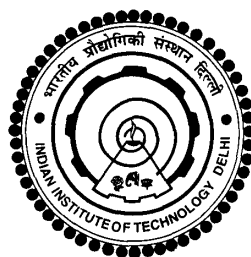


SOLVATION AND SELF-ASSEMBLY OF NANOPARTICLES: A COMPUTATIONAL STUDY

HARI OM SHARANAM YADAV



DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY DELHI
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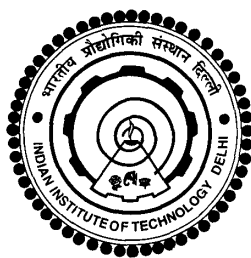
HARI OM SHARANAM YADAV

DEPARTMENT OF CHEMISTRY

Submitted

in fulfillment of the requirements of the degree of Doctor of Philosophy

to the



INDIAN INSTITUTE OF TECHNOLOGY DELHI

FEBRUARY 2018

To My Parents

and

*our beloved Charu Ma'am
(Prof. Charusita Chakravarty)*

Certificate

This is to certify that the thesis titled "**SOLVATION AND SELF-ASSEMBLY OF NANOPARTICLES: A COMPUTATIONAL STUDY**" is being submitted by **Mr. Hari Om Sharanam Yadav** to the Department of Chemistry, Indian Institute of Technology Delhi, for the award of the degree of **Doctor of Philosophy**. This thesis is a record of bona-fide research work carried out by him under the supervision of **(Late) Prof. Charusita Chakravarty** from 3 January, 2011 to 29 March, 2016 and subsequently under our guidance. In our opinion, the thesis has reached the standards fulfilling the requirements of the regulations relating to the degree.

The results contained in this thesis have not been submitted to any other University or Institute for the award of any degree or diploma.

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Abstract

In this thesis, molecular dynamics (MD) simulations are employed to understand two important aspects of nanoparticle self-assembly: the first aspect is examining the structure and solvation thermodynamics of single passivated nanoparticle, hence the dispersion stability of nanoparticles, and the second is computing the effective pair interactions between nanoparticles as a route for understanding self-assembly. The gold (Au) and semiconductor (CdSe) nanocrystals passivated with alkanethiol and alkylamine ligands respectively are taken as systems of interest. The near-critical fluids (ethane and propane) and liquid hydrocarbons (C_6 - C_{12}), which are commonly used in most experiments, are chosen as the solvents for these nanoparticles. The solvation thermodynamics at the single nanoparticle level is studied following the Ben-Naim's formulation of statistical mechanics of solvation. The entropic changes associated with the ligand shell and solvent reorganizations are explicitly calculated using the structural metrics frequently exercised in biomolecular hydrations. The Helmholtz free energy of solvation is estimated by combining the change in entropy with the solvation energy, which is estimated from the pair interactions between the solvent molecules and the nanoparticle. The effective interactions (i.e., the pair potential of mean forces, PMFs) of nanoparticles at two- and three-particle level are computed employing the constrained MD simulations, in which both the isotropic and anisotropic interactions are characterized. Anisotropy arises from instantaneous fluctuation of ligands, which introduces directional characteristic in the interparticle interactions. The role of various factors affecting the assembly process such as solvent density, temperature, nanocrystal size, ligand chain length, and surface coverage on both the aspects are thoroughly examined. Implications of generating coarse-grained potentials for understanding the single-component superlattices (SLs) and binary nanocrystal superlattices (BNSLs) are discussed. Both the solvation and interaction results are found consistent with experiment, suggesting the approach used in work as a good route of obtaining the structural insights into solvation thermodynamics and the effective interactions that could be useful for understanding the dispersion stability and self-assembly of passivated nanoparticles.

सार

इस शोध में, मॉलिक्यूलर डायनामिक्स (MD) सिमुलेशन का प्रयोग करके नैनोपार्टिकल सेल्फ-असेंबली के दो महत्वपूर्ण पहलुओं को समझा गया है: पहला पहलू एकल नैनोकणों की संरचना और सॉल्वेशन थर्मोडायनामिक्स का परीक्षण करना है, अर्थात् नैनोकणों के डिस्पर्सन स्थायित्व को समझना है, और दूसरा, सेल्फ-असेंबली को समझने के लिए एक मार्ग के रूप में दो नैनोकणों के बीच प्रभावी इंटरैक्शन्स की संगणना करना है। अल्केनथायोल और एल्काइलअमीन्स लिगेण्ड्स से निष्क्रियित गोल्ड (Au) और सेमीकंडक्टर (CdSe) नैनोक्रीस्टल्स इस शोध के प्रमुख अंग हैं। प्रायः प्रयोगों में प्रयुक्त किये जाने वाले नियर-क्रिटिकल फ्लूयिड्स (एथेन और प्रोपेन) और लिक्विड हाइड्रोकार्बन्स (C_6-C_{12}) को इन नैनोपार्टिकल्स के लिए सॉल्वेंट्स के रूप में चुना गया है। एकल-नैनोपार्टिकल स्तर पर सॉल्वेशन थर्मोडायनामिक्स का अध्ययन बेन-नैम के द्वारा विकसित स्टैटिस्टिकल मेकैनिक्स पर आधारित सूत्र का प्रयोग करके किया गया है। लिगेण्ड शेल और विलायक के पुनर्गठन के साथ जुड़े एंट्रोपिक परिवर्तनों की गणना बायोमॉलिक्यूलर हाइड्रेशन में प्रयुक्त किए जाने वाले संरचनात्मक मेट्रिक्स का उपयोग करके करते हैं। सॉल्वेशन की हेल्महोल्ट्ज़ मुक्त ऊर्जा, एंट्रोपिक परिवर्तन को सॉल्वेशन ऊर्जा के साथ संयुक्त करके प्राप्त किया जाता है, जिसे नैनोपार्टिकल और विलायक अणुओं के बीच इंटरैक्शन्स से आंका जाता है। दो और तीन नैनोपार्टिकल स्तर पर प्रभावी युग्म इंटरैक्शन्स (अर्थात्, पोटेन्शियल ऑफ मीन फोर्सस, PMFs) का आकलन, कन्स्ट्रैंड MD सिमुलेशन से किया गया है, जिसमें हम आइसोट्रोपिक और अनिसोट्रोपिक इंटरैक्शन्स को पृथक् रूप से कंप्यूट करते हैं। अनिसोट्रोपी लिगेण्ड्स के तात्कालिक फ्लक्चुयेन्स से आता है, जो दो नैनोपार्टिकलों के इंटरैक्शन में दिशात्मक प्रवृत्ति को जन्म देता है। सेल्फ-असेंबली प्रक्रिया को प्रभावित करने वाले विभिन्न कारकों, जैसे कि विलायक के घनत्व, तापमान, नैनोक्रीस्टल्स के आकार, लिगेण्ड्स की लंबाई और सतह कवरेज की भूमिका का विस्तृत अध्ययन किया गया है। सिंगल-कॉम्पोनेन्ट सुपरलैटिसेस (SLs) और बाइनरी नैनोक्रीस्टल सुपरलैटिसेस (BNSLs) को समझने के लिए कोर्स-ग्रेन्ड पोटेन्शियल को विकसित करने के निहितार्थ की चर्चा गयी है। दोनों सॉल्वेशन और इंटरैक्शन्स के परिणाम प्रयोगों के अनुरूप हैं, जो इस बात का सुझाव देते हैं, कि इस अध्ययन में प्रयुक्त किया जाने वाला दृष्टिकोण, सॉल्वेशन थर्मोडायनामिक्स और इंटरैक्शन्स में संरचनात्मक अंतर्दृष्टि प्राप्त करने का एक अच्छा मार्ग है, और ये नैनोपार्टिकलों के डिस्पर्सन स्थायित्व और सेल्फ-असेंबली को समझने के लिए बहुत उपयोगी हो सकता है।

