



# MOLECULAR DYNAMICS SIMULATION OF THE RHEOLOGICAL BEHAVIOUR OF GEL FUELS

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## ABSTRACT

The rheological behaviour of JP-10-based gelled fuels enhanced with nano-aluminium (Al) particles and low-molecular-weight gelators (LMWGs) was studied by molecular dynamics (MD) simulations. Non-equilibrium molecular dynamics (NEMD) methods were used to evaluate shear viscosity across a range of shear rates. The results demonstrate that the hybrid system exhibits non-Newtonian shear-thinning behaviour, with Al particles enhancing shear sensitivity through mechanical interactions, while LMWGs serve to stabilise the gel network. Increasing Al content leads to a reduction in the time constant in Cross model, which accelerates structural degradation under shear. These findings underscore the synergistic roles of Al nanoparticles and LMWGs in fine-tuning the viscosity profiles of gelled fuels for high-shear propulsion systems, offering a molecular-level framework for optimising gelled fuel performance.

**Keywords:** gel fuel, MD, nanoparticle, viscosity

## NOMENCLATURE

$E$	[J]	energy
$F$	[N]	force
$\rho_i$	[C/m <sup>3</sup> ]	electron density
$\phi$	[eV]	interatomic potential energy
$r$	[m]	distance
$\eta$	[mPa·s]	viscosity
$A_1$	[mPa·s]	zero- shear viscosity
$A_2$	[mPa·s]	infinite-shear viscosity
$\tau$	[Pa]	shear stress
$m$	[-]	shear-thinning index
$\dot{\gamma}$	[1/s]	shear rate

## Subscripts and Superscripts

NVT	Canonical Ensemble
NPT	Isothermal-Isobaric Ensemble

## 1. INTRODUCTION

Gelled fuels are modified liquid fuels with unique rheological properties, comprising hydrocarbon fuel, gelling agents, and high-energy particles. The gelling agents form a network that increases viscosity, enabling solid-like behaviour at rest and fluid-like flow under shear forces, ensuring efficient injection and atomization. High-energy particles enhance calorific value and energy density, making gelled fuels suitable for high-performance propulsion systems [1]. Upon injection, they undergo a two-stage breakup: primary fragmentation due to turbulent shear forces, followed by secondary dispersion into finer droplets, which evaporate and ignite under high temperatures. These processes involve complex multiphase flows and non-Newtonian fluid dynamics, presenting challenges for stable combustion [2]. Furthermore, multiscale coupling effects—from microscopic particle dispersion to macroscopic flow dynamics under extreme conditions—affect fuel performance. Investigating rheological properties and microscopic mechanisms is essential for optimizing gelled fuels in aerospace propulsion.

Experimental studies have advanced the understanding of gelled fuel rheology but struggle to capture molecular-scale interactions and extreme conditions. Li et al. [3] demonstrated that shear-thinning and thixotropic properties in organic kerosene gels are influenced by pre-shear effects. Sun et al. [4] found that a 1.0% glycyrrhizic acid hydrogel supports efficient atomization, while higher concentrations hinder fuel breakup. Liu et al. [5] developed stable, shear-thinning gelled fuels using low-molecular-mass gellants, improving combustion. Ma et al. [6] synthesized poly glycyrrhizic acid (PGly) with pH-responsive emulsification for controlled release. Despite these insights, experimental constraints highlight the need for molecular simulations.

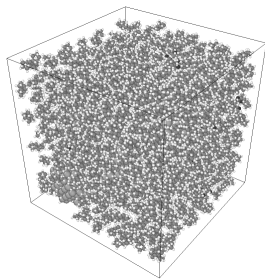
Molecular dynamics (MD) simulations effectively model gel behavior under extreme shear and pressure. Cui et al. [7] identified nanoparticle-induced interfacial effects in copper-water nanofluids, while Loya et al. [8] showed CuO nanoparticles enhance hydrocarbon-based fluid conductivity. Blanco-Díaz et al. [9] linked shear-thinning in ionic liquids to hydrogen bond disruption, and Liu et al. [10] showed that shear alignment reduces lubricant viscosity. These findings establish MD simulations as essential for understanding and optimizing gelled fuel rheology. Experimental studies lack molecular-level insights under extreme conditions, while simulations mainly focus on single-component systems. The interplay between small-molecule gelators, nanoparticles, and their behaviour under such conditions remains unresolved, requiring advanced models to predict rheological properties across shear regimes.

