On the Enhancement of Thermal Properties of Graphene Nanofluids

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... the work of:

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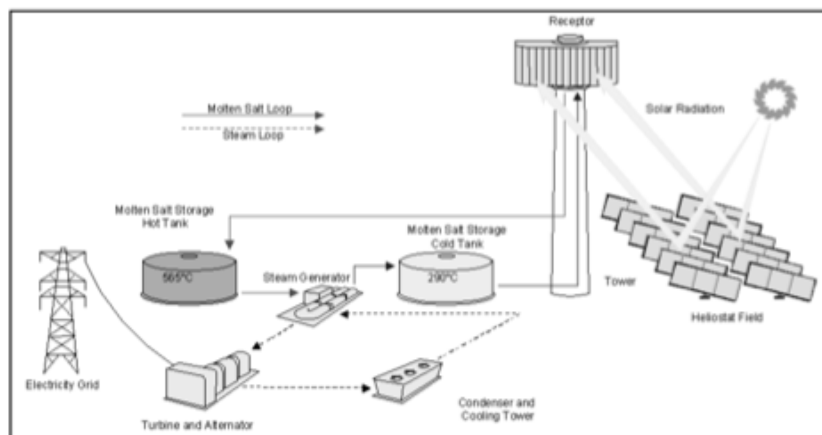
MaX Pilot: Thermal Fluids

<u>Molten salts:</u>

- Heat storage and transport médium
- Allow electric energy generation in the absence of sunlight (with heat stored during daylight)
- Carbonates (M_2CO_3), Chlorides (MCl, MCl_2); Nitrates (MNO_3), and mixtures
- Melting: ~200ºC
- Operation: ~500ºC
- High heat capacity



Nanoparticles to improve the thermal properties of molten salts

Nanoscale Research Letters 2014, **9**:582

NANO EXPRESS **Open Access**

Increment of specific heat capacity of solar salt with SiO_2 nanoparticles

Patricia Andreu-Cabedo[1], Rosa Mondragon[1], Leonor Hernandez[1], Raul Martinez-Cuenca[1], Luis Cabedo[2] and J Enrique Julia[1*]

Acta Materialia 75 (2014) 80–91

Enhanced specific heat capacity of molten salt-based nanomaterials: Effects of nanoparticle dispersion and solvent material

Byeongnam Jo[a,b,*], Debjyoti Banerjee[b]

- Nanofluid: nanoparticles dispersed in the fluid
- High heat capacity increase (reports of up to 100%)
- Accurate quantification?

Table 1 Summary of the previous published works and present work in salt-based nanofluids

Authors	Year	Salt composition	Nanoparticles	Preparation method	Results	Ref
Shin and Banerjee	2011	Li_2CO_3 (62%) + K_2CO_3 (38%)	SiO_2 (10 nm), 1% wt.	Salt + water (1:100) Nanoparticle dispersion in ultrasonic bath (100 min). Drying in hot plate (200°C)	C_p: +19% to +24%	[10]
Shin and Banerjee	2011	$BaCl_2$ (34%) + NaCl (13%) + $CaCl_2$ (40%) + LiCl (13%)	SiO_2, 1% wt.	Salt + water (1:100) Nanoparticle dispersion in ultrasonic bath (100 min). Drying in hot plate (200°C)	C_p: +14.5%	[16]
Lu and Huang	2013	$NaNO_3$ (60%) + KNO_3 (40%)	Al_2O_3 (13 nm, 90 nm), 0.9% to 4.6% wt.	Salt + water (1:100) Nanoparticle dispersion in ultrasonic bath (100 min). Drying in hot plate (105°C)	C_p: −10%, 4.6% wt.	[17]
Tiznobaik and Shin	2013	Li_2CO_3 (62%) + K_2CO_3 (38%)	SiO_2 (5 to 60 nm), 1% wt.	Salt + water (1:100) Nanoparticle dispersion in ultrasonic bath (100 min). Drying in hot plate (200°C)	C_p: +23% to +29%	[11]
Tiznobaik and Shin	2013	Li_2CO_3 (62%) + K_2CO_3 (38%)	SiO_2 (10 nm), 1% wt.	Salt + water (1:100) Nanoparticle dispersion in ultrasonic bath (100 min). Drying in hot plate (200°C)	C_p: +26% C_p: +3% (addition NaOH)	[12]
Shin and Banarjee	2013	Li_2CO_3 (62%) + K_2CO_3 (38%)	SiO_2 (2 to 20 nm), 1% wt.	Salt + water (1:100) Nanoparticle dispersion in ultrasonic bath (100 min). Drying in hot plate (100°C)	Segregation C_p: +124% (zone A) C_p: +0% (zone B)	[13]
Dudda and Shin	2013	$NaNO_3$ (60%) + KNO_3 (40%)	SiO_2 (5 nm, 10 nm, 30 nm, 60 nm), 1% wt.	Salt + water (1:100) Nanoparticle dispersion in ultrasonic bath (100 min). Drying in hot plate (200°C)	C_p: +10% (5 nm) +13% (10 nm), +21% (30 nm), +28% (60 nm)	[18]
Chieruzzi et al.	2013	$NaNO_3$ (60%) + KNO_3 (40%)	SiO_2 (7 nm), Al_2O_3 (13 nm), TiO_2 (20 nm), SiO_2 + Al_2O_3(2 to 200 nm), 0.5% to 1.5% wt.	Salt + water (1:100) Nanoparticle dispersion in ultrasonic bath (100 min). Drying in hot plate (200°C)	C_p: +22.5% (SiO_2 + Al_2O_3 (2 to 200 nm 1.0% wt.)) H: +15% (all np except TiO_2, 1% wt.)	[19]
Jo and Banarjee	2014	Li_2CO_3 (62%) + K_2CO_3 (38%)	Graphite (50 nm) + gum arabic	Salt + water (1:100) Nanoparticle dispersion in ultrasonic bath (120 min). Drying in hot plate (200°C)	Segregation C_p: +100% (material 1) C_p: +33% (material 2)	[14]
Shin and Banarjee	2014	Li_2CO_3 (62%) + K_2CO_3 (38%)	Al_2O_3 (10 nm), 1% wt.	Salt + water (1:100) Nanoparticle dispersion in ultrasonic bath (120 min). Drying in hot plate (100°C)	C_p:+32%	[15]
Ho and Pan	2014	$NaNO_3$ (7%) + KNO_3 (53%) + $NaNO_2$ (40%)	Al_2O_3 (<50 nm), 0.016% to 1% wt.	Salt + nanoparticle aqueous suspension (20% wt.) Nanoparticle dispersion by mechanic stirring at high temperature (180 min.)	C_p: +19.9% (0.063% wt.)	[20]
Present work		$NaNO_3$ (60%) + KNO_3 (40%)	SiO_2 (12 nm), 0.5% to 2.0% wt.	Salt + water (1:10) Nanoparticle dispersion in ultrasonic probe (5 min). Drying in hot plate (100°C)	C_p: +25% (1.0% wt.)	