Permissions

Permissions have been taken from the respective journals for the publications related to work presented in this thesis.

List of Publications Related to Work Presented in this Thesis as on Date of Submission of Thesis

1. Divya Nayar, **Hari O. S. Yadav**, B. Shadrack Jabes and Charusita Chakravarty, “Relating Structure, Entropy and Energy of Solvation of Passivated Metal Nanoparticles”, *J. Phys. Chem. B.* **116**, 13124-13132 (2012).
2. B. Shadrack Jabes, **Hari O. S. Yadav**, Sanat K. Kumar and Charusita Chakravarty, “Fluctuation-Driven anisotropy in effective pair interactions between nanoparticles: Thiolated gold nanoparticles in ethane”, *J. Chem. Phys.* **141**, 154904, (2014).
3. **Hari O. S. Yadav**, Gourav Shrivastav, Manish Agarwal and Charusita Chakravarty, “Effective interactions between nanoparticles: Creating temperature-independent solvation environments for self-assembly”, *J. Chem. Phys.* **144**, 244901, (2016).
4. **Hari O. S. Yadav** and Charusita Chakravarty, “Thiolated gold nanoparticle solvation in near-critical fluids: The role of density, temperature, and topology”, *J. Chem. Phys.* **146**, 174902, (2017).

Contents

Certificate	i
Acknowledgements	ii
Abstract	v
Permissions	vii
Table of Contents	viii
List of Figures	xi
List of Tables	xxv
1 Introduction	1
1.1 Nanoparticle building blocks	1
1.2 Dispersion Stability	2
1.3 Self-Assembly	6
1.4 Factors Affecting the Nanoparticle Self-assembly	9
1.5 Nanoscale Forces	13
1.6 Theoretical Framework for Computational Study	18
1.6.1 Simple Liquids	22
1.6.2 Solvation Thermodynamics of Single Nanoparticle	28
1.6.3 Effective Potentials as Predictors for Self-Assembly	32
1.7 Computational Methods	38
1.7.1 Canonical and Isothermal-Isobaric Ensembles	39
1.7.2 Molecular Dynamics Simulations	43

1.7.3	Systems of Interest	45
1.8	Observables	47
1.8.1	Pressure	47
1.8.2	Diffusivity	49
1.8.3	Thermodynamic Response Functions	50
1.8.4	Particle density and Correlation functions	50
1.8.5	Pair and Excess Entropy	55
1.9	Motivation and Organization of Thesis	56
2	Solvation of Thiolated Gold Nanoparticles in Near-Critical Fluids	59
2.1	Introduction	59
2.2	Computational Details	62
2.2.1	Potential Energy Surface	62
2.2.2	Molecular Dynamics Simulation	63
2.3	Results and discussion	67
2.3.1	Effect of Density, Temperature and Core Size	67
2.3.2	Effect of Ligand Chain Length	79
2.3.3	Effect of Surface Coverage	82
2.4	Conclusions	86
3	Effective Pair Interactions between Thiolated Gold Nanoparticles: The Role of Solvent Density and Temperature	89
3.1	Introduction	89
3.2	Computational Details	92
3.2.1	Potential Energy Surface	92
3.2.2	Molecular Dynamics Simulation	92
3.3	Results and Discussion	94
3.3.1	Nanoparticle-Solvent Interactions	94
3.3.2	Two-body Interactions	97
3.3.3	Three-body Effect	101
3.3.4	Emergent Anisotropy	102
3.4	Conclusions	106

4	Creating Temperature-Independent Solvation Environments for Nanoparticle Self-Assembly	109
4.1	Introduction	109
4.2	Experimental Background	111
4.3	<i>n</i> -Alkanes: Criteria and Consequences of Simple Liquid Behaviour . .	114
4.4	Computational Details	115
4.4.1	Potential Energy Surface	115
4.4.2	Molecular Dynamics Simulation	115
4.5	Results and Discussion	118
4.5.1	Thermodynamic and Transport Properties of <i>n</i> -Alkanes	118
4.5.2	Solvation of a Single Nanoparticle	122
4.5.3	Effective Interactions between a Pair of Nanoparticles	125
4.6	Conclusions	128
5	Effective Pair Interaction between Au and CdSe Nanoparticles	133
5.1	Introduction	133
5.2	Computational Details	136
5.2.1	Potential Energy Surface	136
5.2.2	Molecular Dynamics Simulation	137
5.3	Results and Discussion	141
5.3.1	Thermal Relaxation of CdSe Cores and Ligand Binding Energy	141
5.3.2	Structure and Configurational Entropy of Ligand Shell	143
5.3.3	Properties due to Solvent Reorganization	147
5.3.4	Isotropic Two-body PMFs	150
5.3.5	Emergent Anisotropy in Pair PMFs	154
5.4	Conclusions	159
6	Summary and Future Perspectives	162
	Bibliography	166
	Biodata of the Candidate	205

