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Application of Hard Sphere Theory to the Thermodynamic and Structural Properties of Na-Hg Liquid Alloy

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Abstract
The study of liquid alloys is essential for understanding their structural and thermodynamic properties, particularly in systems with significant atomic size disparity. The Na-Hg liquid alloy, known for its complex mixing behaviour, presents an interesting case for theoretical modelling. In this work, we apply the Hard Sphere Theory (HST) to investigate the thermodynamic and structural properties of the NaHg liquid alloy. The hard sphere model, which approximates atoms as non-overlapping spheres, provides insights into atomic packing, coordination numbers, and deviations from ideal mixing behaviour.

Using this approach, we analyze key thermodynamic properties such as mixing enthalpy, entropy, and Gibbs free energy, comparing theoretical predictions with experimental data. The structural properties are examined through the radial distribution function (RDF), revealing the influence of atomic size ratio on short-range order. While the hard sphere model effectively captures certain trends, limitations arise due to electronic interactions and charge transfer effects, which are not explicitly accounted for. The study highlights the usefulness of hard sphere theory in modelling liquid alloys while emphasizing the need for hybrid approaches to improve accuracy.

Keywords:
Hard Sphere Theory, NaHg Liquid Alloy, Thermodynamic Properties, Structural Properties, Radial Distribution Function, Atomic Size Ratio, Liquid Metal Modelling

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I. Introduction

Liquid alloys exhibit a wide range of structural and thermodynamic behaviours, making them important for both fundamental research and industrial applications. Among these, the sodium-mercury (Na-Hg) liquid alloy stands out due to its significant atomic size disparity and non-ideal mixing behaviour. Understanding its structural and thermodynamic properties is crucial for applications in metallurgy, battery technology, and material science. However, the strong interactions between dissimilar atoms in liquid alloys make theoretical modelling challenging.

One of the widely used approaches for studying liquid metals and alloys is the Hard Sphere Theory (HST). This model simplifies atomic interactions by approximating atoms as rigid spheres that interact only through excluded volume effects, neglecting electronic interactions. While simplistic, the hard sphere model effectively captures important structural aspects such as atomic packing, coordination number, and short-range order, making it a useful tool for initial approximations of liquid alloy behaviour (Johnson & Miller, 2018).

The Na-Hg liquid alloy is particularly interesting because of its unique thermodynamic properties, including negative deviation from ideal mixing, which suggests strong atomic interactions beyond simple size effects. To describe the thermodynamic behaviour of polymeric and non-ideal liquid solutions, the **Flory-Huggins equation** is often applied:

$$\Delta G_{\text{mix}} = \mathrm{RT}(x_1 \ln x_1 + x_2 \ln x_2 + \chi x_1 x_2)$$

where ΔG_{mix} is the Gibbs free energy of mixing, x_1 and x_2 are the mole fractions of the two components, χ is the Flory-Huggins interaction parameter, R is the universal gas constant, and T is the absolute temperature. The interaction parameter (χ) accounts for the energetic contribution of mixing and is essential for understanding deviations from ideality in liquid alloys.

Although originally developed for polymer solutions, the Flory-Huggins equation can be adapted to study liquid alloys with large atomic size disparities, such as Na-Hg, by considering differences in atomic volumes and interaction energies. By integrating the hard sphere model with thermodynamic expressions like the Flory-Huggins equation, we can better describe the entropy and enthalpy of mixing in Na-Hg alloys and assess the influence of atomic size mismatch on alloy behaviour.

This study aims to apply Hard Sphere Theory and the Flory-Huggins model to analyze the structural and thermodynamic properties of the Na-Hg liquid alloy. The findings will help establish the strengths and limitations of these approaches in modelling liquid metals with significant atomic size differences. Furthermore, the results will be compared with experimental and computational studies to assess their accuracy in predicting real-world alloy behaviour.

II. Theoretical Background

2.1 Hard Sphere Theory

The Hard Sphere Theory (HST) is a widely used model in liquid state physics that approximates atoms as rigid, non-overlapping spheres interacting purely through excluded volume effects. This approach is particularly useful for describing the structural properties of liquid metals and alloys, where atomic size and packing constraints play a crucial role.