Andreu-Cabedo *et al. Nanoscale Research Letters* 2014, **9**:582

Nanoparticles to improve the thermal properties of molten salts

ABENGOA RESEARCH

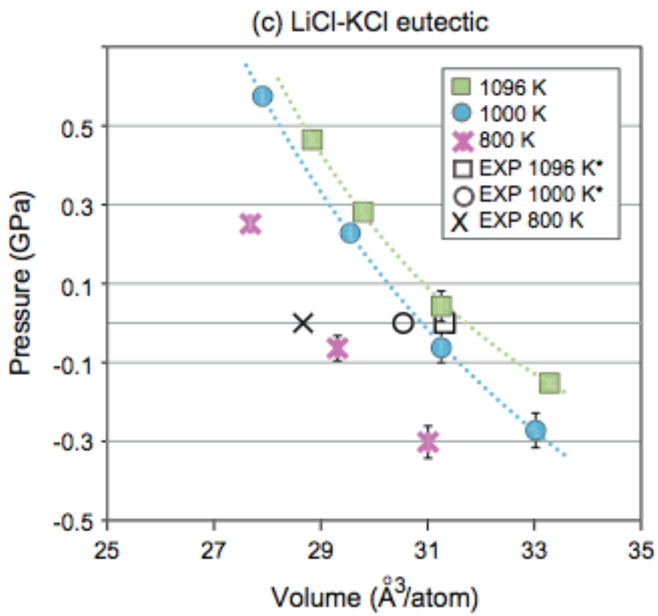
Nanofluids to improve the thermal properties of molten salts

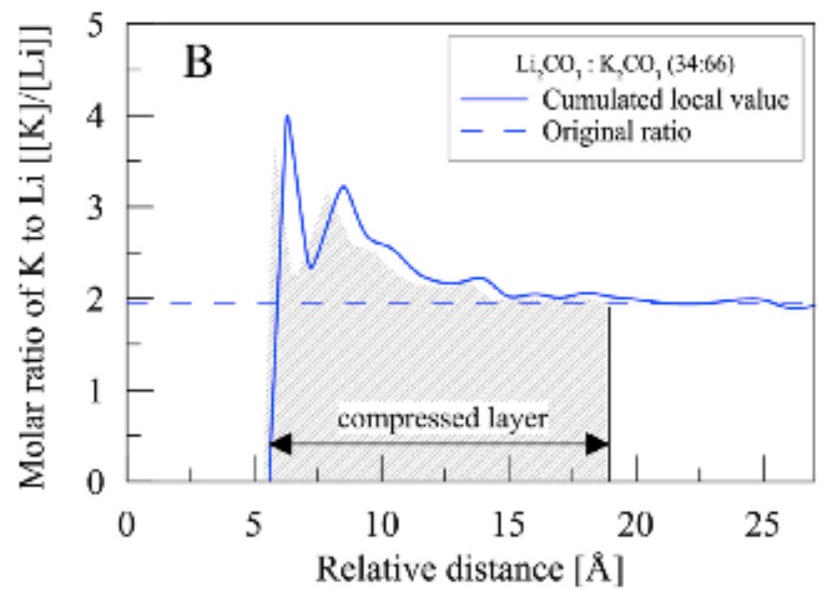
- Nanofluid: nanoparticles dispersed in the fluid
- High heat capacity increase (reports of up to 100%)
- Accurate quantification ?
- Understanding mechanism for increase in heat capacity and other thermal properties

Can we understand and (eventually) predict the thermal properties of liquids with simulation?

- Atomistic simulations provide information about the **structure and thermodynamical properties** of the molten salts, as a function of composition. [Computational Materials Science 83, 362 (2014)]

- They also provide **understanding of the interaction of the molten salt with the embedded Nanoparticles**, and how these affect the structure and properties of the liquid. [Acta Materialia 75, 80 (2014)]





MaX Pilot Target

To elaborate **computational protocols** for the determination of the key **thermal parameters of nanofluids**, to predict and explain the **modification of these properties by the addition of nanoparticles**

Forbes / Energy

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Spain's Renewable Energy Powerhouse Abengoa Teeters Toward Bankruptcy

BUSINESS

Abengoa on verge of largest bankruptcy filing in Spanish history

- The renewable energy and engineering company has filed for creditor protection

EL PAÍS / BLOOMBERG | Madrid | 26 NOV 2015 - 17:14 CET

Abengoa's solar plant in Sanlúcar La Mayor (Seville). / EFE

≡ EL PAÍS Sevilla - 4 MAR 2017 - 15:46 CET ECONOMÍA

MERCADOS MIS AHORROS VIVIENDA MIS DERECHOS FORMACIÓN TITULARES » Retina CincoDías NEGOCIOS

Desmantelado el mayor laboratorio privado de energías renovables

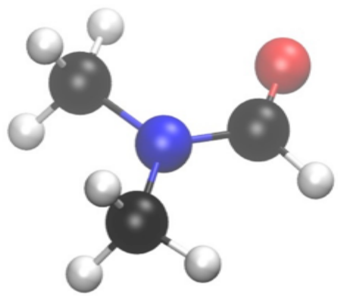
Abengoa Research desaparece con un equipo de 150 investigadores para tecnología puntera

Carlos Sanz-Navarro,
~~Abengoa Resarch.~~

Heat Transfer Fluids

- Room temperature applications - Cooling and termal management
- Graphene nanofluids – very large effect on thermal properties
- Large literature on Graphene nanofluids
- Experimental work at ICN2 (preparation and thermal properties)

DMF: Dimethylformamide



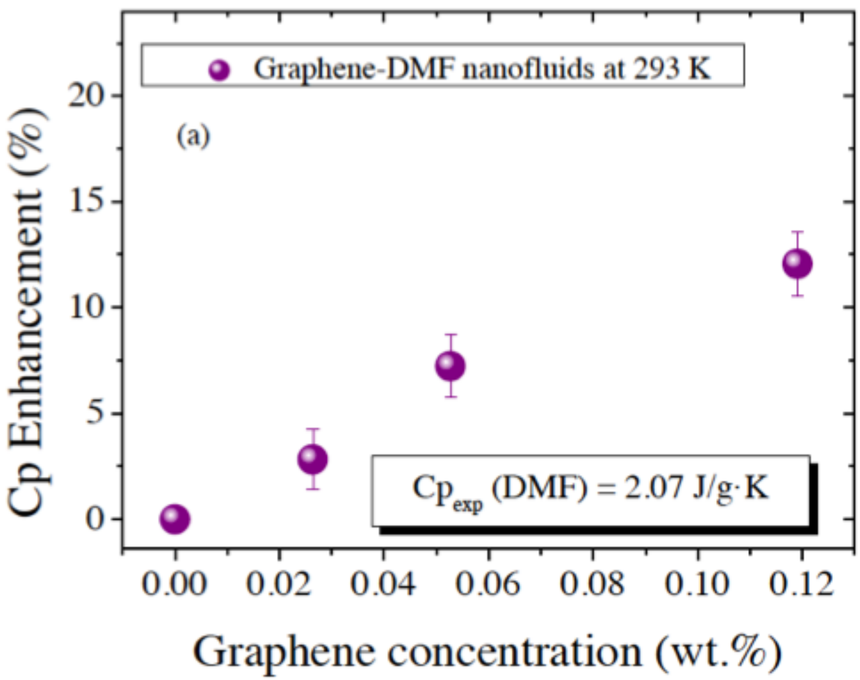
Organic solvent for Graphite Nanoflakes
currently used by P. Gómez (ICN2)

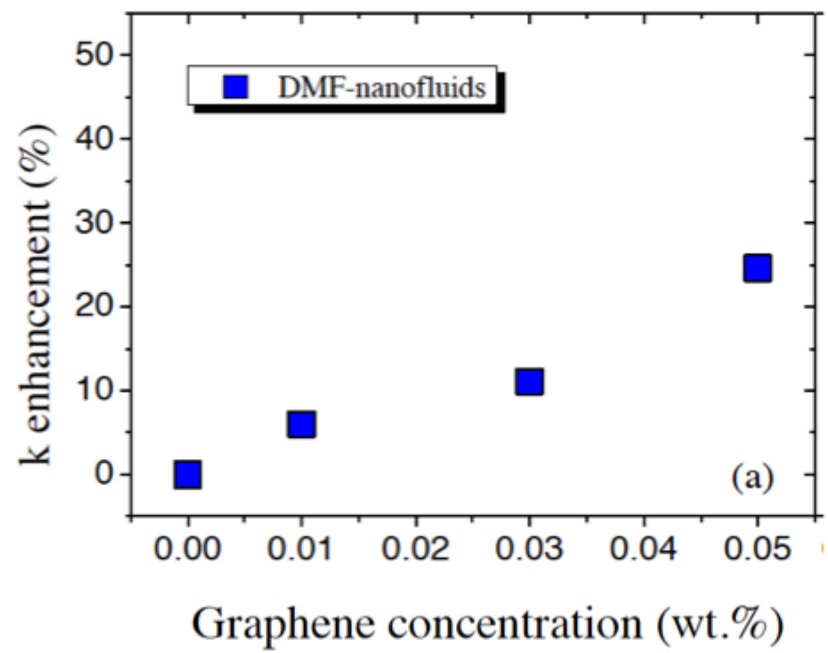
Very stable dispersions - low concentration of NFs: 0 - 0.05 wt %

