

**DEPARTMENT OF MECHANICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY PATNA**



**Synthesis of Nanoparticle Using
Supercritical CO₂**

Bachelor of Technology

in

Mechanical Engineering

by

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under the guidance of

Dr. Ajay Kumar Yadav

CERTIFICATE

This is to certify that the work contained in this thesis titled "**Synthesis of Nanoparticle Using Supercritical CO₂**" is a bonafide research work of **Kumar Ayush Aman**(2201ME38) & **Abhay Vyas**(2201ME02), carried out in the Department of Mechanical Engineering, Indian Institute of Technology Patna, under my supervision and that it has not been submitted elsewhere for a degree.

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Date: 01/12/2026

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Declaration

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B.Tech. Project Title: Synthesis of Nanoparticle Using Supercritical CO₂

This is to certify that Mr/Ms _____

1. has/have sincerely worked on their project,
2. has/have contacted me regularly to update on the progress of the assigned project,
3. has/have received my comments on the preliminary version of the report and presentation and will address those prior to final submission/presentation,
4. may be allowed to present/defend the project before the department.

Remarks (if any):

Dr. Ajay Kumar Yadav

Date: 01/12/2026

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ABSTRACT

Supercritical CO₂ (scCO₂) is used in the Supercritical Anti-Solvent (SAS) process, which has become a highly controllable and clean method for creating nanoparticles. Because of its mild operating conditions, quick mass transfer capability, and environmental friendliness, this project focuses on the production of magnesium nanoparticles using scCO₂. The basic SAS mechanism is based on the quick diffusion of scCO₂ into an organic solvent that contains a dissolved precursor. This drastically lowers the solvent's density and solubility, resulting in instantaneous supersaturation and the precipitation of nanoparticles.

In an experiment, CO₂ was exposed to magnesium chloride dissolved in ethanol with oleylamine serving as a capping agent. Rather than bulk or amorphous agglomerates, distinct particulate deposits were obtained after drying, indicating successful nanoparticle formation. By keeping the particles from merging and allowing for controlled growth, oleylamine played a critical stabilizing role. The experiment lays the groundwork for future optimization under full scCO₂ operation and confirms that SAS is a viable synthesis pathway even in near-supercritical conditions.

Molecular dynamics simulations were used to comprehend nucleation and stabilization at the atomic scale. The absence of long-range crystallinity was confirmed by rapid decay, while the Mg–Mg radial distribution function (RDF) showed a strong first peak at ~3.1 Å, indicating a compact nanoparticle core and short-range atomic ordering. A spherical condensed structure with a slightly disordered surface, typical of nanoscale packing, was depicted in cluster visualizations. Consistent oleylamine attachment on the magnesium surface was demonstrated by the Mg–N RDF, which displayed a sharp peak at about 2.7 Å. This confirms that oleylamine prevents agglomeration and stabilizes the nanoparticle by forming a surface ligand shell rather than integrating into the metallic core.

The simulation and experiment together confirm the creation of a core-shell nanostructure, where the inner magnesium cluster is surrounded by an organic protective layer made of oleylamine. The findings demonstrate that the SAS process is a scalable and sustainable technique with great potential for creating nanoparticles with adjustable size, enhanced stability, and little environmental impact. In order to achieve more control over the properties of nanoparticles, future development will concentrate on carrying out the process under fully supercritical CO₂ conditions and further optimizing synthesis parameters like pressure, temperature, CO₂ exposure duration, and surfactant concentration.

Keywords : Supercritical CO₂ (scCO₂); Supercritical Anti-Solvent (SAS) process; Nanoparticle synthesis; Magnesium nanoparticles; Oleylamine capping; Molecular dynamics (MD) simulation; Radial distribution function (RDF); Core–shell nanostructure; Nucleation mechanism; Environment-friendly synthesis.