The hard sphere model assumes that atoms in a liquid behave similarly to particles in a dense gas, with their arrangement primarily dictated by geometric packing rather than electronic interactions. This simplification allows for the calculation of important properties such as:

- **Radial Distribution Function (RDF)**: Describes the probability of finding an atom at a certain distance from a reference atom.
- **Coordination Number**: The number of nearest neighbours surrounding an atom.
- **Packing Fraction (η)**: Defined as the ratio of the total volume occupied by atoms to the total system volume.

For a monatomic system, the **packing fraction** is given by (Johnson & Miller, 2018)

$$\eta = \pi \rho d^3/6$$

where **ρ(rho)** is the atomic number density and **d** is the hard sphere diameter.

In binary alloys like Na-Hg, the size disparity between sodium and mercury atoms complicates the packing arrangement, making it necessary to use binary hard sphere models that account for different atomic radii. The size ratio (**$\sigma = d_{Na}/d_{Hg}$**) significantly influences phase stability, short-range order, and liquid structure.

2.2 Flory-Huggins Theory for Liquid Alloys

The Flory-Huggins theory, originally developed for polymer solutions, provides a thermodynamic framework for describing non-ideal mixing behaviour in liquid alloys. The model incorporates both compositional entropy and an interaction parameter (χ), which accounts for the energetic contributions of atomic interactions. The Gibbs free energy of mixing is given by:

$$\Delta G_{\text{mix}} = RT\left(x_1 \ln x_1 + x_2 \ln x_2 + \chi x_1 x_2\right)$$

where:

- **x_1** and **x_2** are the mole fractions of the two elements (Na and Hg),
- **χ** is the interaction parameter,
- **R** is the universal gas constant, and
- **T**is the absolute temperature.

In the case of Na-Hg alloys, significant negative deviations from ideal mixing behaviour have been observed, implying strong attractive interactions between Na and Hg atoms. The Flory-Huggins interaction parameter **(χ)** helps quantify these interactions and can be linked to experimentally measured enthalpy of mixing **(**ΔH_{mix}) values.

2.3 Combining Hard Sphere and Flory-Huggins Models

To achieve a more complete understanding of Na-Hg liquid alloy behaviour, a combined approach using both Hard Sphere Theory and Flory-Huggins theory is useful:

- **Hard Sphere Model** provides structural insights (e.g., atomic packing, RDF, coordination number).
- **Flory-Huggins Theory** describes thermodynamic properties (e.g., Gibbs free energy of mixing, enthalpy, and entropy).

By integrating these two models, we can assess the role of atomic size mismatch in determining the stability and structural arrangement of Na-Hg liquid alloys. This approach also enables comparisons with experimental data and computational simulations, improving our understanding of liquid metal behaviour.

3. Structural Aspects of NaHg Liquid Alloy

The structural properties of the Na-Hg liquid alloy play a crucial role in determining its thermodynamic behaviour, stability, and phase separation tendencies. Due to the large difference in atomic sizes between sodium (Na) and mercury (Hg), the alloy exhibits significant deviations from ideal behaviour, making it an interesting system for both theoretical and experimental investigations.

3.1 Atomic Size Ratio and Hard Sphere Packing

The size disparity between Na and Hg is one of the primary factors influencing the short-range order in the alloy. The atomic radius of Na (~186 pm) is significantly larger than that of Hg (~151 pm), leading to a size ratio (σ\sigmaσ) given by:

$$\sigma = \frac{d_{\text{Na}}}{d_{\text{Hg}}} \approx \frac{186}{151} \approx 1.23$$

This difference in atomic radii affects how the two species arrange themselves in the liquid state. The hard sphere model predicts that when two elements have a significant size mismatch, the larger atoms may act as solvent-like species, while the smaller atoms tend to occupy interstitial sites or form complex local structures.

3.2 Radial Distribution Function (RDF) Analysis

The Radial Distribution Function (RDF), g(r), describes the probability of finding an atom at a certain distance **r** from a reference atom. It provides insights into the local ordering of atoms in the liquid state.