List of Figures

1.1	The general profile of potential energy illustrating (a) electrostatic stabilization of nanoparticles in polar solvents and (b) steric stabilization of nanoparticles in non-polar solvents. In plot (b), the components of total potential energy (steric repulsion and van der Waals attraction) are also shown for better understanding. Both figures (a) and (b) have been adapted from Ref. [54] with permission.	3
1.2	Typical example of long-range well-ordered, two-dimensional (2D) assembly of dodecanethiol-passivated gold nanocrystals (6 nm) onto a 3 mm×4 mm substrate. Lower right inset shows the fast Fourier transform of the image. Upper left inset schematically shows the arrangement two adjacent nanoparticles in the monolayer. The figure has been adapted from Ref. [89] with permission.	7
1.3	Illustration of some of the binary superlattices generated in the experiment from the mixture of two different sizes of nanoparticles . . .	8
1.4	Experiment demonstrating the effect of chain length on 2D self-assembly of nanoparticles. TEM images are showing the self-assembled structures of 4.5 nm Pd nanocrystals coated with the ligand of (a) butanethiol, (b) octanethiol, (c) dodecanethiol, and (d) hexadecanethiol. Micrographs have been adapted from Ref. [95] with permission. . . .	9
1.5	Empirical d/l phase diagram for thiolated Pd nanoparticles of different chain lengths	10
1.6	Effect of temperature on single-component self-assembly of nanoparticles	11

1.7	Experiment illustrating the effect of temperature on binary assembly of nanoparticles.	12
1.8	Effect of nature of solvent (polarity) on self-assembly of nanoparticles. The images are high resolution scanning electron micrographs (HRSEM) of self-assembled structures of dodecanethiol-coated gold nanocrystals drop-casted from (a) hexane, (b) toluene, and (c) chloroform. The images have been adapted from Ref. [99] with permission.	13
1.9	Effect of length scale on interparticle interaction of colloids. Plot shows the pair interactions, $U_{LJ}(r)$, of different sizes of colloidal particles made of Lennard-Jones (12-6 LJ) atoms, where $2a$ is the diameter of colloid particles, which is simply a multiple of the diameter (σ) of LJ atom. Both the interaction and pair separation are shown in reduced units in which ϵ denotes the well-depth of LJ interaction. This plot of effective pair interactions of LJ colloid particles has been adapted from Ref. [105] with permission.	14
1.10	Depletion interaction of nanoparticles in solution. (a) illustrates the excluded volume (dashed circles) when two interacting nanoparticles (yellow spheres) are far apart in solvent (gray spheres). (b) shows the excluded volume when nanoparticles come in close proximity. Red convex corresponds to the excess volume gained due to the overlap of excluded volume of nanoparticles. Black arrows display the direction of resulting force due to overlap of excluded volumes. Schematic diagram has been redrawn using Ref. [101].	17

1.11	The variation of length and time scales in the nanoparticle self-assembly from computational viewpoint. (a) TEM image of a single CdSe nanoparticle composed atoms and ligand molecules, (b) [111] projection of hcp superlattice of CoPt ₃ nanocrystals, (c) Micrograph of macroscopic 3D superlattices of CdSe nanoparticles. The length and time scales of these systems in computational model are specified below the respective images. Image (a) has been adapted from Ref. [126], (b) and (c) from Ref. [127] with permission.	19
1.12	Schematic representation of the computational approach for understanding the solvation and self-assembly of passivated metal and semiconductor nanoparticles	21
1.13	Pressure (P)–temperature (T) phase diagrams of pure liquid argon and gold metal.	25
1.14	Radial distribution function of a typical atomic liquid	26

- 1.15 Schematic diagram illustrating the simulation setup for the PMF of thiolated gold nanoparticles. The snapshots are taken from molecular dynamics simulations of $\text{Au}_{140}(\text{SC}_{10})_{62}$ nanoparticles interacting in vacuum at temperature, $T = 311\text{K}$. Au_{140} nanocrystals are shown in light yellow color. The sulfur atom of the ligands shown as red beads are attached to the alkyl chains made up of line segments representing the C–C bond. (a) Explains the two-body interaction and dipolar behaviour of passivated nanoparticles. The centers of mass of the gold core, (Au_{COM} with position coordinate, $\mathbf{r}_1$) and the ligand cloud, ($\text{Ligand}_{\text{COM}}$) are shown schematically. The mass of ligand monomers is assumed to be identical in the calculation of center of mass of ligand cloud. The mass dipole, ($\vec{\Delta}$) is defined as a vector connecting the geometric centers of the gold core, (Au_{COM}) and the ligands, ($\text{Ligand}_{\text{COM}}$). The angle θ between the mass dipole, ($\vec{\Delta}$) and the inter-particle axis, ($\mathbf{r}_{12}$) joining the centers $\mathbf{r}_1$ and $\mathbf{r}_2$ of two adjacent gold cores is also shown. (b) Exhibits the simulation setup for interaction studies of three-particle system. The centers of mass of metal cores of three nanoparticles form an isosceles triangle, are shown using vectors $\mathbf{r}_1$, $\mathbf{r}_2$, and $\mathbf{r}_3$ respectively. The midpoint of positions $\mathbf{r}_1$ and $\mathbf{r}_2$ is labeled as $\mathbf{r}_C$. The mean force between the position $\mathbf{r}_C$ and third nanoparticle along vector $\mathbf{r}_{3C}$ is sampled from a constraint simulation keeping separation, $r_{12}=|\mathbf{r}_2 - \mathbf{r}_1|$ fixed. Bisect angle, α between vectors $\mathbf{r}_{3C}$ and $\mathbf{r}_{31}$ is used to obtain the mean force along vector $\mathbf{r}_{31}$ or $\mathbf{r}_{32}$ using equation (1.6.34). 34
- 1.16 Nanocrystals of interest. Figure (a) and (b) show the snapshots of gold (Au) nanocrystals having fcc structure and truncated octahedron morphology, and (c) shows the snapshot of thermally optimized CdSe nanocluster generated from wurtzite lattice of bulk material. 46