This study develops a MD model to analyze rheological properties of gelled fuels under varying shear rates using non-equilibrium molecular dynamics (NEMD). The primary contributions are: (i) constructing a complex model incorporating aviation kerosene, low molecular weight gelators (LMWG), and nano-aluminum particles at different mass fractions, and (ii) elucidating the shear response of high-energy hydrocarbon fuels under extreme conditions, linking macroscopic behavior to molecular interactions. The article is organized as follows: Section 2 presents the modelling method. Section 3 summarizes the simulation setting details including the mass fraction and numerical settings. Section 4 gives the results and discussion. Section 5 shows the conclusion.

## 2. METHODOLOGY

### 2.1. MD model

This study employed Packmol [11] and LAMMPS [12] for MD simulations of JP-10-based gel fuel. As shown in Fig.1, the system involved three key components: JP-10 (modeled as exo-tetrahydrodicyclopentadiene) serving as the high-energy-density base fuel, diacetone-D-mannitol as the gel-forming LMWG, and Al nanoparticles for combustion enhancement.



**Figure 1. Molecular model of JP-10 gel fuel**

The simulations utilized hybrid force fields to describe interparticle interactions. Organic components (JP-10 and LMWGs) were modeled with the Polymer Consistent Force Field (PCFF) [13] selected for its proven reliability in polymer/organic systems. Metallic interactions in nano-aluminum particles were addressed through the Embedded Atom Method (EAM) potential [14]. A mixed potential approach (Heinz et al., 2008) enabled cross-interaction modeling between different material phases.

Derived from the CFF91 framework, the PCFF potential function originally described small organic molecules and proteins, later extending to polymers and inorganic materials. Its mathematical formulation provides comprehensive coverage of bond stretching, angle bending, torsional interactions, and van der Waals forces critical for gel network characterization.

The Embedded Atom Method (EAM) potential, a semi-empirical model for metallic systems, decomposes atomic energy into two components: pairwise interatomic interactions and embedding energy derived from local electron density. This framework enables efficient simulation of metal/alloy behaviour by accounting for both direct atomic bonds and the energy cost of embedding atoms within their electron cloud environment. The functional expression is formulated as Eq. (1).

$$E_{\text{total}} = \sum_i F(\rho_i) + \frac{1}{2} \sum_{i \neq j} \phi(r_{ij}) \quad (1)$$

where  $F(\rho_i)$  represents the embedding energy of atom  $i$  which depends on the total electron density  $\rho_i$  surrounding the atom.  $\phi(r_{ij})$  represents the pairwise interaction energy between atoms, which depends on the distance  $r_{ij}$  between the atoms.

### 2.2. Non-equilibrium conditions

The SLLOD equations, originally developed by Hoover and Ladd [15], provide a validated framework for simulating shear flow in molecular dynamics. Refinements by Tuckerman et al. [16] enhanced their capability to model nonlinear velocity gradients, enabling transport property analysis in complex fluids. In LAMMPS implementations, these equations govern particle dynamics under shear by updating velocities/positions via applied velocity gradients, with triclinic simulation boxes enabling consistent shear strain application.

Simulation protocols involved sequential equilibration stages: initial Packmol-generated configurations underwent iterative energy minimisation through temperature-cycling relaxation. Subsequent NVT/NPT ensembles stabilised system density prior to nonequilibrium studies. For NEMD runs, adaptive step adjustments

ensured sampling adequacy across shear rates. Also, multiple parallel simulations per shear rate were statistically averaged to enhance data reliability.

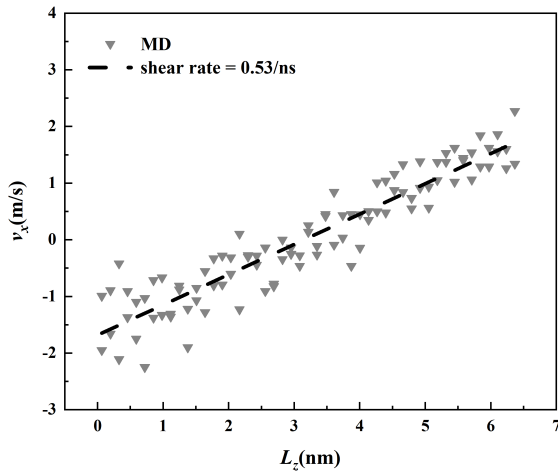
### 3. COMPUTATIONAL SETTINGS

The gel fuel model contains 10% nano-aluminium particles by mass, ensuring consistent metallic additive proportions. LMWG was tested at 2% mass fractions to exploit its efficient gelation at minimal concentrations. Component quantities were determined from molecular weights (JP-10, LMWG, Al) for precise formulation control.