Introduction

One well-known method for creating nanoparticles with regulated size and shape is the Supercritical Anti-Solvent (SAS) process. The basic idea depends on supercritical carbon dioxide's (scCO₂) quick diffusion into a solvent. Solvent density and solubility power are drastically reduced when scCO₂ comes into contact with the solute-solvent system. A high degree of supersaturation is produced by this quick change, which causes abrupt nucleation and nanoparticle precipitation.

For example, optimizing grain sizes to the nanoscale can significantly increase the hardness of metals, and using nanomaterials increases the energy efficiency of explosives and propellants due to accelerated reaction kinetics. Nanoscale particles in pharmaceuticals allow for improved bioavailability, targeted drug delivery, and increased solubility. Similarly, faster transistors, high-density memory, and effective sensors are made possible by nanostructured materials in electronics.

The main focus of this work is the production of nanoparticles using supercritical carbon dioxide (scCO₂), a highly effective and environmentally friendly bottom-up method. Each synthesis pathway is explained in detail, along with the corresponding mechanisms, simulation results, and industrial significance.

1. Nanomaterials: Classification and Properties

There are nanomaterials that are generally categorized into three structural types according to the number of dimensions in the nanoscale regime:

1. **Nanoparticles (3D confinement):** These possess nanoscale dimensions in all three directions (x, y, z). They include metallic nanoparticles such as gold (Au) and silver (Ag), semiconductor nanoparticles such as quantum dots, and ceramic particles. They find extensive applications in catalysis, drug delivery, and imaging.
2. **Nanofilms (2D confinement):** In this case, two dimensions (width and length) are macroscopic, while thickness is in the nanometer scale. Nanofilms are most important in protective coatings, optical devices, and thin-film transistors.
3. **Nanowires or Nanotubes (1D confinement):** These are materials with nanoscale diameters but micrometre-scale lengths. Such materials include carbon nanotubes, nanorods, and semiconductor nanowires for energy devices and nanoelectronics.

The **properties of nanomaterials** differ drastically from bulk materials:

- Greater hardness and strength resulting from grain refinement.
- Greater reactivity owing to high surface-to-bulk ratios.
- Quantum confinement effects changing optical and electronic characteristics.
- Customizable solubility, magnetic susceptibility, and catalytic effectiveness.

2. Methodology

Molecular Dynamics Computational Simulation:

To visualize the mechanism of nucleation, a realistic SAS environment was simulated using Molecular Dynamics (MD).

- **System Initialization:** PACKMOL was used to initialize the system. Along with CO₂ and oleylamine, which served as a surfactant, magnesium (Mg) atoms were distributed in an ethanol solvent.
- **Equilibration:** To stabilize the environment, the system was equilibrated using NPT (constant Number, Pressure, Temperature) and NVT (constant Number, Volume, Temperature) ensembles.
- **Simulation Conditions:** In order to observe atomic interactions during the anti-solvent process, the simulation was created to replicate the high-pressure conditions necessary for the supercritical state.

3. Approaches for Nanoparticle Synthesis

Synthesis of nanomaterials can be broadly classified into two pathways:

3.1 Top-Down Approach

Here, bulk materials are broken down to the nanoscale by mechanical, chemical, or lithographic methods. These include:

- **Mechanical Milling:** Grinding of materials to sizes of nanometers.
- **Laser Ablation:** High-energy laser shatters materials into nanoparticles.
- **Lithography:** Photo lithographic or electron-beam methods utilized in electronics.

Advantages: Easy, sometimes scalable, and doesn't involve complex chemistry.

Limitations: Defects on the surface, non-uniform particle size, and no precise control.

3.2 Bottom-Up Approach

In this, nanoparticles are constructed atom by atom or molecule by molecule by self-assembly or chemical reactions. Sol-gel processes, chemical vapor deposition, and **supercritical fluid techniques** are some examples.

Advantages: Precise control over particle size, morphology, and composition.

Limitations: Sophisticated equipment, slower processes, and increased cost in some instances.