NFs: 100 – 400 nm diameter;   1-10 layers

Experimental Results

Thermal properties: Specific Heat and Thermal Conductivity

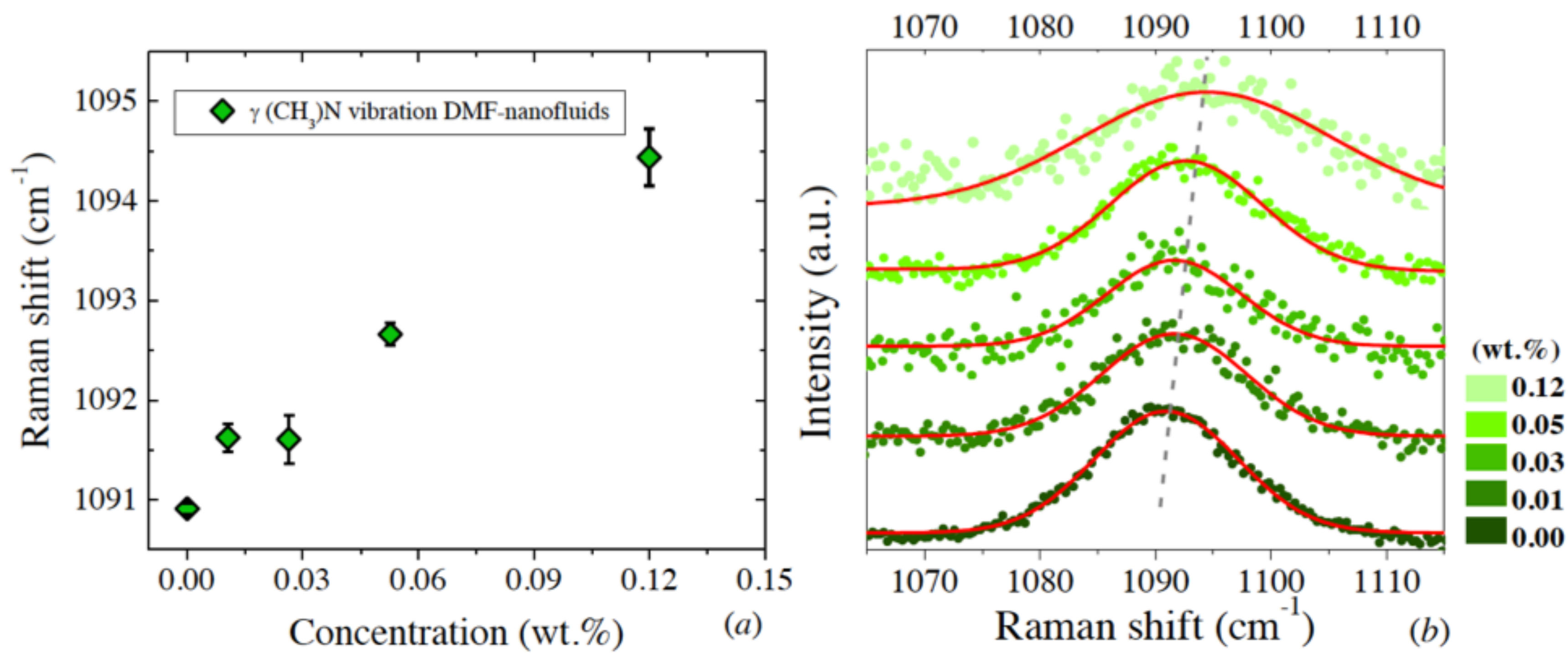




Experiments: R. Rodriguez, E. Chavez, P. Gomez, C. Sotomayor – ICN2

Experimental Results

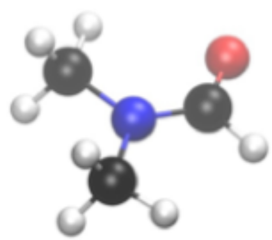
Raman spectra - DMF modes

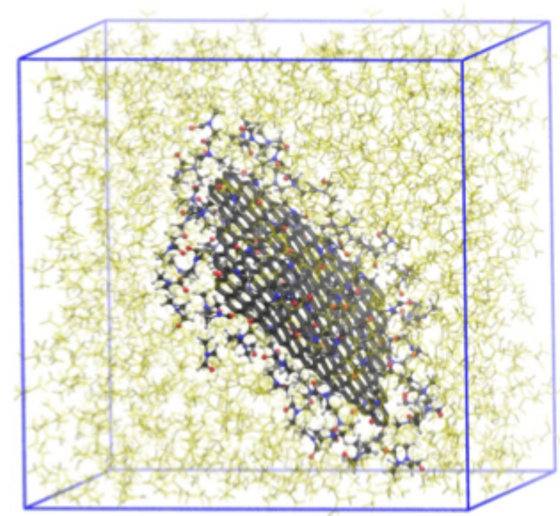


Experiments: R. Rodriguez, E. Chavez, P. Gomez, C. Sotomayor – ICN2

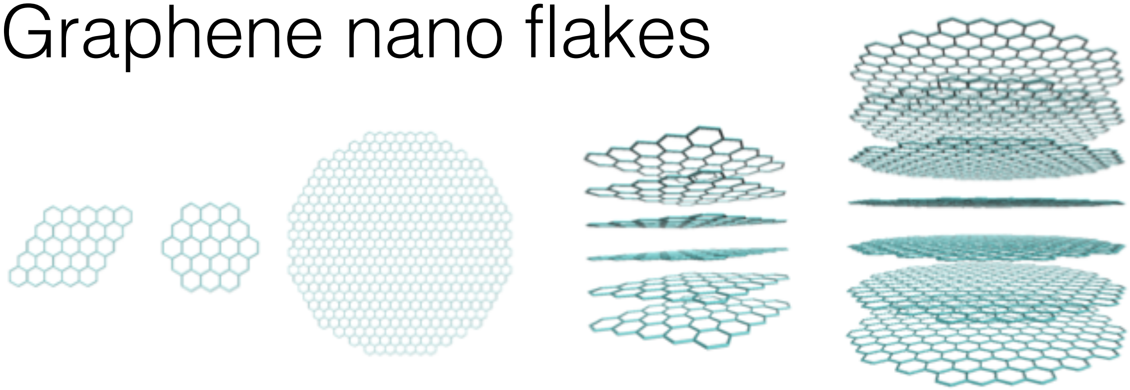
Nanofluid: Graphene flakes in DMF

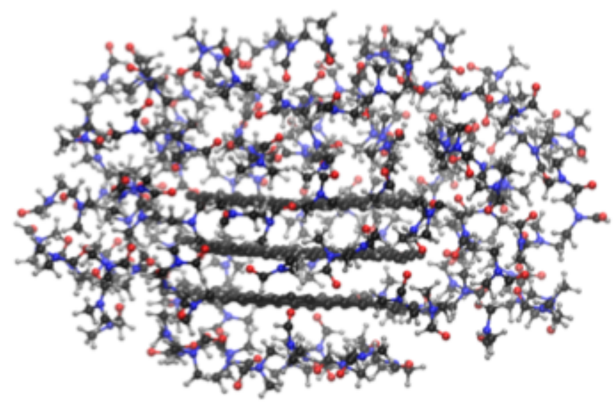
- MD simulation
- LAMMPS;   GAFF/OPLS force fields
- Equibration; NVT; NPT