- 2.1 Liquid-vapour coexistence curve for ethane and propane in reduced temperature, T_r and reduced density, ρ_r plane from the TraPPE-UA potential. Both temperature and density are reduced by the corresponding critical values of solvents. The coexistence data for ethane and propane shown by solid and open circles have been taken from Ref. [125]. The dotted horizontal and vertical lines represents the critical isotherm and isochore which respectively divide the phase diagram into $T_r > T_c$ or $T_r < T_c$ and $\rho_r > \rho_c$ or $\rho_r < \rho_c$, where T_c and ρ_c correspond to the critical temperature and density of the solvents. The other points represent the state points used for solvation of thiolated gold nanoparticles. The simulation in propane solvent is carried out only for isotherm, $T_r = 1.02$, corresponding to the blue points. 66
- 2.2 Pair correlation function, $g_{ns}(r)$, between solvent monomers and the center of mass of the gold cluster passivated with the decanethiol ligands in ethane solvent. Plot (a) shows the $g_{ns}(r)$ for Au_{38} nanoparticle at different densities, $\rho_r = 0.1, 0.5$ and 3.0 for the isotherms, $T_r = 1.02, 1.15$, and 1.25 ; (b) shows the $g_{ns}(r)$ for Au_{140} nanoparticle at different densities, $\rho_r = 0.1, 0.5$ and 3.0 for the isotherms, $T_r = 1.02$ and 1.15 . The $g_{ns}(r)$ at other densities are not shown for the clarity reasons. 67
- 2.3 Ensemble-averaged solvation energy, ΔU_{ns} , of decanethiol-passivated gold nanoparticles as a function of reduced density, ρ_r , of solvent along different isotherms. Data of both nanoparticle systems are labeled using the arrows. The ΔU_{ns} in ethane are shown using solid lines, whereas the ΔU_{ns} of Au_{38} nanoparticle in propane corresponding to the isotherm, $T_r = 1.02$ is shown using a black dashed line. 71

2.4	Solvation properties of Au ₃₈ nanoparticle passivated with decanethiol ligands as a function of reduced density, ρ_r , of solvent along different isotherms. (a) Partial molar volume at infinite dilution, $\bar{v}_n^\infty$, (b) solvent excess, n_s^E , (c) pair entropy of solvation due to local ordering of solvent, ΔS_{ns}^{loc} , (d) total entropy of solvation with local and long-range correction terms, ΔS_{ns}^{tot} , and (e) solvation free energy, ΔA_{ns} . The solvation quantities computed in ethane are shown using the solid line-points. The dashed lines show the results in propane along the isotherm, $T_r = 1.02$. As a result of minor differences in the solvation quantities at higher densities ($\rho_r \geq 2.0$), plots corresponding to the isotherm, $T_r = 0.9$, in ethane are not shown.	72
2.5	Solvation properties of Au ₁₄₀ nanoparticle passivated with decanethiol ligands in ethane as a function of reduced density, ρ_r , for different isotherms. (a) Partial molar volume at infinite dilution, $\bar{v}_n^\infty$, (b) solvent excess, n_s^E , (c) pair entropy of solvation due to local ordering of solvent, ΔS_{ns}^{loc} , (d) total entropy of solvation with local and long-range correction terms, ΔS_{ns}^{tot} , and (e) solvation free energy, ΔA_{ns}	75
2.6	Schematic diagram illustrating the inherent anisotropy of nanoparticle. Part (a) shows a snapshot of an Au ₃₈ nanoparticle passivated with decanethiol ligands in vacuum at $T_r = 1.02$. Part (b) is a model of this nanoparticle, in which yellow circle represents the Au ₃₈ core, and distorted light blue circle represents asymmetric cloud of the ligand shell. The mass dipole, $\vec{\Delta}$, determining the extent of anisotropy is shown using the black arrow, which is a vector connecting the geometric centers of the gold core and the ligand chains	76

2.7	Mean square value of the magnitude of the mass dipole, $\langle \Delta^2 \rangle$, as a function of reduced density, ρ_r , of the solvent. Plot (a) shows the comparison for Au ₃₈ nanoparticle at common reduced temperature in ethane and propane solvent; (b) and (c) show the variation of $\langle \Delta^2 \rangle$ for Au ₃₈ and Au ₁₄₀ nanoparticles in ethane for different isotherms. The unit of ensemble averaged $\langle \Delta^2 \rangle$ is Å ²	77
2.8	A comparison of the probability distribution, $P(\Delta^2)$, of the square magnitude of the mass dipole for decanethiol-passivated Au ₃₈ nanoparticle in vacuum at $T_r = 1.02$ for TraPPE-UA [125] and Paul <i>et al.</i> 's UA force field [289].	78
2.9	Pair correlation function, $g_{ns}(r)$, of solvent monomers for Au ₁₄₀ nanoparticle with different chain lengths (n) of alkanethiol ligands in ethane at critical density, and temperature, $T_r = 1.02$	80
2.10	Probability distribution, $P(\Delta^2)$, of the square magnitude of the mass dipole, for the Au ₁₄₀ nanoparticle with different chain lengths (n) of alkanethiols at temperature, $T_r = 1.02$ in (a) vacuum, and (b) ethane at reduced density, $\rho_r = 1.0$	81
2.11	Solvation properties of the Au ₃₈ nanoparticle with different surface coverage of decanethiol ligands in ethane at reduced density, $\rho_r = 1.0$ and temperature, $T_r = 1.02$. (a) Pair correlation function, $g_{ns}(r)$, between solvent monomers and center of mass gold nanocluster, (b) Partial molar volume at infinite dilution, $\bar{v}_n^\infty$, (c) Solvent excess, n_s^E , (d) Pair entropy of solvation due to local ordering of solvents, ΔS_{ns}^{loc} , and (e) Total entropy of solvation with local and long-range correction terms, ΔS_{ns}^{tot} . The quantities shown in subfigures (b) to (e) are obtained from integration of $g_{ns}(r)$ (see Section II) with respect to r between the limits, $r_c = 0$ to 50 Å.	83

