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# Effect of gold nanoparticles on structure and dynamics of binary Lennard-Jones liquid: Wave-vector space analysis

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## HIGHLIGHTS

- MD simulations at constant *NVT* are performed for BLJ/gold-nanoparticles mixture.
- Results are interpreted in terms of mode coupling theory of dynamic glass transition.
- It is found that the gold nanoparticles have a 'softening' effect on liquid dynamics.
- The effect depends fundamentally on the microscopic interactions.
- Unlike BLJ host atoms, relaxation dynamics of gold nanoparticles is nearly exponential.

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## ABSTRACT

Molecular dynamics simulations at constant $(N, V, T)$ are used to study the mutual effects of gold nanoparticles on the structure and dynamics of Kob–Andersen binary Lennard-Jones (BLJ) liquid within the framework of mode coupling theory of dynamic glass transition in the reciprocal space. The results show the 'softening' effect of the gold nanoparticles on the liquid dynamics in terms of (i) reducing the mode coupling crossover temperature $T_c$ with respect to that of the bulk BLJ (i.e. BLJ without nanoparticles), (ii) decreasing the time interval of $\beta$-relaxation, and (iii) decreasing the exponent $\gamma$ characterizing the power-law behavior of the $\alpha$-relaxation time. This softening effect is explained in terms of the van der Waals *attraction* between the gold atoms comprising the nanoparticle and the BLJ host atoms, such that adsorption of host atoms onto the nanoparticle surface creates more space or free-volume for the other atoms to diffuse. By the same token interactions of purely excluded-volume-type are expected to result in the opposite effect. It is also noted that, much unlike BLJ host particles, the dynamics of gold nanoparticles is much less dependent on the wave-vector and that it exhibits a nearly exponential behavior in the $\alpha$-relaxation regime.



## 1. Introduction

Nanoparticles are the building blocks of nanoscience and nanotechnology. They possess unique physical and chemical properties that are significantly different from those of the bulk materials in part because of their high surface area to volume ratio. The diffusion of nanoparticles in polymer melts [1–6], and molecular liquids [7,8], is a matter of considerable

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**Table 1**
The mutual interaction parameters of A, B, and C particles in reduced BLJ units.

| Atomic pair | $\sigma_{\mu\nu}$ (in units of $\sigma_A$) | $\epsilon_{\mu\nu}$ (in units of $\epsilon_A$) |
|---|---|---|
| A–A | 1 | 1 |
| B–B | 0.88 | 0.5 |
| C–C | 0.77 | 22.18 |
| A–B | 0.80 | 1.5 |
| A–C | 0.885 | 4.814 |
| B–C | 0.825 | 3.33 |

interest from both theoretical and technological point of view. In particular, the gold nanoparticle has attracted a great deal of attention due to its chemical stability [9–11]. It has been used in micro-electronic devices [12–14], and also as drug delivery agent in medicine [15,16]. Hence, the study of stability [17] and dynamics of gold nanoparticles in glassy liquids [18] is of immense interest for technological applications. Furthermore, from a more fundamental point of view, a rational combination of nanoparticles and supercooled liquids can open new ways to further develop our knowledge about how molecules move in supercooled liquids [19,20].

The mode coupling is a first principle theory that describes the dynamics of atoms in a viscous liquid during the early stages of supercooling [21]. Extensive work has been developed based on the mode coupling theory (MCT) both numerically [22] and experimentally [23] to describe the behavior of mildly supercooled liquids close to their melting point. The Kob–Andersen binary Lennard-Jones (BLJ) liquid is a famous prototype for studying the behavior of molecular glass-forming liquids. The behavior of this model has been investigated in detail by Kob and Andersen upon supercooling within the framework of the MCT [22], and it has been parameterized by Weber and Stillinger to simulate $Ni_{20}P_{80}$ in the supercooled liquid state [24]. Furthermore, Gallo et al. investigated the confined BLJ atoms, embedded in an off-lattice matrix of fixed nanospheres both in the direct and the reciprocal space [25].

Both simulations and experimental observations indicate that the effect of nanoparticles on viscous liquids is in general system-dependent. Nanoparticles sometimes have a softening effect on the host fluid in terms of decreasing the MCT crossover temperature [26], while in other cases just the opposite effect is resulted [6]. So an important point at issue is to discover the main physical factors that bring about these rather opposite behaviors in viscous liquid/nanoparticle mixtures. More recently, we reported the direct space results from the molecular dynamics simulations of BLJ liquid in the presence of gold nanoparticles [26], in order to study the mutual effects of gold nanoparticles on structure and dynamics of BLJ in the direct space. In particular, we reported two major differences between the dynamics of BLJ particles in the presence of gold nanoparticles as compared to the bulk BLJ (BLJ without the gold nanoparticles). The first difference was about the enhanced mobility of the minority B particles with respect to the majority A particles, and the second was related to the substantial decrease in MCT crossover temperature $T_c$ and the corresponding dynamic exponent $\gamma$.

In this work, we focus on the behavior of the density correlators as a new development on the above mentioned work [26]. We present the $q$-space results of constant $(N, V, T)$ molecular dynamics simulations in order to study the relaxation dynamics at different length scales within the framework of the MCT. The system studied in this work consists of a gold nanoparticle composed of 13 gold atoms (called C particles) in a BLJ liquid of 800 A particles and 200 B particles with masses $m_A = m_B = 1$. The mass of gold nanoparticle is $64\, m_A$. All particles are placed inside a cubic box with an edge length $L = 9.486\, \sigma_A$, which is slightly expanded with respect to the bulk simulations of Ref. [22] (without nanoparticles), in order to have a total number density equal to that of Ref. [22], thus allowing for a meaningful comparison of the results. The periodic boundary conditions imply that our simulations correspond to an impurity concentration of 1.3% in the thermodynamic limit, i.e. 13 gold atoms in the form of a stable gold nanoparticle for every $10^3$ BLJ host atoms. We also reproduced some of the results of Ref. [22] relevant to our work for the purpose of comparison.

The interaction potential between the pairs of particles is that of the Lennard-Jones potential:

$$V(r) = 4\epsilon_{\mu\nu}[(\sigma_{\mu\nu}/r)^{12} - (\sigma_{\mu\nu}/r)^{6}], \tag{1}$$

where indices $\mu, \nu \in \{A, B, C\}$. The values of the parameters for A and B particles are those of the Kob–Anderson BLJ. All potentials are truncated and shifted at a distance of $2.5\, \sigma_A$. For the C particles, the interaction parameters reported in Ref. [27] are used. The gold nanoparticle is first produced by a process of simulated annealing, and then introduced in the simulation box. The interaction parameters between the BLJ host particles and the C particles comprising the gold nanoparticle are obtained from the Lorentz–Berthelot combination rules as listed in Table 1. The range of temperatures investigated in equilibrium is $0.4 \leq T \leq 4.0$. Further details of the molecular dynamics simulations can be found in Ref. [26]. The results are reported in the reduced BLJ units such that the lengths are measured in units of $\sigma_A$, the energies in units of $\epsilon_A$, and the time intervals in units of $\sqrt{m_A\sigma_A^2/48\epsilon_A}$. The temperature has $\epsilon_A/k_B$ as its unit, where $k_B$ is the Boltzmann constant.

The rest of this paper is organized as follows. In Section 2, the main results of MCT relevant to this work are briefly reviewed. Section 3 presents the simulation results for the static structure factors, and the self-intermediate scattering functions of various atoms together with the corresponding MCT scaling fits. The results thus obtained are compared with the bulk BLJ, and the paper is concluded with a discussion and summary in Section 4.