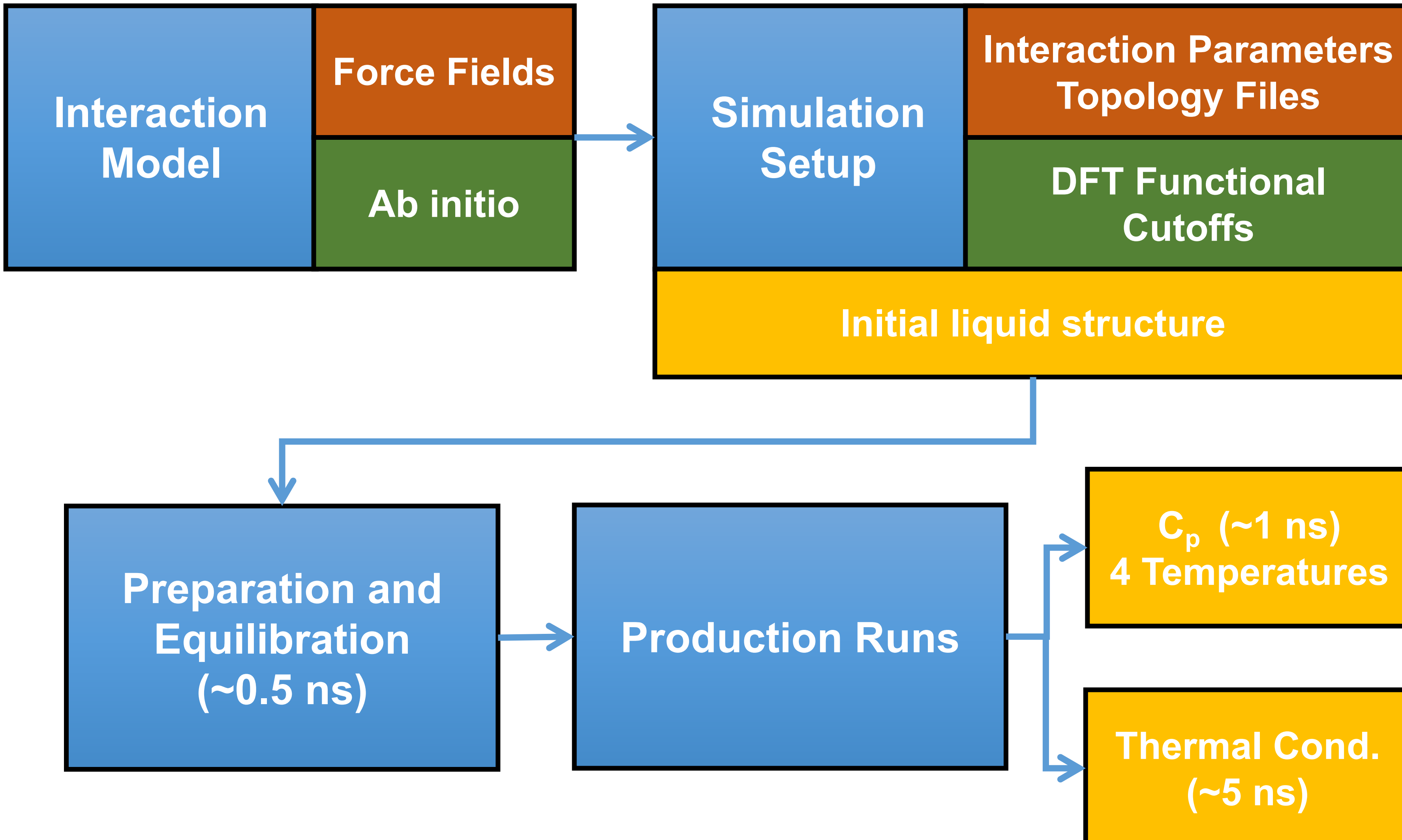


Graphene nano flakes

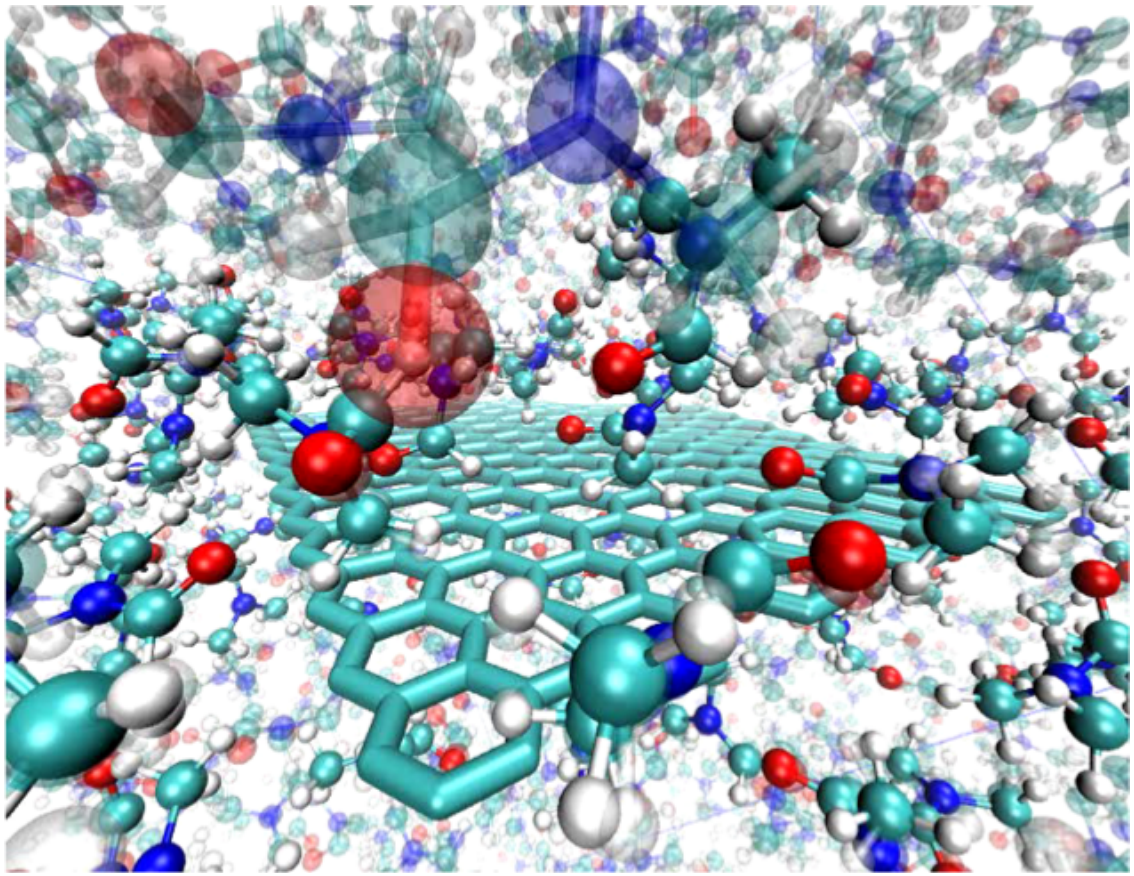




Workflows


Interaction Model
Force Fields
Ab initio
Simulation Setup
Interaction Parameters
Topology Files
DFT Functional
Cutoffs
Initial liquid structure
Preparation and Equilibration (~0.5 ns)
Production Runs
C_p (~1 ns)
4 Temperatures
Thermal Cond.
(~5 ns)