All simulations adhered to standard conditions (298 K, 1 atm). The conjugate gradient method performed energy minimisation to optimise molecular configurations. Thermal regulation employed combined Langevin (stochastic collisions) and Nose-Hoover (deterministic coupling) thermostats, while pressure was maintained via a Nose-Hoover barostat. This dual-thermostat approach balanced computational efficiency with thermodynamic accuracy under shear conditions.

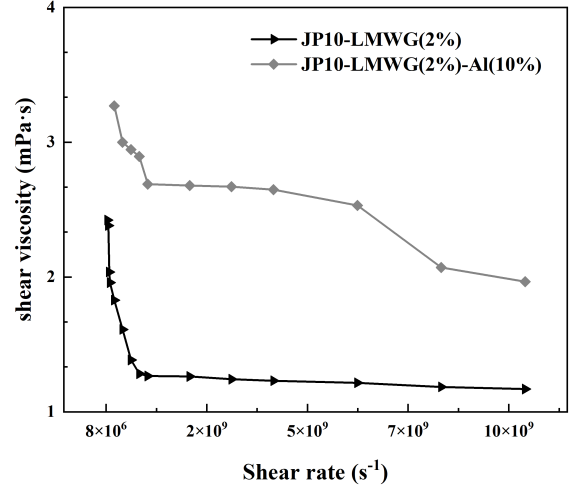
## 4. RESULTS AND DISCUSSION

### 4.1. Rheological behaviour at ambient conditions



**Figure 2. Fitting curves of molecular velocity**

NEMD simulations quantified the shear viscosity of gel fuel systems across shear rates spanning  $4 \times 10^7 \text{ s}^{-1}$  to  $2 \times 10^{11} \text{ s}^{-1}$ . As illustrated in Fig.2, thermal fluctuations dominate at shear rates below  $8 \times 10^8 \text{ s}^{-1}$ , exemplified by the unstable velocity profiles observed at  $2 \times 10^8 \text{ s}^{-1}$ , a regime where measurement uncertainties preclude reliable viscosity determination. Beyond this threshold, shear-induced forces suppress thermal noise, enabling stable velocity gradients and reproducible viscosity measurements.



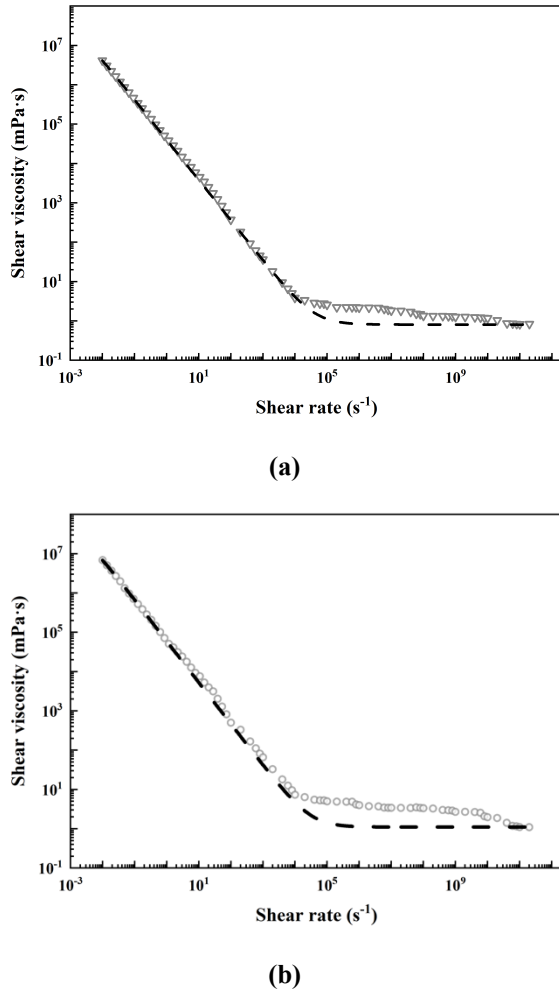
**Figure 3. Shear viscosity of gel fuel systems at different shear rates**