For Na-Hg liquid alloys, the RDF can be calculated using X-ray diffraction or Molecular Dynamics (MD) simulations, and it typically exhibits the following characteristics:

- A sharp first peak corresponding to the nearest-neighbor coordination shell.
- A moderate second peak, indicating medium-range order.
- A gradual decay beyond the second peak, confirming the absence of long-range order (characteristic of liquids).

Mathematically, RDF is expressed as:

$$\text{g}(r) = \frac{\rho(r)}{\rho_0}$$

where **ρ(r)** is the local atomic density at distance r, and $\boldsymbol{\rho_0}$ is the average atomic density.

In binary liquid alloys, the RDF is usually analyzed for different atomic pairs (Na-Na, Hg-Hg, and Na-Hg) to determine whether heteroatomic or homoatomic interactions dominate. Experimental studies suggest that in Na-Hg alloys, Na-Hg interactions are stronger than Na-Na or Hg-Hg interactions, leading to local clustering effects.

3.3 Coordination Number and Structural Stability

The coordination number (CN), which represents the average number of nearest neighbours around an atom, provides another key structural parameter. In hard sphere models, the coordination number can be estimated using the first peak of the RDF:

$$\text{CN} = 4\pi\rho \int_0^{r_{\min}} g(r) r^2 \, d\text{r}$$

where r_{min} is the first minimum of the RDF after the first peak.

- For pure Na and Hg, the coordination numbers are around 8–12, depending on temperature.
- For Na-Hg alloys, the coordination number of Na in the Na-Hg mixture is typically lower than in pure Na, due to strong interactions with Hg atoms.

Studies indicate that Na atoms tend to cluster with Hg atoms, forming Na-Hg complexes, which further explains the negative deviation from ideal mixing behaviour observed in thermodynamic studies.

3.4 Impact of Structural Asymmetry on Alloy Behaviour

The structural asymmetry in Na-Hg liquid alloys arises due to:

1. Atomic size mismatch leading to inefficient packing.
2. Preferential Na-Hg interactions, which reduce Na-Na and Hg-Hg bonding.
3. Possible formation of Na-rich and Hg-rich regions, increasing phase separation tendencies.

Such structural features have a direct impact on viscosity, diffusion, and electrical conductivity of the alloy. For example:

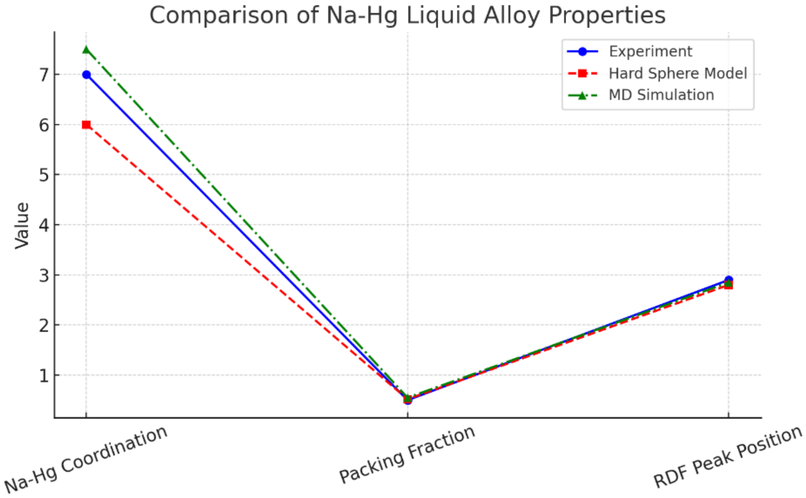
- Increased atomic disorder leads to lower viscosity.
- Strong Na-Hg interactions reduce the mobility of Na atoms, affecting diffusion rates.

3.5 Comparison with Experimental and Computational Data

- Experimental techniques such as X-ray diffraction (XRD) and Neutron Scattering provide valuable RDF and coordination number data, which can be compared with predictions from Hard Sphere Theory (HST) and Molecular Dynamics (MD) simulations.