DMF with Graphene NPs

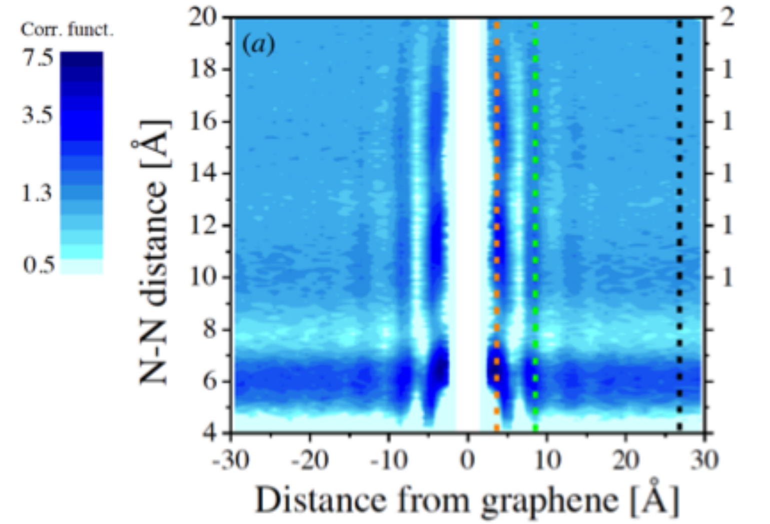


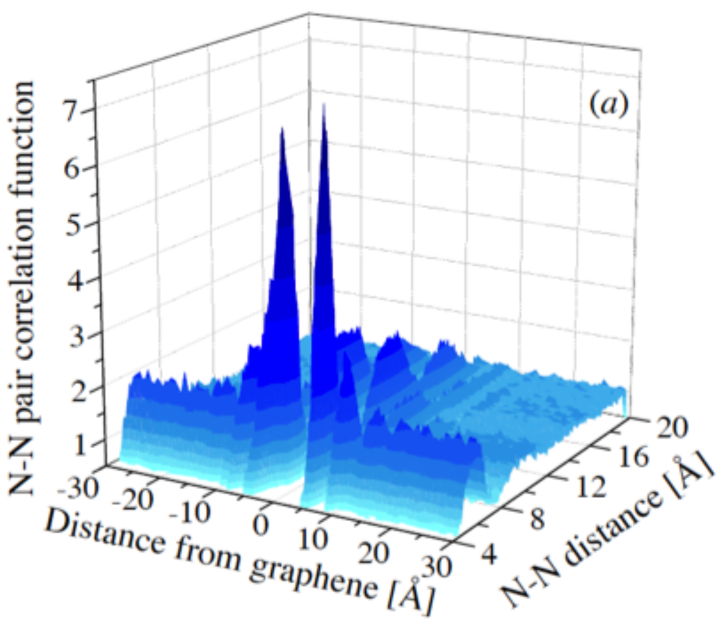
6 ps movie
(out of a 1 ns simulation)

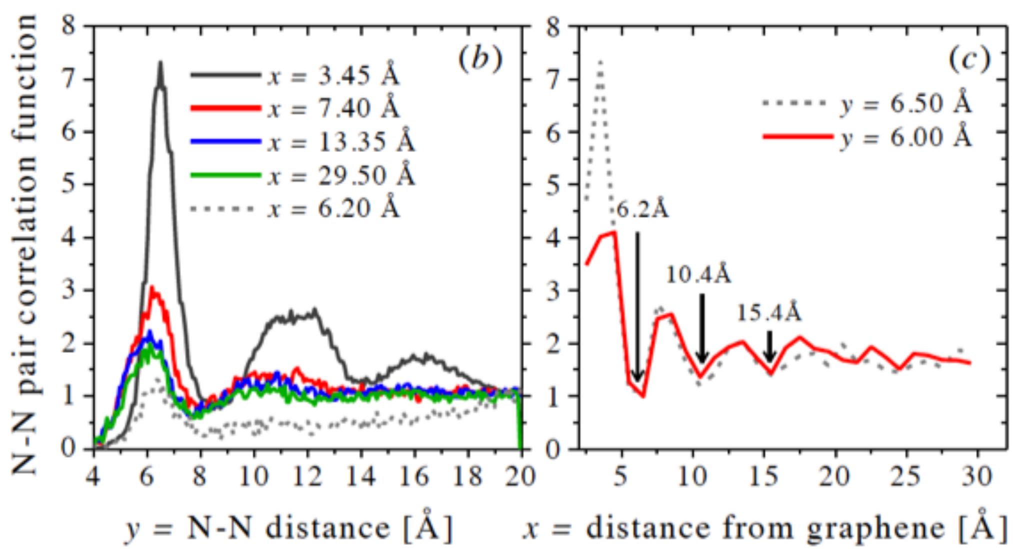
Layering of DMF on graphene flake

Radial distribution in the plane as a function of the height abov

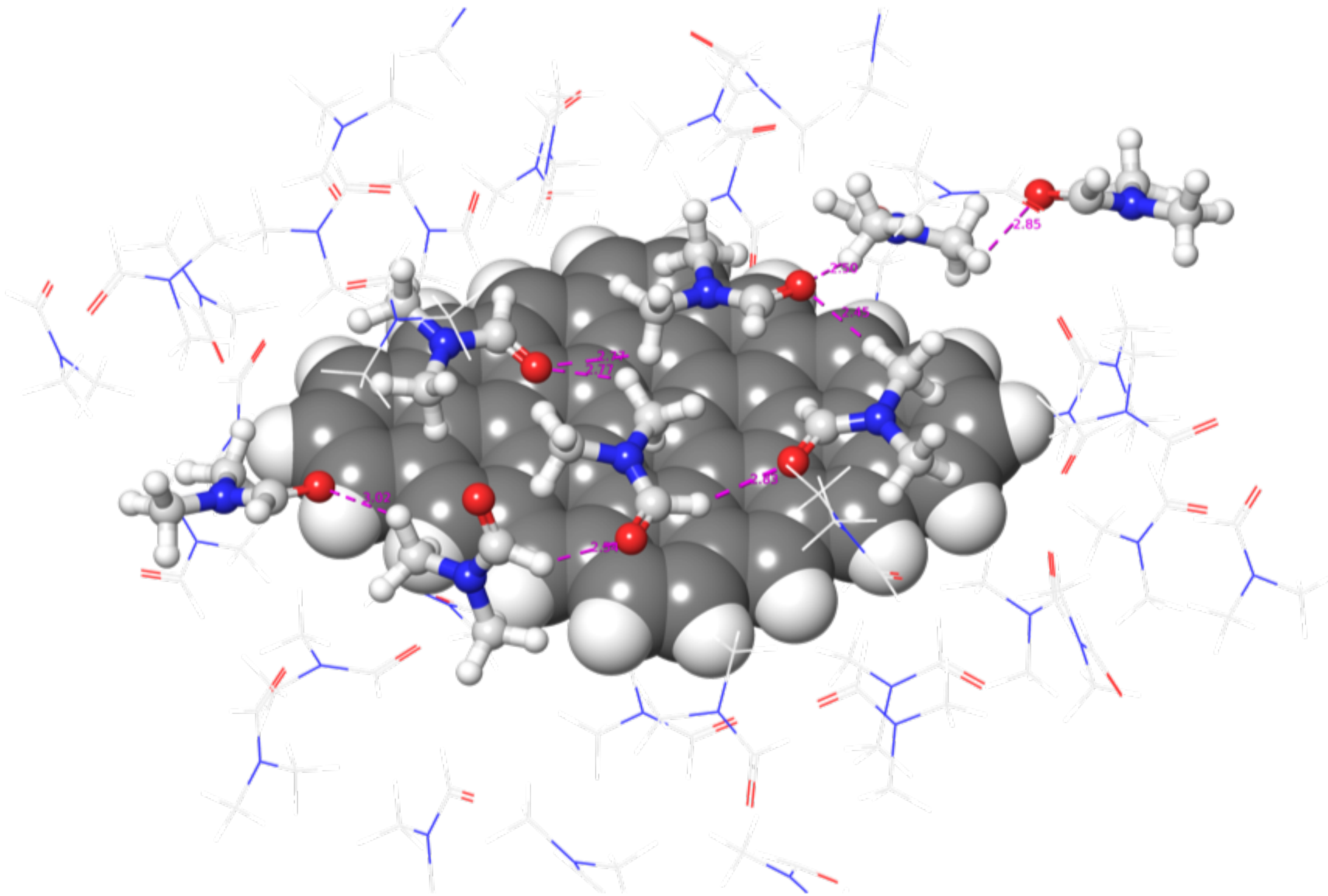
- there is strong layering observed
- in the first layer, the DMF is mainly lying flat on the grap
- 3 coordination shells can be seen around a DMF molecu layer (could be more on larger flakes)
- 3 layers can be observed onto the surface