2.12	Probability distribution, $P(\Delta^2)$, of the square magnitude of the mass dipole for the Au_{38} nanoparticle with different surface coverages of decanethiol ligands at temperature, $T_r = 1.02$, in (a) vacuum, and (b) ethane at reduced density, $\rho_r = 1.0$. The $P(\Delta^2)$ distribution for symmetrical coating at 25% coverage is shown with green lines. . . .	86
3.1	Direct and solvent-induced contributions to the potential of mean forces (PMFs) between the gold nanoparticle and solvent monomer. Plot (a) shows the direct solute-solvent interaction energy, U_{ns} as function of r for $\text{Au}_{38}(\text{SC}_{10})_{24}$ and $\text{Au}_{140}(\text{SC}_{10})_{62}$ nanoparticles at temperature, $T_r = 1.02$ and solvent density, $\rho_r = 3.0$ where r corresponds to the distance between the center of mass of gold nanocrystal and solvent monomer. For multisite nanoparticles made up of hard core and soft corona of ligands, U_{ns} are estimated from spherical averaging of pair interactions. The solvent-induced contribution, $\omega_{ns}(r)$ for $\text{Au}_{38}(\text{SC}_{10})_{24}$ at different temperatures and density, $\rho_r = 1.0$ is shown in (b); for $\text{Au}_{38}(\text{SC}_{10})_{24}$ and $\text{Au}_{140}(\text{SC}_{10})_{62}$ at different densities (ρ_r) of solvent along the isotherm, $T_r = 1.02$ are shown in plots (c) and (d).	96
3.2	Potential of mean force, $V_{PMF}(r_{12})$ as a function of pair separation, r_{12} at different temperatures (T_r) along the given isochore (ρ_r) for a pair of $\text{Au}_{38}(\text{SC}_{10})_{24}$ nanoparticles. Hamaker interaction energy, $U_{Hamaker}$ between two bare gold nanocrystals is shown using the black dotted line and interaction parameter is taken from the previous studies. [191, 314].	98

3.3	Isotropic pair potential of mean force in two-body (shown in left column as function of r_{12}) and in three-body system (shown in right column as function of r_{31}) at different densities (ρ_r) along the isotherm, $T_r = 1.02$ for $\text{Au}_{38}(\text{SC}_{10})_{24}$ (a & c) and $\text{Au}_{140}(\text{SC}_{10})_{62}$ nanoparticles (b & d), respectively. Hamaker interactions, $U_{Hamaker}$ between bare gold nanocrystals are shown using the black dotted lines. Note that $V_{PMF}(r_{31})$ is also a two-body PMF in presence of third nanoparticle and one should not consider it as three-body PMF. See Figure 1.15 for more details.	99
3.4	Anisotropic parameters as a function of pair separation, r_{12} for $\text{Au}_{38}(\text{SC}_{10})_{24}$ nanoparticle at different temperatures (T_r). The mean square value of the magnitude of mass dipole, $\langle\Delta^2\rangle$ and mean angle, $\langle\cos(\theta)\rangle$ between the mass dipole Δ and inter-particle axis (r_{12}) in vacuum and ethane solvent with density, $\rho_r = 1.0$ are shown in (a) and (b), respectively. Due to insignificant effect of temperature, the comparison of anisotropic parameters for solvent density, $\rho_r = 3.0$ are not shown. Units of $\langle\Delta^2\rangle$ is in $\text{\AA}^2$	103
3.5	Anisotropic parameters as a function of pair separation, r_{12} at different densities (ρ_r) of solvent along the isotherm, $T_r = 1.02$. The mean square value of the magnitude of mass dipole, $\langle\Delta^2\rangle$ and mean angle, $\langle\cos(\theta)\rangle$ between the mass dipole Δ and inter-particle axis (r_{12}) for $\text{Au}_{38}(\text{SC}_{10})_{24}$ nanoparticle are shown in (a) and (b), and for $\text{Au}_{140}(\text{SC}_{10})_{62}$ nanoparticle are shown in (c) and (d), respectively.	105
3.6	Comparison of anisotropic parameters, $\langle\Delta^2\rangle$ and $\langle\cos(\theta)\rangle$, calculated in two- and three-body interactions for $\text{Au}_{140}(\text{SC}_{10})_{62}$ at $\rho_r = 1.0$ and $T_r = 1.02$	106

- 4.1 Experimental Clausius-Clapeyron plot of the saturated vapour pressure, (P_{vap}) against inverse temperature, ($1/T$) for n-alkanes [330]. The data for n-octane produced from simulation using the TraPPE-UA potential is shown as a dashed line for comparison. [125]. 112
- 4.2 Liquid-vapour coexistence curve for alkanes in temperature (T) and reduced monomer density (ρ_m^*) plane from the TraPPE-UA potential. The diagram was constructed from data for state points with $T > 300$ K from Refs. [125, 333]; the low-temperature below 300K portion of the curve was generated by us from zero pressure coexistence simulations [196]. The reduced monomer density is defined as: $\rho_m^* = \sigma^3 \rho_m$, where σ denotes the Lennard-Jones length parameter of methylene unit. The vertical dashed line shown at $\rho_m^* = 1.85$ corresponds the constant monomer density of alkanes. 114
- 4.3 Simulation snapshot illustrating the [111]-[111] orientation of two interacting $\text{Au}_{140}(\text{SC}_{10})_{62}$ nanoparticles in vacuum at 331.1 K at the pair separation of 28 Å. In [111]-[111] orientation, Au_{140} core of both nanoparticles (yellow color) face each other with their two [111] facets. The common edge joining these two facets are in parallel. The sulfur atoms are shown as the red beads, whereas the alkyl tails with the line segments. The centers of mass of the gold core, (Au_{COM}) and the ligand cloud, (Ligand_{COM}) are shown schematically. The mass dipole, ($\vec{\Delta}$) is defined as a vector connecting the geometric centers of the gold core, (Au_{COM}) and the ligands, (Ligand_{COM}). The angle, θ between the mass dipole, ($\vec{\Delta}$) and the inter-particle axis, ($\vec{r}$), joining two adjacent gold cores is also shown. Ligands from front surface of nanocrystals have been removed for clarity reason. 118

