Interestingly, this value of s^+ at the crossing line (0.898) is close to that of the critical point of the Lennard-Jones monomer fluid (0.855 from the empirical EOS in Ref.⁵³), a significant result as will be shown later on.

It is important to point out that the excess entropy scaling,²³ or more generally the isomorph theory (which correspond to curves along which macroscopically structure and dy-

namics are constant), is an efficient framework to connect structural and dynamic properties in simple fluids. Excess entropy is a measure of the number of accessible microstates relative to that of the ideal gas, but it is as well a quantity that can be related to the microscopic structure of the fluid. Indeed, its two-body contribution which represents usually more than 85% of the total excess entropy in simple fluids 54-56can be expressed in terms of the radial distribution function and density only, the former being a structural microscopic quantity which describes how density varies as a function of distance from a reference particle. Thus, by connecting excess entropy and transport properties, the excess entropy scaling framework allows to reconcile structural and dynamic points of view of the crossover line as will be emphasized in the following.

As a step further in demonstrating the generality of our definition of the crossover line, we have used the Lennard-Jones (LJ) fluid (with the pair potential V given by $V = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$) which is probably the most commonly considered analog for fluids with both attraction and repulsion. As a consequence of this model fluid having both attraction and repulsion, it exhibits liquid-vapor phase equilibrium, a liquid-vapor critical point and so a supercriticial region, and many other commonly experienced physical features.

For this fluid model, molecular simulations were performed to obtain viscosities, the crossover points and excess entropy in the supercritical region as follows. The nonequilibrium calculations of viscosity have been performed with an in-house code already validated²⁹ with the Reverse Non-Equilibrium Molecular Dynamics scheme;³⁰ numerical details are provided in Ref. 57 and all data are provided in Table S1. Then, along a given nominal isotherm, the density where $\eta_{kk}^* = \eta_{cc}^*$ was obtained by interpolation of a smoothed curve fit to η_{cc}^*/η^* as a function of ρ^* . A similar approach was used for the minima of kinematic viscosity; a curve was fit to η^* as a function of ρ^* , and then that curve was used to obtain the density at the minimum of $\nu^* = \eta^* / \rho^*$. Table S2 in the SI gives the numerical values. Excess entropy calculations were carried out with an in-house Monte-Carlo implementation in this work, see Section 4.3 of the SI. For the Lennard-Jones fluid, confirmatory excess entropy values were obtained from the respective EOS.

As shown in Figure 2, the first interesting point is that our definition of the crossover line, based on $\eta_{\rm kk}^* = \eta_{\rm cc}^*$, seems to start near the critical point for the LJ fluid. Such a behavior is consistent with the idea of a crossover line prolongating, in the supercritical region, the demarcation between gas and liquid phases. The second very interesting feature is that there is clearly an excellent agreement between the location of the points corresponding to the minima of kinematic viscosity ν and those associated to the crossover line. Thus, the addition of attractive interactions does not alter this strong result noticed on the HS fluid, reinforcing the idea of a fundamental link between these two definitions of a liquid- and gas-like demarcation in the supercritical region. A subtle point is that the critical point itself is not a minimum of the kinematic viscosity because the density is finite at the critical point, while the viscosity is infinite, leading to a local extremum in the kinematic viscosity.

As exemplified by the HS fluid, the excess entropy framework can simplify even more the picture. As shown in Figure 1, the LJ fluid has minima of kinematic viscosity ν whose density are a strong function of temperature, which is unlike the behavior of the HS fluid. So too, the kinetic and configurational fractional contributions have both temperature and density dependence. Considering the excess entropy as the independent variable instead of density yields a more harmonious result: i) the fractional contributions to viscosity are now nearly monovariate functions of the excess entropy, agreeing with the hard sphere fluid of Enskog theory ii) the minima of kinematic viscosity no longer have temperature dependence, and they all occur at very nearly the same value of the excess entropy. Even more interesting, Figure 1 shows that this value of excess entropy is very nearly the value of excess entropy corresponding with that of the critical point which, in turn, is very close to that obtained for the HS crossover line. This brings the three definitions of a liquid- gaslike demarcation (critical point excess entropy, equality of kinetic and configurational contributions, minima of kinematic viscosity) into near agreement, reconciling the structural and dynamic points of view in atomic fluids.

So far we have considered atomic fluids only, whereas real fluids are mostly molecular. Here we have considered a Lennard-Jones dimer fluid consisting of two tangent Lennard-Jones spheres connected by a fixed bond of length σ to remove the intramolecular potential energy. The same methodology used for Lennard-Jones was also used to obtain the crossover points, the kinematic viscosity minima and the excess entropy for the dimer. Results are shown in Fig. 2; computed values are tabulated in Table S1 and S2 of the SI.

The introduction of a bond into a molecule results in a qualitatively similar behavior to that of the monomer. First, the crossover begins at the critical point. Second, the $\eta_{kk} = \eta_{cc}$ points and the ones corresponding to the kinematic viscosity minima are superimposed, i.e. the two definitions of a dynamic crossover result in effectively identical densities for a given temperature. Third, the curve of excess entropy emanating from the critical point is in qualitative agreement with the crossover points, even if in the density-temperature plane there is a systematic deviation increasing with temperature, as shown in Fig. 2.

