



# Hard-sphere behavior in the dynamics of all mono-atomic liquids at the de Gennes minimum



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## ABSTRACT

We show that the position of the de Gennes minimum in scattering spectra, where the dynamics of liquids slow down, is given by a hard-sphere expression for a range of mono-atomic liquids that crystallize in a close packed structure. This expression relates the position of the minimum to the number density of the liquid, without any adjustable or unknown parameters. We argue that this implies that a liquid can be viewed as a close packed structure of the cages that represent the confinement of atoms by their neighbors. We further show that some metals deviate from this expression, namely those metals that crystallize in a structure that is not close packed. Our expression should prove very useful in identifying what liquids to study in inelastic scattering experiments given that deviations from normal fluid behavior can already be predicted based on the peak position of the static structure factor.

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## 1. Introduction

The equations of hydrodynamics tell us how long length scale fluctuations in liquids decay back to equilibrium. These equations tell us how long fluctuations last for, and how fast they can propagate through the liquid, or how quickly they diffuse away from the point of origin. All this is captured in the Rayleigh-Brillouin triplet that is visible in light scattering experiments [1].

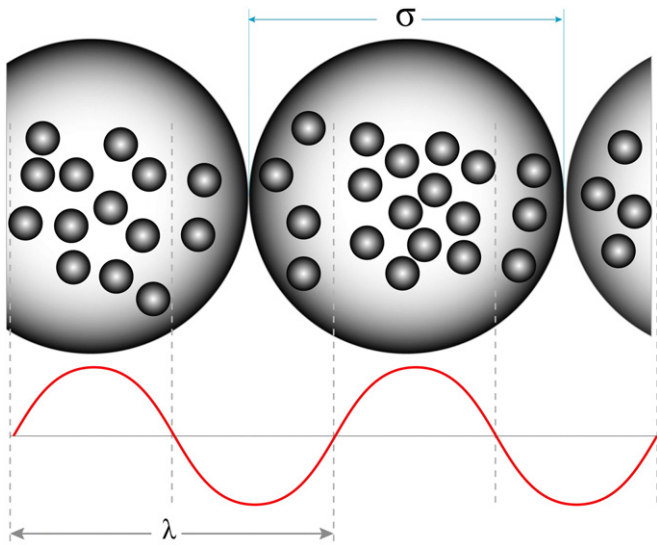
When photons, or neutrons for that matter, are scattered by a liquid, they can create or absorb a sound wave in an inelastic scattering event, or they can probe the diffusion of particles in a quasi-elastic event. The former shows up as two peaks in the scattered intensity located at energy transfers corresponding to  $\hbar c_s q$ , with  $c_s$  the speed of propagation of sound waves and  $\hbar q$  the amount of momentum transferred to the liquid [1]. The wavenumber  $q$  is related to the probing wavelength  $\lambda$  by  $q = 2\pi/\lambda$ . The width, in energy, of these sound modes increases quadratically with  $q$  in the hydrodynamic regime, similar to the  $q$ -dependence of the width of the quasi-elastic feature.

Liquids can also support fluctuations on shorter length scales [2–4], an example of which is shown in Fig. 1. The shorter the length scale of the fluctuation, the more energy it will cost to create. The extreme case would be a fluctuation of wavelength  $\lambda = 2d_{avg}$  ( $d_{avg}$  being the average interatomic separation) where, essentially, we are looking at a fluctuation consisting of a particle next to a hole. Clearly, creating such a hole would be very costly in energy. In this range of wavenumbers, between the hydrodynamic regime and the peak of the dispersion, the width of the excitations increases approximately linearly with  $q$  [3–5].

When the wavelength of the fluctuation is decreased even further, the cost in energy actually goes down again, until there is a minimum in the region where the wavelength corresponds to the interatomic separation  $d_{avg}$ . When we probe the liquid on this length scale, by transferring an amount of momentum to it given by  $q_{min} = 2\pi/d_{avg}$ , we find that fluctuations take longer to decay. This is known as the de Gennes narrowing [6], or structural slowing down; in scattering experiments we observe that the overall width (in energy) of the spectra reaches a local minimum [1]. Intuitively this all makes perfect sense: when we try to create a density disturbance of a wavelength corresponding to the natural length scale of the liquid, it would cost a minimum amount of energy. Conversely, such fluctuations would last for a relatively long time since we are actually probing individual particles locked up in a cage of their neighbors.

The de Gennes region has received extra scrutiny since this is the region where sound modes can cease to propagate, and where the halfwidths of neutron and X-ray scattering spectra follow hard-sphere predictions [4]. In this paper we show that the position (in  $q$ ) where de Gennes narrowing occurs can be accurately predicted, for most mono-atomic liquids, by a hard-sphere relation between the liquid number density  $n$  and the interatomic separation. However, this hard-sphere relation does not imply a hard-sphere potential, rather it simply reflects that the particles in a liquid collide with their neighbors.