4.4	Comparison of the pair correlation functions for (a) alkane monomer units, $g_{ss}(r)$ and (b) centers of mass of n-alkane chains, $g_{cc}(r)$ at given temperatures and constant reduced monomer density. In part (a), the peaks corresponding to the contributions from bond, angle and dihedral are labeled. The distance, r/σ is shown in reduced unit where σ denotes the Lennard-Jones length parameter of methylene unit.	120
4.5	Log-log plot of mean square displacement (MSD) as a function of time (t) for monomer of n-alkanes of different chain length at the given temperatures.	122
4.6	Solvation properties of single thiolated gold nanoparticle in n-alkane solvents. (a) Pair correlation function, $g_{ns}(r)$, between solvent monomers and center of mass gold cluster (b) solvent excess number, n_s^E (c) partial molar volume at infinite dilution, v_{ns}^∞ (d) solvation pair entropy due to local ordering of solvents, ΔS_{ns}^{loc} and (e) total entropy of solvation with local and long-range correction terms, ΔS_{ns}^{tot} . The quantities, (b) to (e) are obtained from the integration of $g_{ns}(r)$ (see section II) with respect to r between limits $r_c = 0$ to $50 \text{ \AA}$	123
4.7	Probability distribution, $P(\Delta^2)$ for single passivated gold nanoparticle in (a) vacuum and (b) n-alkane solvents. Here, Δ , denotes the magnitude of the vector connecting the centers of mass of the gold core and the ligand shell.	125
4.8	Isotropic potential of mean force, $V_{PMF}(r)$ as a function of pair separation, r , between two decanethiol-coated gold nanoparticles at given temperatures in (a) vacuum and (b) alkane solvents for [111]-[111] orientation. The inset of figure (a) and (b) show a comparison of PMFs for [111]-[111] and [100]-[100] orientations at 331.1 K in the respective medium. The PMF for cross orientation, [100]-[111] is also shown using the black dashed line in the inset of figure (b).	127

4.9	Fluctuation-driven anisotropy in passivated nanoparticles as a function of pair separation, r , for [111]-[111] orientation at different temperatures. The mean square value of the magnitude of the mass dipole, $\langle \Delta^2 \rangle$ are shown in (a) and (c). Mean angle between the mass dipole and interparticle axis are shown in (b) and (d).	129
5.1	Magnitude of dipole moment, $ \mu $, of thermally relaxed bare CdSe nanocrystals in the Debye (D) units as a function of number of atoms, N , in the nanocrystals at 300 K. The dipole moment of the SNP10 in vacuum is additionally shown in the plot as a blue point for the comparison.	143
5.2	Density contours of carbon pseudo-atoms of ligand tails for (a) GNP10, (b) GNP16, (c) SNP10, and (d) SNP16 in vacuum at 300 K. The density contours are shown in terms of pseudoatoms per $\text{\AA}^3$. The center of mass of inorganic core is taken as the origin, and the density profile is computed in terms of z-axis coordinate and cylindrical radial coordinate (r), and averaged over all azimuthal angles at a given point (z, r).	144
5.3	Density profiles of carbon pseudoatoms of ligand chains for (a) GNP10, (b) GNP16, (c) SNP10, and (d) SNP16 in hexane at 300 K.	145
5.4	Probability distribution, $P(\Delta^2)$, for GNP10, GNP16, SNP10, and SNP16 at the single particle level in (a) vacuum and (b) hexane at 300 K, where Δ^2 denotes the square of the magnitude of mass dipole connecting the geometric centers of core and ligand shell of nanoparticles.	146
5.5	Pair correlation function, $g_{ns}(r)$, of solvent monomers around GNP10, GNP16, SNP10, and SNP16 in hexane at 300 K. The $g_{ns}(r)$ is computed from the center of mass of inorganic core of nanoparticles. . . .	148

- 5.6 Two-body isotropic potential of mean force, $V_{PMF}(r)$, between two passivated nanoparticles as a function of pair separation, r . Plot (a) shows the comparison of V_{PMFs} for GNP10-GNP10, GNP10-SNP10, and SNP10-SNP10, and (b) for GNP10-SNP10 and GNP16-SNP16 pair interactions in vacuum and hexane at 300 K. The PMFs of nanoparticles in vacuum and hexane are distinguished in the plots by two color regions. Hamaker interactions of Au-Au, Au-CdSe, and CdSe-CdSe cores from the experiments [53, 94, 101, 106, 314, 383], and the PMF, $V_{core-core}$, of Au-CdSe cores computed from the simulation are shown using the dashed lines. 151
- 5.7 Schematic diagram illustrating the method for calculating the anisotropic parameters, $\vec{\Delta}$ and $\cos \theta$, in binary interaction of Au and CdSe nanoparticles. The snapshot is taken from molecular dynamics simulation of interaction between Au and CdSe nanoparticles passivated with the decanethiol and decylamine ligands respectively in vacuum at 300 K for the pair separation of 50 Å. Alkyl tails of ligands are shown in cyan, nitrogen and sulfur atoms in red, hydrogens of amine functional groups in green, gold core in yellow, cadmium in blue, and selenium atoms in orange colors. Mass dipole $\vec{\Delta}$ denotes the vector connecting the centers of mass of gold core (Au_{COM}) and the ligand shell ($Ligand_{COM}$), and θ tells its orientation with respect to the interparticle axis, $\vec{r}$ 153
- 5.8 Probability distribution, $P_r(\cos \theta)$, at different interparticle distances, r , for GNP10-GNP10 (a and a'), GNP10-SNP10 (b and b'), and SNP10-SNP10 (c and c') pair interactions in vacuum and hexane at 300 K, where θ is the orientation angle of mass dipole with respect to the interparticle axis, $\vec{r}$. The distribution of $\cos \theta$ for the other separations are not shown due to the clarity reason. 155