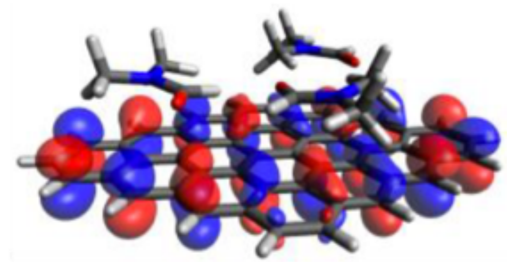


Layering of DMF on graphene flake

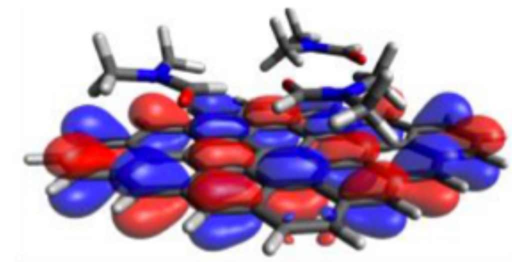


π-stacking

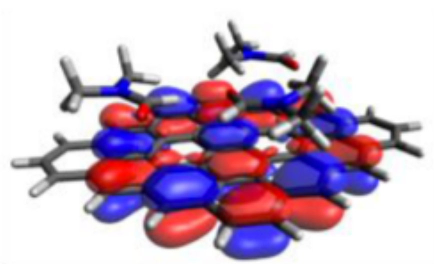
DFT Calculations



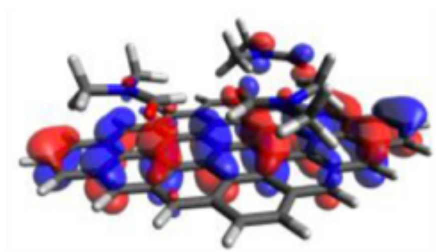
LUMO



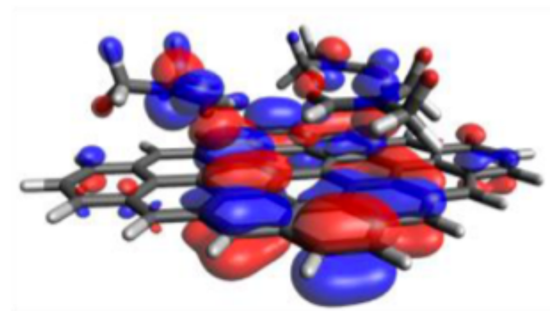
HOMO (0.13)



HOMO-1 (0.17)



HOMO-2 (0.21)



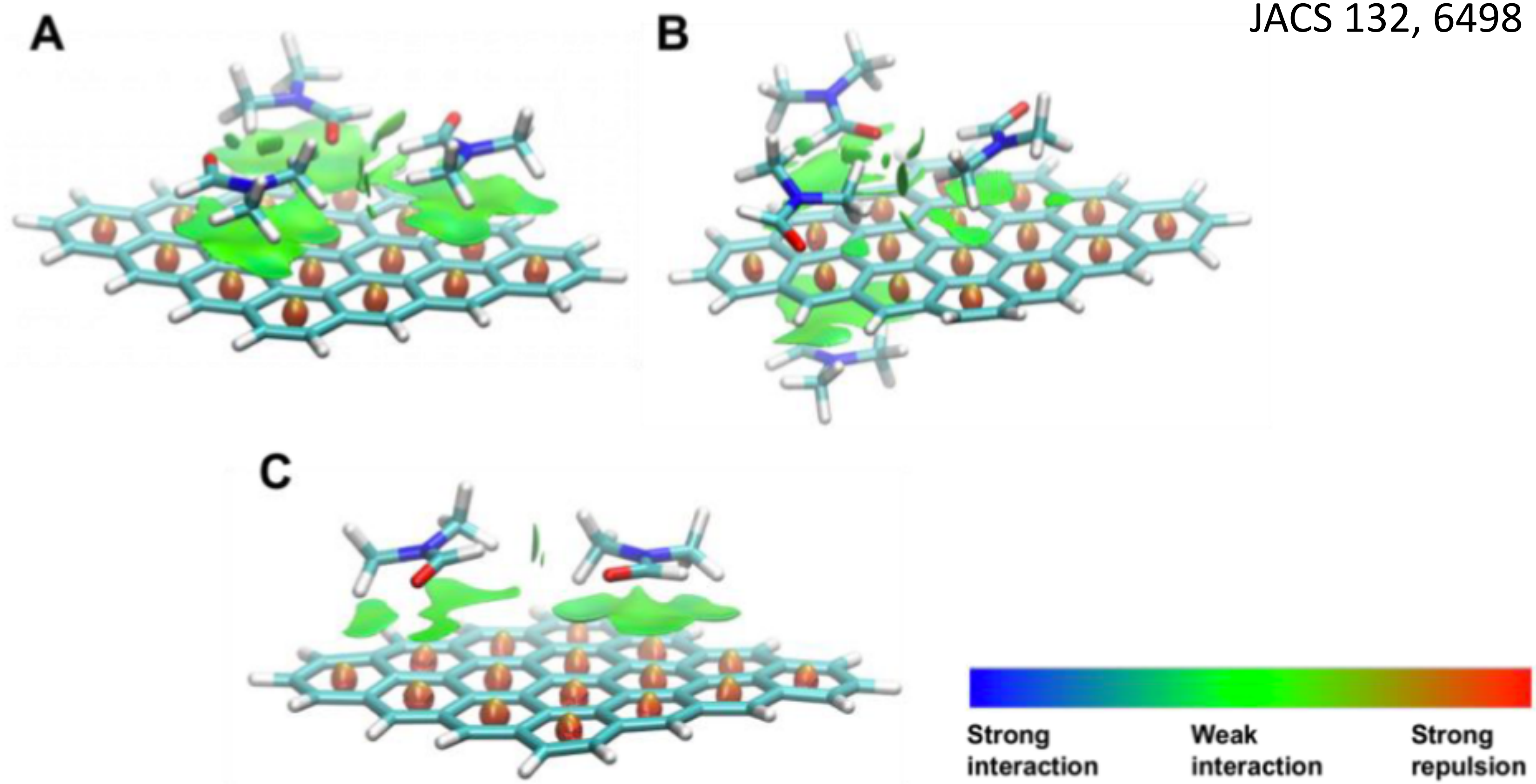
HOMO-3 (0.22)