The incorporation of 10% nano-aluminium particles elevates shear viscosity by 18 - 32% relative to gelator-only systems, as demonstrated in Fig.3. This enhancement stems from nanoparticle-mediated reinforcement of the gel network's mechanical integrity. Notably, particle-free systems exhibit shear-thinning behaviour until reaching a viscosity plateau above  $2 \times 10^9 \text{ s}^{-1}$ , indicative of a critical shear rate where structural reorganisation counterbalances further viscosity reduction. The divergence in rheological response underscores the nanoparticles' role in stabilising the gel matrix under extreme shear conditions.

### 4.2. Correlation formulation

This section details the rheological characterisation of JP-10-based gel fuel across shear rates spanning  $1 \times 10^{-2}$  to  $2 \times 10^{11} \text{ s}^{-1}$ . Experimental measurements [17] provided low shear-rate data ( $1 \times 10^{-2}$  -  $1 \times 10^2 \text{ s}^{-1}$ ), complemented by NEMD simulations for high-rate regimes ( $4 \times 10^7$  -  $2 \times 10^{11} \text{ s}^{-1}$ ). The intermediate shear-rate range ( $1 \times 10^2$  -  $4 \times 10^7 \text{ s}^{-1}$ ), inaccessible to reliable simulation due to computational constraints and viscosity instabilities, was bridged through interpolation. The Cross model further enabled extrapolation to ensure rheological curve continuity across the full shear spectrum. The model is expressed as Eq. (2).

$$\eta(\dot{\gamma}) = A_2 + \frac{A_1 - A_2}{1 + (\tau \cdot \dot{\gamma})^m} \quad (2)$$



**Figure 4. Rheological curves of gel fuels fitted using Cross model (a)  $C_{JP-10} = 98\%$ ,  $C_{LMWG} = 2\%$ ,  $\tau = 1160.55$ ,  $m = 0.98$ ; (b)  $C_{JP-10} = 88\%$ ,  $C_{LMWG} = 2\%$ ,  $C_{AI} = 10\%$ ,  $\tau = 828.48$ ,  $m = 0.96$**

As shown in Fig.4., nano-aluminium additives (10% mass) increased infinite-shear viscosity, indicating enhanced structural integrity, while reducing characteristic time  $\tau$ , implying faster shear-induced network breakdown. Higher LMWG content with nanoparticles marginally lowered shear-thinning sensitivity ( $m$ ), attributed to strengthened gel-particle interactions. At extreme shear rates ( $>2 \times 10^{10} \text{ s}^{-1}$ ), viscosity fell below pure JP-10 levels, signalling complete structural collapse, though MD scaling constraints contributed to fitting deviations.

## 5. SUMMARY

This study utilised molecular dynamics simulations to analyse the rheological properties of JP-10-based gel fuels, revealing the critical influence of nano-aluminium particles and LMWGs on shear viscosity. Nano-aluminium additives (10% mass fraction) enhanced viscosity at low shear rates through structural reinforcement, while LMWGs stabilised the three-dimensional gel network, dictating bulk rheological responses.

The Cross model outperformed the Power-law model in characterising non-Newtonian behaviour, accurately capturing the transition from gel-like (Newtonian plateau) to liquid-like (shear-thinning) regimes at elevated shear rates. This approach resolved limitations of conventional models in describing multiphase systems, particularly the viscosity collapse observed beyond  $2 \times 10^{10} \text{ s}^{-1}$  where simulated values dropped below pure JP-10 levels. These findings validate molecular dynamics as a robust tool for probing complex fluid systems, offering practical guidelines for tailoring gel fuel formulations. The synergy between nanoparticle reinforcement and gellants concentration optimisation provides a pathway to enhance fuel performance in aerospace propulsion and munitions systems requiring stability under extreme shear conditions. The use of specific modelling assumptions and extrapolation of intermediate values may introduce uncertainties. In future work, we plan to incorporate reactive potentials or machine-learned force fields to address these limitations and enhance the predictive capability of our model.

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