5.9	Emergent anisotropy as a function of interparticle separation, r , in the GNP10-GNP10, GNP10-SNP10, and SNP10-SNP10 pair interactions at 300 K. The mean square value of the magnitude of the mass dipole, $\langle \Delta^2 \rangle$, for vacuum and hexane are shown in (a) and (c), and mean value of $\cos \theta$, where θ is the angle between the mass dipole and interparticle axis, are shown in (b) and (d) respectively.	156
5.10	Angular potentials, $V_{PMF}(r, \cos \theta)$, at different pair separations, r , in the interaction of GNP10 and SNP10 in (a) vacuum and (b) hexane at 300 K.	158
5.11	Simulation snapshots of GNP16-SNP16 pair at different separations, r , in vacuum and hexane at 300 K. The color coding of atoms is same as used in Fig. 5.7. Hexane molecules are not shown for clarity. . . .	159

List of Tables

2.1	12-6 Lennard-Jones parameters of non-bonded interactions for alkanethiol passivated gold nanoparticles in ethane solvent.	63
2.2	Parameters for bonded interactions of alkanethiol ligands and solvents. Intermolecular bonds in thiol ligand are modeled using harmonic stretching potential; $U(r) = (1/2k_r)(r - r_0)^2$, where k_r is the force constant and r_0 is the equilibrium bond length. Bond angles are modeled using harmonic bending potential; $U(\theta) = (1/2k_\theta)(\theta - \theta_0)^2$ where, k_θ is the force constant and θ_0 is the equilibrium bond angle. The triple cosine potential is used for 1-4 torsional interactions given by: $U(\phi) = 1/2A_1(1 + \cos(\phi)) + 1/2A_2(1 - \cos(2\phi)) + 1/2A_3(1 + \cos(3\phi))$, where A_1 , A_2 , and A_3 are constants. The gold-thiol interaction is modeled using the switched and shifted version (at 6.2 Å) of pairwise additive m - n potential; $U(r_{ij}) = (E_0/(n - m))(m(r_0/r_{ij})^n - n(r_0/r_{ij})^m)$, where E_0 is the well depth, r_0 is the equilibrium distance, m and n are constants.	64
2.3	Radius of gyration (R_g) of methylene (CH_2) monomers of passivating decanethiol chains from the center of mass of the gold core, and ligand configurational entropy per (CH_x/SH) atom (S_L) of the $\text{Au}_{38}(\text{SC}_{10})_{24}$ nanoparticle at different densities in ethane and propane solvent along the isotherm, $T_r = 1.02$, where ρ and ρ_r denote the densities of fluids in real and reduced units, respectively.	69

2.4	Radius of gyration (R_g) of methylene (CH_2) monomers of passivating decanethiol chains from the center of mass of gold core, and ligand configurational entropy per (CH_x/SH) atom (S_L) of the $\text{Au}_{140}(\text{SC}_{10})_{62}$ nanoparticle at different reduced densities (ρ/ρ_c) in ethane along the isotherms, $T_r = 1.02$ and 1.15	70
2.5	Solvation properties of the Au_{140} nanoparticle with different chain lengths (n) of alkanethiol ligands at critical density, and reduced temperature, $T/T_c = 1.02$ in ethane. The radius of gyration (R_g) of methylene (CH_2) groups of passivating chains from the center of mass of gold core, entropy of ligand shell (S_L), pair entropy due to local ordering of solvent molecules (ΔS_{ns}^{loc}), total pair entropy (ΔS_{ns}^{tot}) including the long range correction terms, average solute-solvent interaction energy (ΔU_{ns}), solvation free energy (ΔA_{ns}), solvent excess (n_s^E), and partial molar volume ($\bar{v}_n^\infty$) are specified. Note that n denotes the number of carbon atoms in the passivating thiol chains. . .	80
2.6	Solvation properties of the Au_{38} nanoparticle with varying surface coverages of decanethiol ligands at critical density, and temperature, $T/T_c = 1.02$ in ethane. The radius of gyration (R_g) of methylene (CH_2) groups of passivating chains from the center of mass of gold core, entropy of ligand shell (S_L), pair entropy due to local ordering of solvent molecules (ΔS_{ns}^{loc}), total pair entropy (ΔS_{ns}^{tot}) including the long range correction terms, average solute-solvent interaction energy (ΔU_{ns}), solvation free energy (ΔA_{ns}), solvent excess (n_s^E), and partial molar volume ($\bar{v}_n^\infty$) are noted.	84

3.1	A summary of fitting parameters for V_{PMF} curves of $\text{Au}_{38}(\text{SC}_{10})_{24}$ nanoparticles at different temperatures along the given isochore. The V_{PMFs} curves in vacuum and in solvent for a density, $\rho_r = 1.0$, are fitted to a Morse function, $D_e((1 - \exp(-a(r - r_e)))^2 - 1)$ with $a = \alpha/r_e$, where D_e denotes the energy well depth and r_e represents the equilibrium pair separation. The V_{PMF} curves at density, $\rho_r = 3.0$ are fitted to a exponential function, $B \exp(-b(r - r_d))$ with $b = \beta/r_d$. The constants, α and the β are the dimensionless range parameters. .	98
3.2	Fitting parameters for pair V_{PMF} curves of two-body and three-body systems at different densities along isotherm $T_r = 1.02$ for $\text{Au}_{38}(\text{SC}_{10})_{24}$ and $\text{Au}_{140}(\text{SC}_{10})_{62}$ nanoparticles. The V_{PMF} curves for densities $\rho_r \leq 1.0$ are fitted with Morse function, $D_e((1 - \exp(-a(r - r_e)))^2 - 1)$, whereas the V_{PMF} curves for density, $\rho_r = 3.0$, are fitted to a functional form, $B \exp(-b(r - r_d))$. The physical meaning of parameters of both fitting functions have been explained in the caption of Table 3.1.	100
4.1	Bulk properties of the alkane solvents along the experimental liquid-vapour coexistence curve [330]. The critical parameters for an alkane, C_n , are denoted by P_c , T_c and ρ_c . At a common reduced vapour pressure of $P/P_c = 7.45 \times 10^{-5}$, the liquid-vapour coexistence temperatures (T) of alkanes are noted. The vapour pressure (P_{liq}), mass densities of liquid (ρ_{liq}) and vapour phase (ρ_{vap}), and monomer density of the liquid phase (ρ_m) of alkanes at their respective temperature (T) are specified in last four columns.	113