π-stacking

DFT Calculations

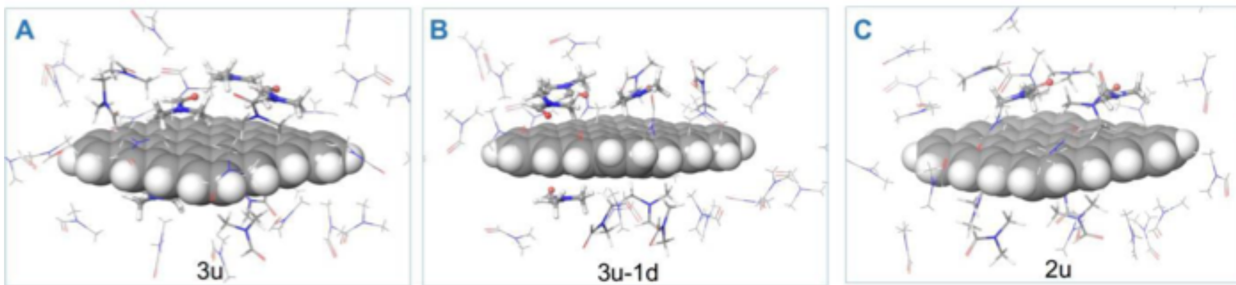
Reduced Density Gradient

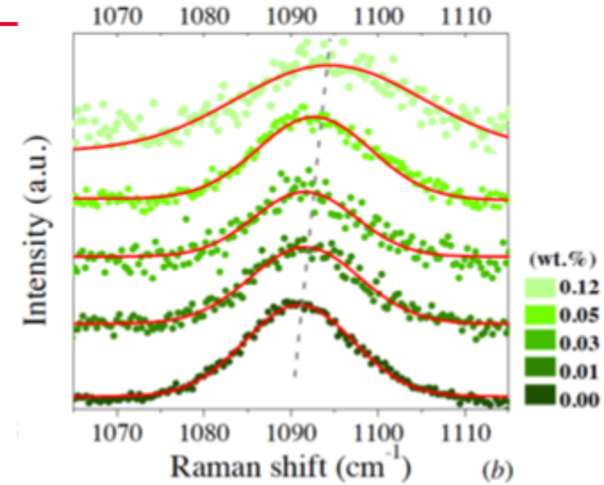
Johnson, Keinan, Mori, Contreras, Cohen and Yang
JACS 132, 6498 (2010)



Raman shifts

DFT Calculations





Experimental frequencies [cm^{-1}]		Theoretical frequencies [cm^{-1}] B3LYP/6-311G(d, p)			
DMF	**0.05 wt %**	**DMF**	**A**	**B**	**C**
1090.9	1092.6	1092.9	1096.3	1113.0	1094.2
1438.5	1439.8	1430.7	1443.7	1442.5	1440.3

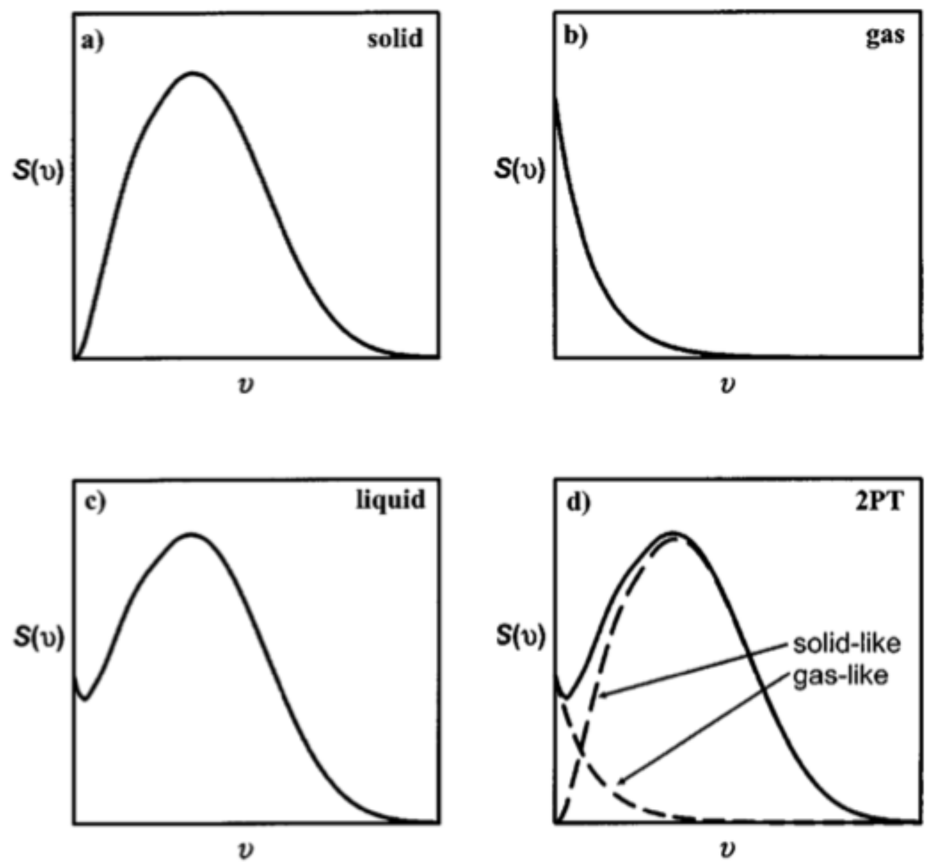
Specific Heat in liquids

Vibrational Density of States

$$S(\upsilon)=\frac{2}{kT}\lim_{\tau\to\infty}\int_{-\tau}^{\tau}C(t)e^{-i2\pi\upsilon t}dt.$$

$$C(t) = < v(t)v(0) >$$

- Solid: quasiharmonic approximation (quantum effects)
- Gas: diffusion and anharmonicity

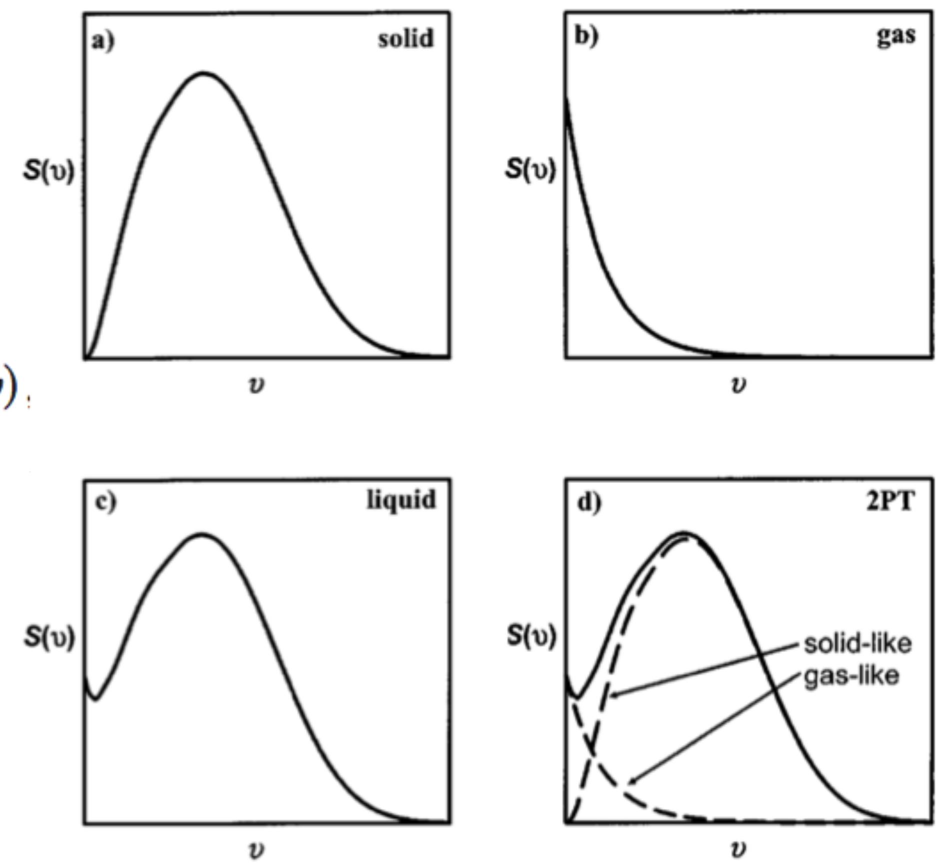


Specific Heat in liquids

Two Phase Thermodinamic Model (2PT)
(Lin, Blanco and Goddard, JCP 2003)

$$P = \int_0^\infty d\upsilon S^s(\upsilon) W_P^{\mathrm{HO}}(\upsilon) + \int_0^\infty d\upsilon S^g(\upsilon) W_P^g(\upsilon),$$