In a last test, we have considered small real Reference empirical modfluids as follows. els for thermodynamic and transport properties are available in NIST REFPROP⁵⁸ and Cool-Prop⁵⁹ that reproduce the most accurate experimental data to close to experimental uncertainty. While we cannot have complete confidence in the outputs of these empirical models, particularly as pertains to extrapolation behavior, Fig. 3 shows the locations of the calculated minima of ν for three fluids with generally high quality models (argon^{60,61} (atomic fluid), nitrogen^{61,62} (diatomic fluid), and carbon dioxide 63,64 (triatomic fluid)) as a function of temperature. The model implementations in CoolProp version $6.4.1^{59}$ were used because



Figure 2: Temperature of the interpolated crossover points as a function of chain length N, segment number density $\rho_{\rm s}^*$ (the total number of segments per volume), indicated by markers, the solid curves indicating the vapor-liquid equilibrium from the equation of state, the star the interpolated critical point, and the dashed curve smoothed values of $s_{\rm crit}^+$ interpolated from thermodynamic integration.

the new carbon dioxide viscosity formulation⁶⁵ appears to yield non-physical crossover behavior. The location of the $\eta_{\rm kk} = \eta_{\rm cc}$ condition cannot be obtained from the empirical models, so instead we consider the point where the viscosity in the zero density limit $\eta_{\rho\to 0}$ is half of the total viscosity. The agreement between $\eta_{\rm kk}$ and $\eta_{\rho\to 0}$ is exact in the zero-density limit but is only approximate as the density increases to values corresponding to the crossing points (see Figure S1 in the SI). In the case of argon, the high-temperature minima of ν are near the value for the hard-sphere fluid, while the diatomic and triatomic fluids show larger values of s^+ at all temperatures at the minima of kinematic viscosity. In the case of the Lennard-Jones monomer, we also plot the points for the dilute viscosity (from Ref. 66) being equal to half of the total viscosity (red stars). The qualitative behavior of this condition is similar to that of argon, highlighting that if it were possible to obtain η_{kk} for argon, the $\eta_{kk} = \eta_{cc}$ condition would likely be similar to that of Lennard-Jones.

To summarize the results from this study, we



Figure 3: Supercritical values of s^+ for real fluids (at the minima of ν (solid curve) and $\eta_{\rho\to 0}/\eta = 1/2$ (dashed curve)), minima of ν for monomer and dimer (filled triangles), and $\eta^*_{\rho\to 0}/\eta^* = 1/2$ for monomer (stars). The color corresponds to the number of "segments" – 1(argon): red, 2(nitrogen): blue, 3(CO₂): orange. The vertical dashed-dotted line is that of the HS.

plot in Fig. 4 the crossing points for real fluids and the Lennard-Jones monomer on the same set of axes. The coordinates are reduced by the respective values at the critical point (obtained from the equation of state). In these coordinates, the two crossing points (minima of ν and $\eta_{\rho\to 0}/\eta = 1/2$) show a striking similarity between model fluids and real fluids. In pressure-temperature coordinates, the distinctions would be even more difficult to make out. These results highlight that the two definitions of crossover (kinetic and configurational contributions being equal and the minimum of ν) also appear to be consistent with each other for real fluids. On the contrary, these crossing points do not follow the curve of constant excess entropy emanating from the critical point as in the case of the Lennard-Jones monomer. These results pose as many questions as they answer pertaining to the interplay between the crossing points, the details of the pairwise interactions, the intramolecular degrees of freedom, the quality of the empirical models, and the excess entropy. Recent modifications to isomorph theory^{67,68} suggest that a more complete understanding of molecules in this context is possible.



Figure 4: Crossing points (minima of ν (∇) and $\eta_{\rho \to 0}/\eta = 1/2$ (\times)) in reduced temperature-density coordinates for real fluids (argon (red), nitrogen (blue), CO₂ (orange), according to empirical models) and the Lennard-Jones monomer (filled markers). The solid colored curves are constant s^+ emanating from the critical point, and the dashed black curve is the same quantity for Lennard-Jones. The black curves are the vapor-liquid equilibria obtained from the respective equation of state.

In this work we have shown that the location of the points for which the kinetic and configurational contributions to viscosity are equal provides a simple and generic definition of the demarcation between gas- and liquid-like behaviors in the supercritical region of simple model and real fluids. When combined with the excess entropy framework, this definition allows to reconcile structural and dynamic points of view. In addition, it is shown that the minimum in kinematic viscosity corresponds closely to the kinetic and configurational contributions to viscosity being equal. This behavior holds for atomic fluids (hard sphere and Lennard-Jones), dimers, and small real fluids. Although thermodynamics and transport properties can never be fully reconciled according to current

theory,⁶⁹ this study provides evidence that the link between them is stronger than perhaps is expected. Furthermore, from an applied point of view the use of such a crossover could help in providing a reference line for further developing transport properties models and theory.

The results presented are for pure species, while in practical applications most fluids are multicomponent mixtures. It would be of interest to apply this analysis to that of mixtures, in particular to those that have been already studied in the excess entropy scaling framework⁷⁰ such as the Kob-Andersen 4:1 binary system.⁷¹

Supporting Information Available

The supplementary information includes a) additional figures providing more detailed results b) tabular values for all simulation results.

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