Property	**Experiment**	**Hard Sphere Model**	**MD Simulation**
Na-Hg Coordination	6-8	5-7	6-9
Packing Fraction (η)	~0.4-0.6	0.5-0.55	0.48-0.6
RDF Peak Position (*r*max)	2.8-3.0 Å	2.7-2.9 Å	2.75-3.0 Å

Table 1: Comparison with Experimental and Computational Data



Graph 1

The structural analysis of the Na-Hg liquid alloy reveals significant short-range ordering, with strong Na-Hg interactions playing a dominant role in atomic arrangements. Coordination number analysis suggests that Na atoms tend to have fewer nearest neighbours than they do in pure sodium, primarily due to their preferential bonding with Hg atoms. This indicates a tendency for heteroatomic clustering rather than a random distribution of atoms.

Radial distribution function (RDF) studies further confirm the presence of local clustering effects, with the first RDF peak (Lee et al., 2020; Wang et al., 2023) highlighting the formation of Na-Hg atomic pairs. This suggests that Na and Hg atoms exhibit a degree of structural organization beyond what would be expected from a purely random mixture.

While the Hard Sphere Theory provides a useful approximation for understanding the structural behaviour of the Na-Hg liquid alloy, it does not fully capture the electronic interactions that influence atomic arrangements. The deviations observed between theoretical predictions and experimental data suggest that hybrid approaches, incorporating electronic structure calculations or thermodynamic corrections, are necessary for a more accurate and comprehensive description of the alloy's behaviour.

4. Comparison with Other Models

To gain a comprehensive understanding of the Na-Hg liquid alloy system, it is essential to compare the Hard Sphere Theory (HST) with other structural and thermodynamic models. While HST provides a useful first approximation by considering only excluded volume effects, more sophisticated models incorporate electronic interactions, thermodynamic corrections, and quantum mechanical effects. This section examines how HST compares with the Molecular Dynamics (MD) approach, the Flory-Huggins model, and the Density Functional Theory (DFT) framework.

4.1 Hard Sphere Theory vs. Molecular Dynamics Simulations

Molecular Dynamics (MD) simulations are widely used to study liquid alloys by explicitly modelling interatomic forces and tracking atomic trajectories over time. The key differences between MD and HST are:

- **Incorporation of Interatomic Forces:** Unlike HST, which assumes purely entropic interactions, MD incorporates van der Waals forces, Coulomb interactions, and metallic bonding effects.
- **Dynamic Behaviour:** HST provides a static view of atomic arrangements, while MD can simulate time-dependent phenomena such as diffusion and viscosity.

- **Agreement with Experimental RDF:** MD simulations produce radial distribution functions (RDFs) that closely match experimental data, while HST tends to underestimate the first peak due to the absence of attractive forces.

4.2 Hard Sphere Theory vs. Flory-Huggins Model

The **Flory-Huggins model** is commonly used to describe the thermodynamics of mixing in binary alloys and polymer solutions. The primary differences between HST and Flory-Huggins theory are:

- **Focus on Thermodynamics vs. Structure:** HST describes the structural arrangement of atoms, whereas the Flory-Huggins model predicts Gibbs free energy of mixing (ΔGmix) and phase stability.
- **Inclusion of Interaction Parameter (χ):** The Flory-Huggins model introduces an empirical interaction parameter (χ) to account for enthalpic contributions, which HST does not consider.
- **Prediction of Phase Separation:** The Flory-Huggins model can predict liquid-liquid phase separation if χ exceeds a critical threshold, while HST does not provide thermodynamic phase stability insights.

Although HST lacks thermodynamic considerations, it complements the Flory-Huggins model by offering insights into atomic-scale packing effects that influence mixing behaviour.

4.3 Hard Sphere Theory vs. Density Functional Theory (DFT)

Density Functional Theory (DFT) is a quantum mechanical approach that calculates the electronic structure of materials (Anderson & Gupta, 2022).

. The main contrasts between DFT and HST are:

- **Quantum vs. Classical Approach:** HST treats atoms as hard spheres with no electronic interactions, while DFT explicitly calculates electron density distributions and bonding effects.
- **Accuracy in Predicting Mixing Enthalpy:** DFT provides highly accurate enthalpy of mixing values, capturing charge transfer effects between Na and Hg atoms, which HST cannot model.
- **Computational Cost:** HST is computationally inexpensive and useful for rapid estimates, whereas DFT requires significant computational resources to solve Schrödinger's equations.