The **bottom-up approach using supercritical CO₂** possesses efficiency, accuracy, and environmental integrity and thus holds great promise.

4. Supercritical Fluids in Nanoparticle Synthesis

A **supercritical fluid (SCF)** is a substance under conditions above its critical temperature and critical pressure, where it displays hybrid properties of both liquids and gases.

- **Gas-like diffusivity:** SCFs permeate quickly, into solids or solutions.
- **Liquid-like solvating power:** They dissolve some solutes well.
- **Eco-friendly processing:** They may be removed completely after synthesis, with little residue.

Comparison of scCO_2 and scH_2O

Property	scCO_2	ScH_2O
Critical Temperature	31.1 °C	374 °C
Critical Pressure	73.8 bar	221 bar
Polarity	Non-polar	Polar
Reactivity	Inert	Highly reactive (H^+/OH^-)
Applications	Organics, polymers, pharmaceuticals	Oxides, sulfides, ceramics

Why scCO_2 ?

- Needs milder conditions than scH_2O , so it is energy-efficient.
- Inert and non-toxic.
- Environmentally benign, as CO_2 can be reused.
- Applicable to a broad spectrum of organic and pharmaceutical processes.

5. Methods of Nanoparticle Production Using SCFs

A number of synthesis pathways have been established:

1. **Hydrothermal Method:** Performed in aqueous solution under high temperature and pressure. Deploys crystalline nanoparticles but is restricted at extreme conditions.
2. **Rapid Expansion of Supercritical Solution (RESS):** Solute dissolved in scCO_2 is depressurized quickly, resulting in the precipitation of nanoparticles. This offers perfect size control but is restricted to solutes in solubility in scCO_2 .

3. **Reprecipitation Solvent Evaporation (RESOLV):** Involves the dissolution of a solute in a volatile solvent, injection into a non-solvent, and solvent evaporation. Most widely used for the synthesis of drug and polymer nanoparticles.
4. **Supercritical Antisolvent (SAS) Process:** The most general and versatile, SAS employs scCO_2 as an antisolvent. A solute dissolved in an organic solvent is introduced into scCO_2 , which lowers the solvent density and solvating power, leading to precipitation of nanoparticles.

6. Experimental Procedure

7.1 Materials :

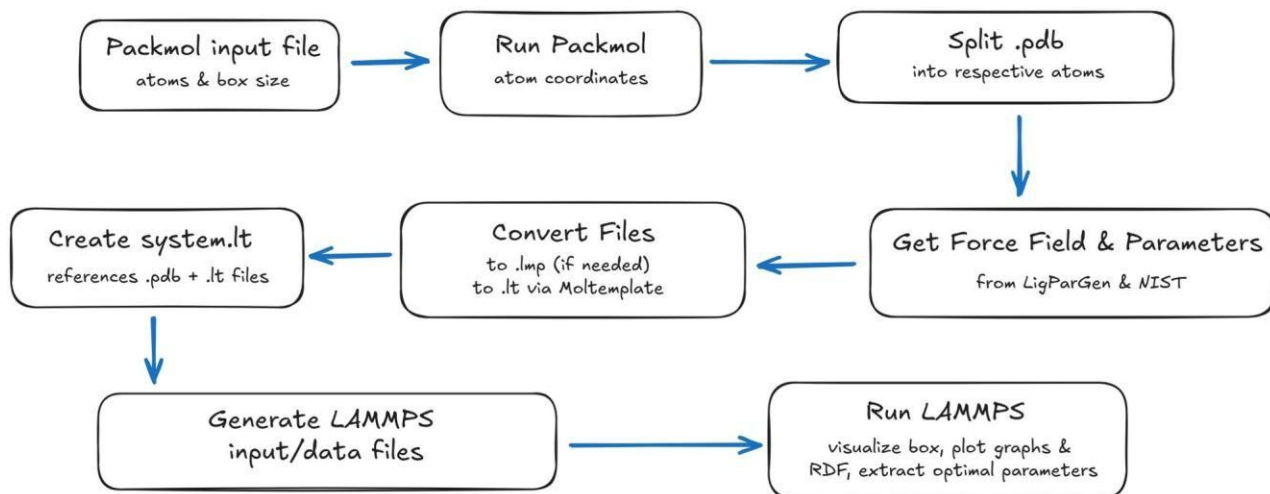
- **Precursor:** Due to its high ethanol solubility and suitability for SAS synthesis, magnesium chloride (MgCl_2) was chosen.
- **Solvent:** Since ethanol is miscible with both the precursor and the anti-solvent (CO_2), it was selected.
- **Capping Agent :** To control particle growth through steric stabilization and avoid excessive aggregation, oleylamine was added.