4.2	Bulk properties of n-alkane solvents along the liquid-vapour coexistence curve from simulation using the TraPPE-UA potential. At common reduced monomer density, $\rho_m^* = 1.85$, temperatures (T), pressures (P_{liq}) and mass densities (ρ_{liq}) of alkanes in NVT condition are noted. The isothermal compressibilities (κ_T) are derived from NPT simulations. The correlation coefficient (R) and inverse power law (γ_{UW}) coefficients at the given state point are reported. The dimensionless quantities shown here are based on TraPPE Lennard-Jones parameters for length ($\sigma = 3.95$ Å) and energy ($\epsilon = 0.3825$ kJ mol ⁻¹) of methylene (CH ₂) monomer of alkane solvents.	119
4.3	Structural, thermodynamic, and transport properties of n-alkanes at common reduced monomer density, $\rho_m^* = 1.85$. The pair entropies, S_2^{all} and S_2 are calculated with and without taking the bond, angle and dihedral contributions respectively (see figure 3). The diffusivity, D is calculated from the mean square displacements of alkane monomers using the Einstein diffusion equation [196]. The dimensionless diffusivity, D^* is obtained using the formula: $D^* = D\rho_m^{1/3}/(k_B T/m)^{1/2}$ where ρ_m , k_B , and m denote the monomer density, Boltzmann constant, and mass of the CH ₂ monomer of alkane solvent. The variable $(\rho_m^*)^{\gamma_{UW}}/T^*$ uses the monomer density of solvent and temperature in reduced unit.	121
4.4	Solvation properties of single nanoparticle at constant reduced monomer density of n-alkane solvents. The partial molar volume of nanoparticle, $\bar{v}_n^\infty$ is calculated using the pair correlation function, $g_{ns}(r)$ in NVT simulation and reported for two different integration cutoff of 40 Å and 50 Å. The solvent excess, n_s^E , the entropic contribution due to local ordering of solvent, ΔS_{ns}^{loc} and total entropy solvation, ΔS_{ns}^{tot} as sum of local and long range correction terms are shown for solvents of varying chain length.	124

4.5	The summary of fitting parameters for V_{PMF} curves in vacuum and solvent. The V_{PMFs} in vacuum are fitted to a Morse function, $D_e((1 - \exp(-a(r - r_e)))^2 - 1)$ with, $a = \alpha/r_e$ where D_e measures the well depth at equilibrium pair separation, r_e . The V_{PMFs} in solvent are fitted to a functional form, $B \exp(-b(r - r_d))$ with, $b = \beta/r_d$. Here, α and β both denote dimensionless range parameters.	128
5.1	Non-bonded (12-6 LJ and coulomb) interaction parameters for gold and CdSe nanoparticles in vacuum and n -hexane.	137
5.2	Parameters of bonded interactions for passivating ligands (alkanethiols and alkylamines) and hexane solvent. Inter-molecular bonds are modeled using the harmonic stretching potential; $U(r) = (1/2k_r)(r - r_0)^2$, where k_r is the force constant and r_0 is the equilibrium bond length. Bond angles are modeled using the harmonic bending potential; $U(\theta) = (1/2k_\theta)(\theta - \theta_0)^2$, where k_θ is the force constant and θ_0 is the equilibrium bond angle. Torsional interactions are modeled using one of a set of cosine series potential given by; $U(\phi) = a_0 + \sum_{i=1}^6 a_i \cos(i\phi)$, and $U(\phi) = 1/2A_1(1 + \cos(\phi)) + 1/2A_2(1 - \cos(2\phi)) + 1/2A_3(1 + \cos(3\phi))$, where a_0 , a_i , A_1 , A_2 , A_3 are constants and ϕ is the current dihedral angle. The gold-sulfur interaction is modeled using the pair additive Morse potential; $U(r) = D_e((1 - \exp(-k(r - r_e)))^2 - 1)$, where r_e is the equilibrium distance, D_e is the well depth, and k controls the width of the potential.	138
5.3	Initial diameter (d_0), radius of gyration (R_g), asphericity (A_s), and the binding energy (U_B) of single hexylamine ligand of thermally relaxed CdSe nanocrystals at 300 K.	142

5.4	Structural and thermodynamic quantities of solvation of single passivated Au ₁₄₀ and CdSe nanoparticles in hexane at 300 K. The S_L^0 and S_L^h denote the configurational entropy of ligand shell per CH _x /SH group in vacuum and hexane respectively. The difference of S_L^h and S_L^0 is noted as ΔS_L , represents change in the ligand shell entropy on solvation. The solvent excess, n_s^E , partial molar volume, $\bar{v}_n^\infty$, pair entropy due to local ordering of solvent, ΔS_{ns}^{loc} , and the total pair entropy, ΔS_{ns}^{tot} , as sum of the local and long range correction terms are reported at the integration cutoff of 50 Å.	147
5.5	Fitting parameters for isotropic pair V_{PMF} curves of gold (Au ₁₄₀) and semiconductor (CdSe) nanoparticles with the ligand chain length of 10 and 16 carbon atoms in vacuum and hexane at 300 K. The pair PMFs in vacuum are fitted to a Morse function, $D_e((1 - \exp(-a(r - r_e)))^2 - 1)$, where $a = \alpha/r_e$, and D_e denotes the free energy well depth at the equilibrium pair separation, r_e . The PMFs in hexane are fitted to a functional form, $B \exp(-b(r - r_d))$, where $b = \beta/r_d$, B is the pre-exponential factor, and r_d is the pair separation. Both the α and β are the dimensionless range parameters.	152