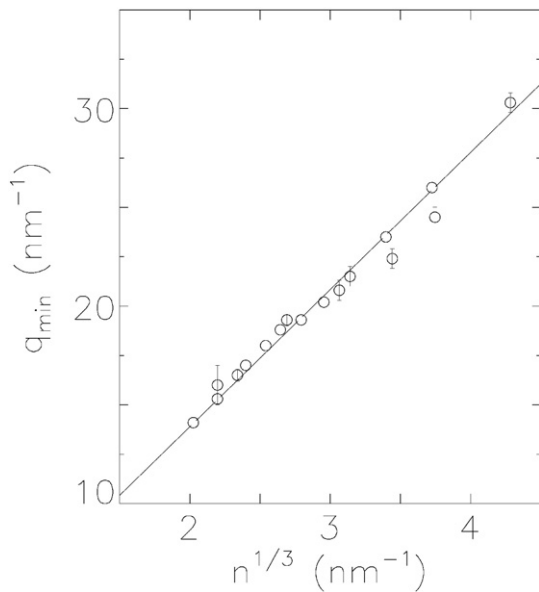
We also show that some mono-atomic liquids, notably Ga [7] and Hg [8], deviate from our prediction: these are the liquids that crystallize in unusual structures. By comparing the position of the de Gennes narrowing to the density of the liquid, it is possible to predict which liquids will display interesting and unusual dynamics.



**Fig. 1.** Just as a disturbance of a wavelength  $\lambda$  spanning quite a few particles (smaller spheres) can be viewed as a departure from the average density (9 atoms on average in between the dashed lines in this figure), when we are probing the liquid on a much shorter length scale, then the atom itself represents a departure from the average density. This is represented by the larger spheres of diameter  $\sigma$  a distance  $d_{\text{avg}}$  apart. The centers of the atoms represent regions with a density higher than average, whereas in between the atoms the density is lower than average. The situation shown here for the larger spheres is for the very high density case  $\sigma \approx d_{\text{avg}}$ . Figure rendered by Alexander Schmetts.

## 2. Results

First we show the validity of our relationship between the position of the de Gennes narrowing and the liquid density, and then we will show how this position can be accurately approximated based on the static structure factor  $S(q)$ . The latter is useful since it allows



**Fig. 2.** The position  $q_{\text{min}}$  of the de Gennes minimum for a range of mono-atomic fluids (symbols) compared to the estimate of Eq. (1) (solid line). The details are given in Table 1. The simple fluids (inert gases and metals) follow the prediction quite well, whereas Hg and Ga (symbols below the line) clearly deviate from this prediction. The latter is not entirely unexpected as these two elements do not condense into a close packed structure. Typical errorbars on  $q_{\text{min}}$  are  $\pm 0.5 \text{ nm}^{-1}$  (for details, see Table 1), with the errorbars of the outliers shown explicitly.

for a quick identification of those liquids that merit further, time-consuming inelastic experiments.

Doing so, we demonstrate the validity of a new relationship between a microscopic quantity that plays a key role in the dynamics of liquids ( $q_{\text{min}}$ ) and the macroscopic density. Doing so, we not only arrive at an easy predictor for which liquids are bound to show unusual dynamics, we also find support for a simple picture as to why hard-sphere predictions are able to capture so much of the dynamics of real fluids even when those real fluids do not interact through a potential that (remotely) resembles a hard-sphere interaction.

We show the positions of the de Gennes minimum for a range of fluids in Fig. 2, and list their values in Table 1. As can be seen, the dependence of the positions on the number density  $n$  is such that they increase linearly with  $n^{1/3}$ , as expected: increasing  $n$  by a factor of 8 must lead to a decrease in the average separation by a factor of 2. The straight line that goes through the points, and which captures the exact linear dependence covering a factor of 10 in  $n$ , is given by

$$q_{\text{min}} = \frac{2\pi}{d_{\text{avg}}} = \frac{2\pi}{[\pi/(3n\sqrt{2})]^{1/3}} = 6.945n^{1/3} \quad (1)$$

## 3. Theory

The average separation  $d_{\text{avg}}$  between particles depends on how closely the particles are packed: the more closely the atoms are packed, the smaller the average separation between them. Imagine we stack cubes of side  $d$  in a simple cubic structure. In this case we would find the separation  $d_{\text{avg}}$  between the nearest neighbor cubes to be  $d$ , and the structure's atomic packing fraction  $nd^3$  would equal 1. Such a packing would work well if the atoms were to cut out cubic volumes for themselves while they jiggle around in the cages formed by the neighbors, however, this is not likely to be the case in a fluid. The densest packing we can have is for spheres stacked in a close packed structure whose packing fraction equals  $\pi/(3\sqrt{2})$ . Thus, without assuming beforehand what the shape is of the volume cut out by a jiggling atom, it seems reasonable to expect that the shortest average separation we can expect to find in liquids is given by  $nd_{\text{avg}}^3 = \pi/(3\sqrt{2})$ . This reasoning leads to the estimate of Eq. (1). Intuitively it is clear that the average separation between atoms is lower when the atoms are close packed rather than arranged in the more open simple cubic structure. Eq.(1) merely captures this intuition in a numerical factor.

We show in Fig. 3 the reason why an expression based on close packed hard-spheres captures the position of the de Gennes minimum even in cases where the atoms do not touch each other. In a liquid, every atom carves out a little space for itself by colliding with its neighbors. The higher the temperature, the more energetic the collisions and the larger the cage the atom forms for itself. The atoms are essentially locked up in their cages, and even when they do manage to escape their cage, they immediately find themselves in a new cage since they are always surrounded by their neighbors. On short length scales, these cages form a close packed structure, since any other stacking arrangement would correspond to large holes in the liquid, which is, from an energy point of view, so unfavorable that such defects quickly disappear. This picture also nicely captures why the details of the inter-atomic interaction do not play much of a role in the exact position of  $q_{\text{min}}$ : cages always form, and their sizes are determined by the amount of kinetic energy available to the collision process.

## 4. Discussion and conclusions

Having validated Eq.(1) by comparing the length scale of the slowing down of the dynamics of liquids to the number density, we now turn the equation around in order to use it as a predictor for identifying which liquids would merit further investigation of the dynamics when only

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