7.2 Preparation : After dissolving the MgCl_2 in ethanol, oleylamine was added. To guarantee the complete dissolution of the precursor and the uniform dispersion of the surfactant, the mixture was constantly stirred.

7.3 Precipitation : The prepared solution was exposed to CO_2 gas in a chamber. A decrease in solubility was caused by this exposure, which served as the anti-solvent step.

7.4 Morphology : The samples were examined under a microscope after being isolated and dried. The pictures verified that precipitated solids were present, confirming that the particle synthesis was successful.

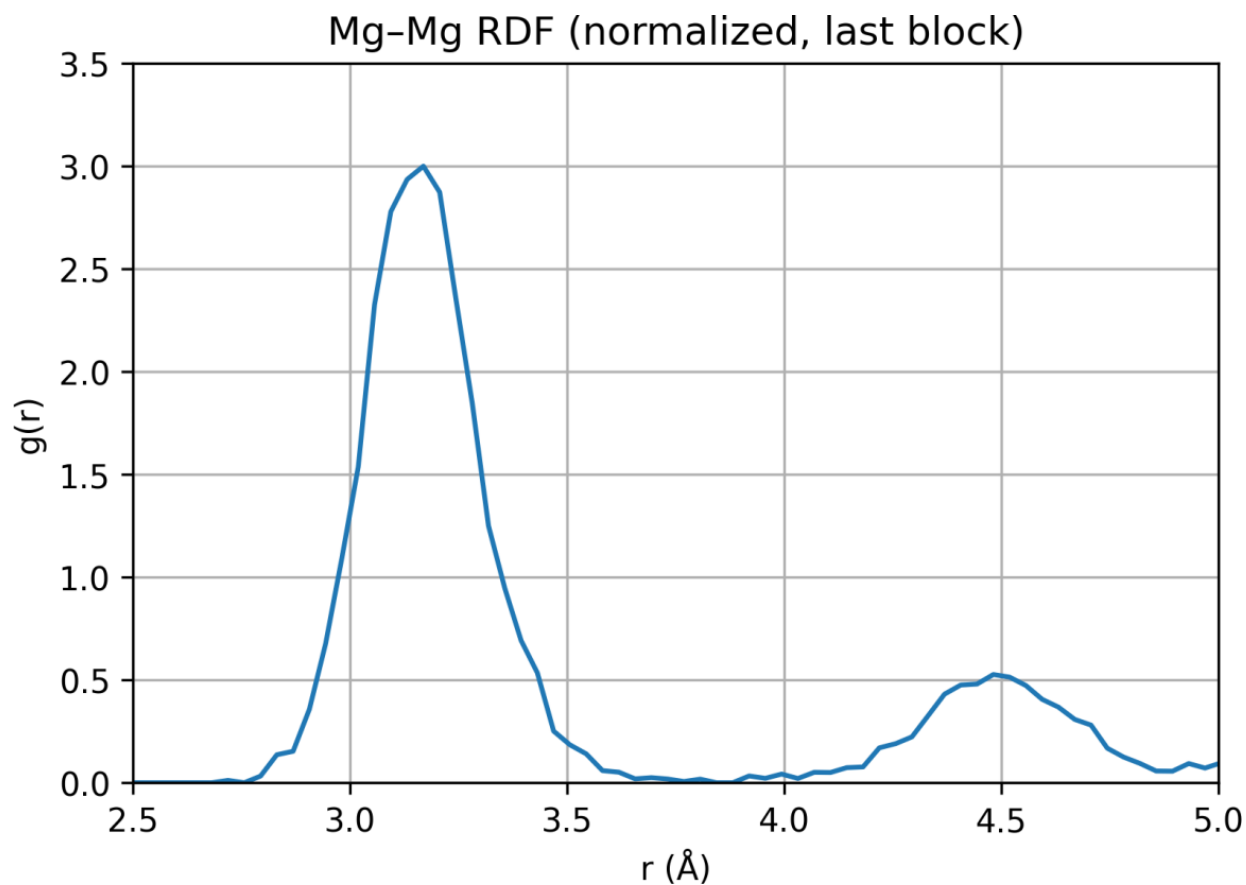