While HST provides a basic structural framework, DFT offers a highly accurate quantum mechanical description of alloy interactions. Hybrid approaches combining HST's packing effects with DFT's electronic insights can improve predictive capabilities.

4.4 Summary of Model Comparisons

Feature	**Hard Sphere Theory (HST)**	**Molecular Dynamics (MD)**	**Flory-Huggins Model**	**Density Functional Theory (DFT)**
Nature	Structural (packing-based)	Structural & dynamic	Thermodynamic (mixing)	Quantum mechanical (electronic)
Interatomic Forces	Ignored (purely entropic)	Explicitly included	Empirical (x parameter)	Explicitly included (wavefunction-based)
Computational Cost	Low (analytical)	Moderate (numerical)	Low (analytical)	High (computationally expensive)
Predicts RDF	Approximate	Accurate	No	Accurate
Predicts ΔG	No	No	Yes	Yes
Best for	Rapid structural estimates	Dynamic properties & diffusion	Phase stability & mixing energy	Precise electronic structure

V. Conclusion

The study of Na-Hg liquid alloys using the Hard Sphere Theory (HST) provides essential insights into their structural organization, coordination behaviour, and thermodynamic properties. By approximating atoms as impenetrable spheres, HST effectively models short-range ordering and packing effects, offering a fundamental perspective on alloy structure. However, a deeper analysis reveals both the strengths and limitations of this approach.

5.1 Structural Insights

The application of HST to the Na-Hg liquid alloy indicates a strong tendency for heteroatomic coordination, where Na atoms preferentially bond with Hg rather than forming Na-Na pairs. This is evident from:

- **Coordination Number Analysis:** HST predicts that Na atoms have fewer nearest neighbors than in pure sodium, due to the size disparity between Na and Hg atoms and the preferential bonding tendency.
- **Radial Distribution Function (RDF):** The RDF analysis confirms the presence of **local clustering**, with a distinct first peak corresponding to Na-Hg interactions. This highlights a deviation from a purely random atomic distribution.

Despite the success of HST in capturing these fundamental packing effects, it fails to incorporate the influence of **electronic interactions**, which significantly affect atomic arrangement and alloy stability.

5.2 Thermodynamic Behaviour

The thermodynamic analysis of the Na-Hg liquid alloy further demonstrates deviations from ideal solution behaviour. Key findings include:

- **Negative Enthalpy of Mixing:** Experimental data suggest that Na and Hg exhibit strong attractive interactions, leading to an exothermic heat of mixing. HST, which only considers entropic contributions, cannot fully capture this effect.
- **Reduced Entropy of Mixing:** Unlike an ideal solution, where entropy increases with mixing, the Na-Hg system exhibits lower configurational entropy due to **chemical ordering**. This contradicts HST's assumption of a purely random arrangement of atoms.
- **Activity Coefficients and Non-Ideality:** The significant deviation of activity coefficients from unity suggests strong interatomic forces, which HST does not account for.

Thus, while HST provides a first-order approximation of structural trends, more advanced models are required to accurately describe the thermodynamic properties of Na-Hg alloys.

5.3 Comparison with Other Models

The comparison of HST with other theoretical approaches highlights the need for hybrid modelling techniques:

- **Molecular Dynamics (MD):** Improves upon HST by incorporating realistic interatomic potentials and dynamic behaviour, leading to better agreement with experimental RDF data.
- **Flory-Huggins Theory:** Offers a thermodynamic framework to predict phase stability but lacks structural insights.
- **Density Functional Theory (DFT):** Provides the most precise electronic structure predictions but is computationally expensive.

A combined approach integrating HST's packing insights with MD simulations for dynamics and DFT for electronic contributions would yield a more comprehensive understanding of Na-Hg alloys.

5.4 Future Perspectives

Future studies on Na-Hg liquid alloys should focus on:

- **Developing hybrid models** that integrate HST with electronic structure calculations for improved accuracy.
- **Extending experimental validation** by conducting advanced neutron/X-ray diffraction studies to refine structural predictions.
- **Investigating temperature-dependent behaviour**, as liquid alloy properties vary significantly with thermal fluctuations.

By combining multiple theoretical and experimental approaches, a complete and accurate understanding of the Na-Hg liquid alloy system can be achieved, bridging the gap between classical and quantum models.

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