8 Approach and Workflow



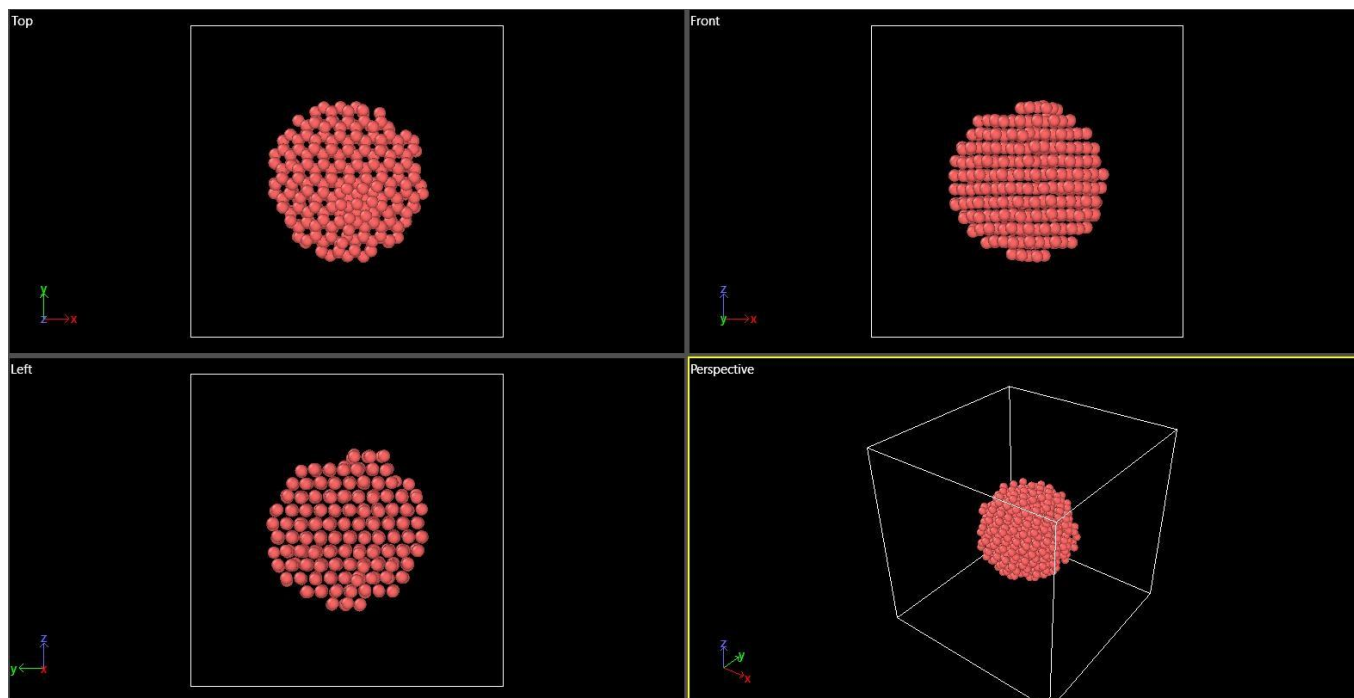
9 Simulation and Results

A condensed magnesium nanoparticle was created by the molecular dynamics simulation, and its structural properties were examined using both the final atomic configuration and the radial distribution function (RDF). When used in tandem, these tools offer complementary insights into the type of ordering found in the simulated system.

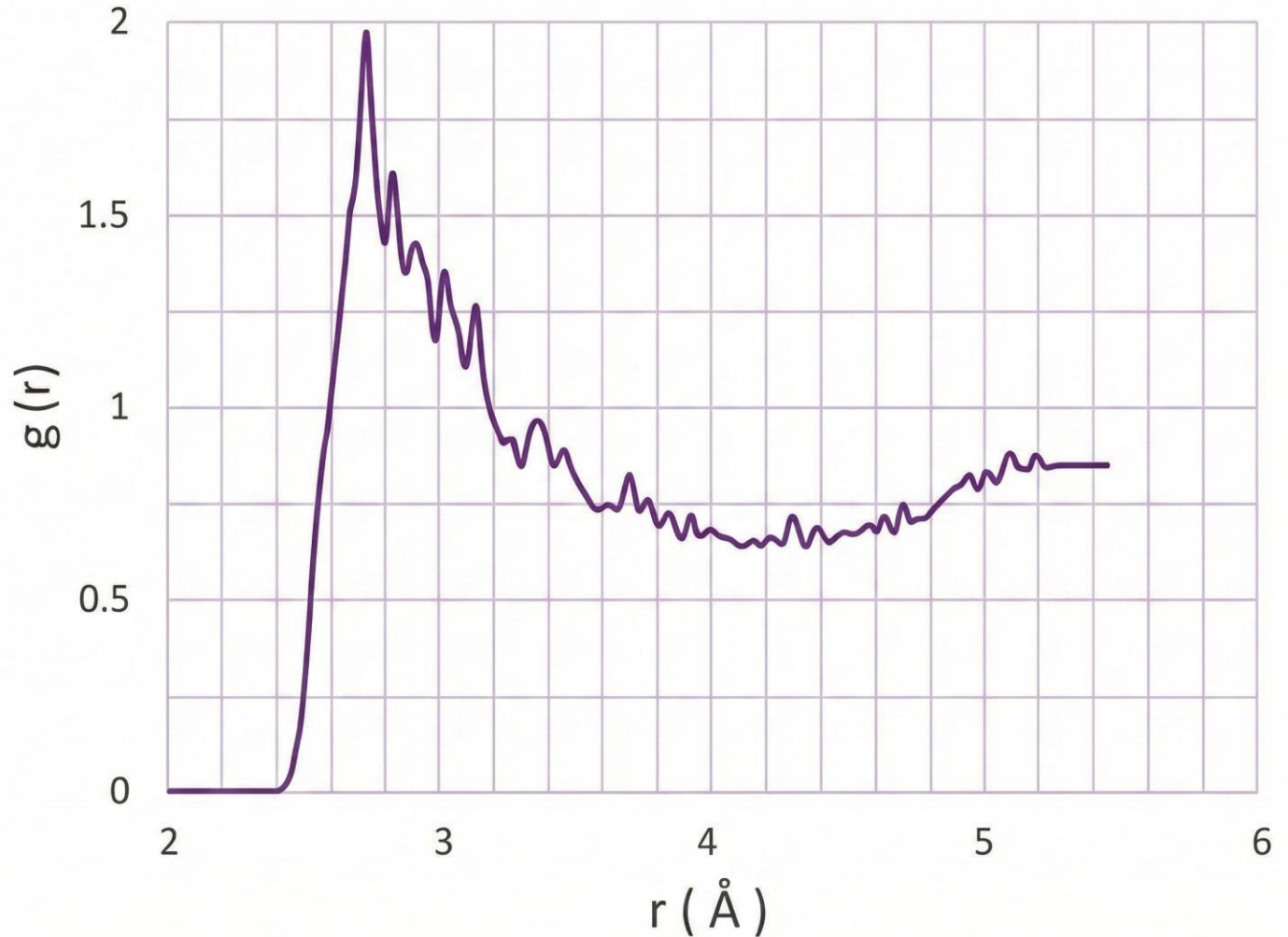
- Strong short-range Mg–Mg coordination but no long-range periodicity, reflecting only local atomic ordering rather than bulk crystallinity, is indicated by the prominent first peak at ~ 3.1 Å followed by a fast decay.
- The observed cluster confirms a nanoparticle-type packing where high surface-to-volume ratios disturb extended crystalline order by displaying a compact, ordered core with a disordered surface layer.
- A higher first peak also indicates that the Mg–N interaction is strong and well-defined, meaning oleylamine consistently prefers this bonding distance.
- Overall, the RDF shows that oleylamine forms a well-defined first coordination shell around Mg (sharp first peak), confirming successful surface capping, while atoms farther away lose ordering and behave like a random distribution.



Radial Distribution Function of Mg–Mg



The final equilibrated simulation yielded the radial distribution function (RDF) of Mg–Mg atoms and the corresponding atomic cluster visualization.



Radial Distribution Function $g(r)$ for Mg–N (Oly) Interactions

- The nitrogen in oleylamine maintains a preferred bonding distance from magnesium, as indicated by the first RDF peak at about 2.7 Å. A protective ligand layer is created by this steady Mg–N interaction.
- Oleylamine keeps MgO nanoparticles from getting too close because it binds firmly at this distance. Agglomeration is prevented and surface contact is decreased.
- An ordered ligand attachment on the MgO surface is indicated by a strong, sharp peak. This suggests effective stabilization and regulated growth of nanoparticles.

10 Conclusion

The formation and stabilization of the magnesium nanoparticle during the simulation are clearly depicted by the RDF analysis. Once equilibrium is reached, the distribution of atoms surrounding a reference magnesium atom changes from a random lattice to a highly ordered arrangement. The formation of a compact, condensed nanoparticle core is reflected in the sharp and prominent first peak in the Mg–Mg RDF, which shows that magnesium atoms regularly settle at a preferred interatomic separation. This shows that the system effectively moves toward a structure resembling a nanoparticle during equilibration and that the force field accurately depicts realistic Mg–Mg bonding behavior.

In parallel, the interaction between the surfactant and the nanoparticle during formation is revealed by the Mg–Oleylamine RDF. Oleylamine maintains a coordinated positioning around the magnesium surface rather than inside the metallic core, as evidenced by the stable peak at a distinctive separation. This behavior is significant because it demonstrates that oleylamine does not directly participate in the magnesium core, but rather functions as a surface-anchoring capping agent.

The structural mechanism anticipated in SAS-based nanoparticle formation is validated by these RDF curves taken together. They demonstrate how the system spontaneously arranges itself into a core-shell structure, where magnesium atoms group together internally and oleylamine envelops the particle on the outside to provide steric stabilization.

11 Future Goals

- To enable the SAS process to occur in its optimal state and generate nanoparticles with improved control and consistency, repeat the experiment under true supercritical CO₂ conditions.
- Beyond what optical and SEM imaging can reveal, use higher-resolution characterization tools (like XRD or TEM) to verify the crystal structure and precise particle size at the nanoscale
- . To control particle size and shape in a predictable manner, adjust the synthesis parameters, including temperature, pressure, CO₂ exposure duration, and surfactant concentration.

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