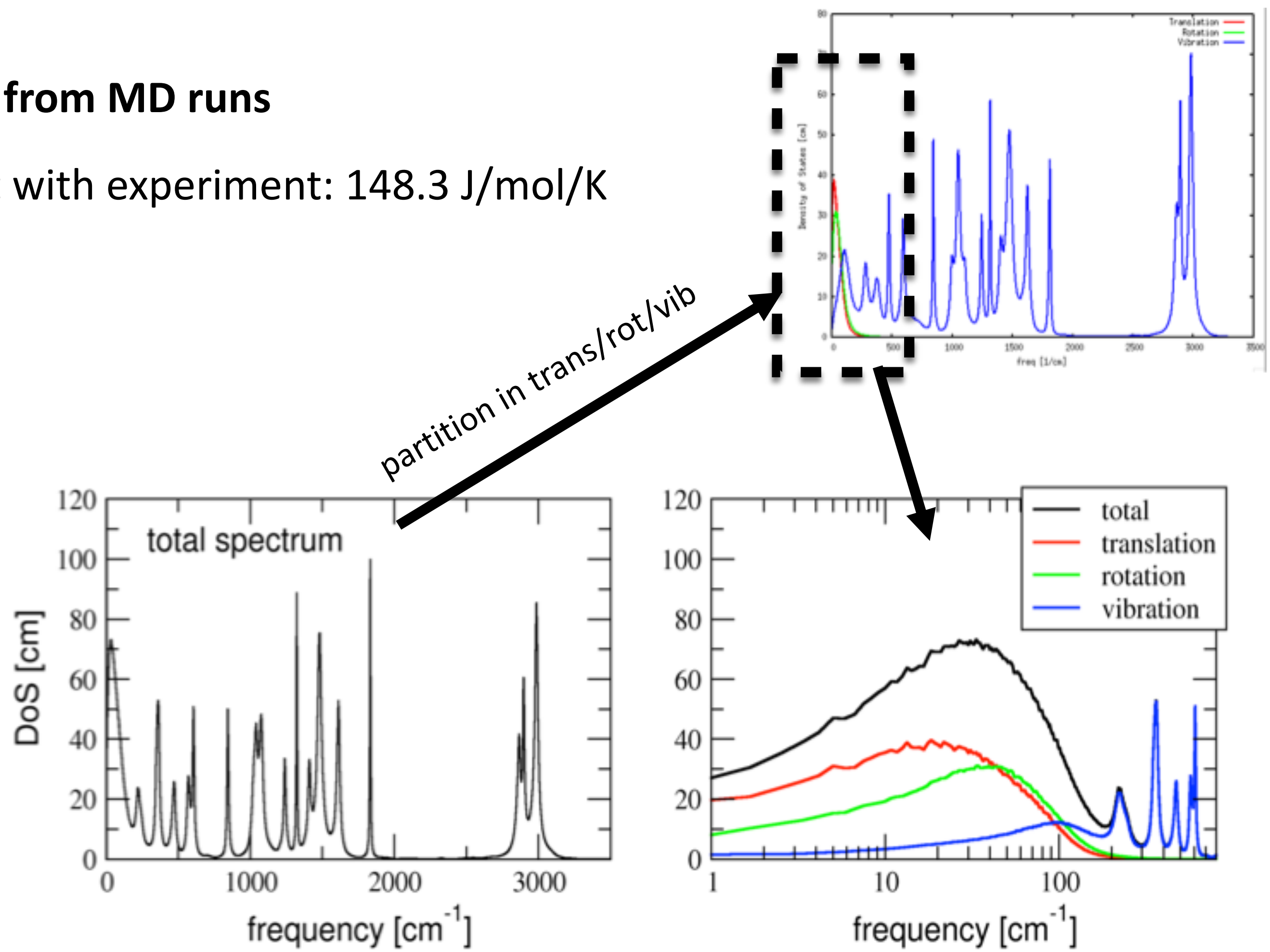
$$W_{\mathrm{solid}}^{C_v}(v) = \frac{\exp(-\beta h v)}{[1 - \exp(-\beta h v)]^2}$$



Heat Capacity of DMF

Cp = 149.2 J/mol/K from MD runs

Excellent agreement with experiment: 148.3 J/mol/K



DMF with Graphite Nanoflakes

Preliminary results:

Specific heat of the nanofluid is close to the sum of its components

3.9 wt% samples (different NF sizes)

Sample		Cp (J/g/K)				
Flake size C-atoms	DMF molecules	flake(g)	DMF(l)	DMF(l)+flake(g)	nanofluid	difference
24	100	0.423	2.041	1.996	2.077	0.081
54	225	0.961	2.041	2.000	2.049	0.049
138	575	0.991	2.041	2.001	2.040	0.039
348	1450	1.174	2.041	2.008	2.005	-0.003

Thermal Conductivity

Thermal conductivity calculated from Green-Kubo equation from a long classical MD simulation

$$\kappa = \frac{V}{k_B T^2} \int_0^\infty \langle J_x(0) J_x(t) \rangle \, dt = \frac{V}{3 k_B T^2} \int_0^\infty \langle \mathbf{J}(0) \cdot \mathbf{J}(t) \rangle \, dt$$

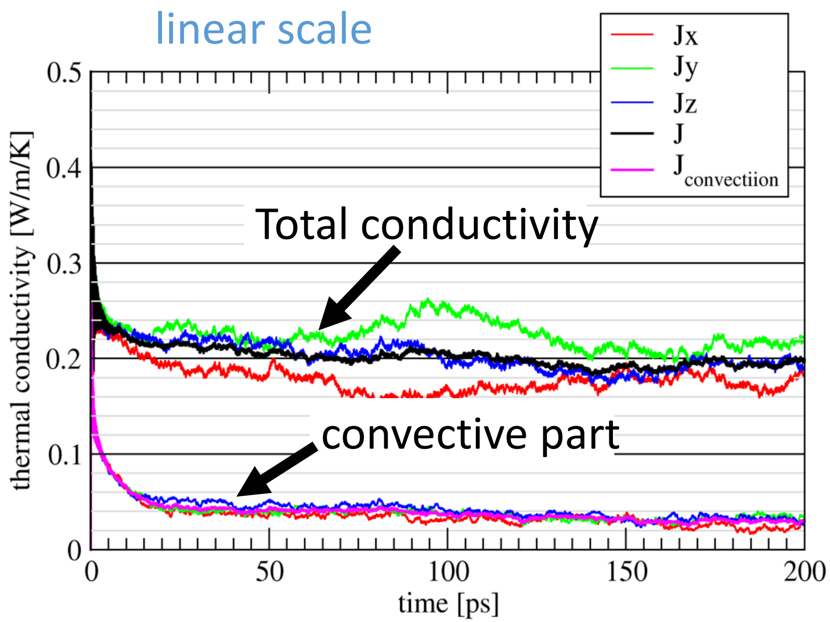
heat flux

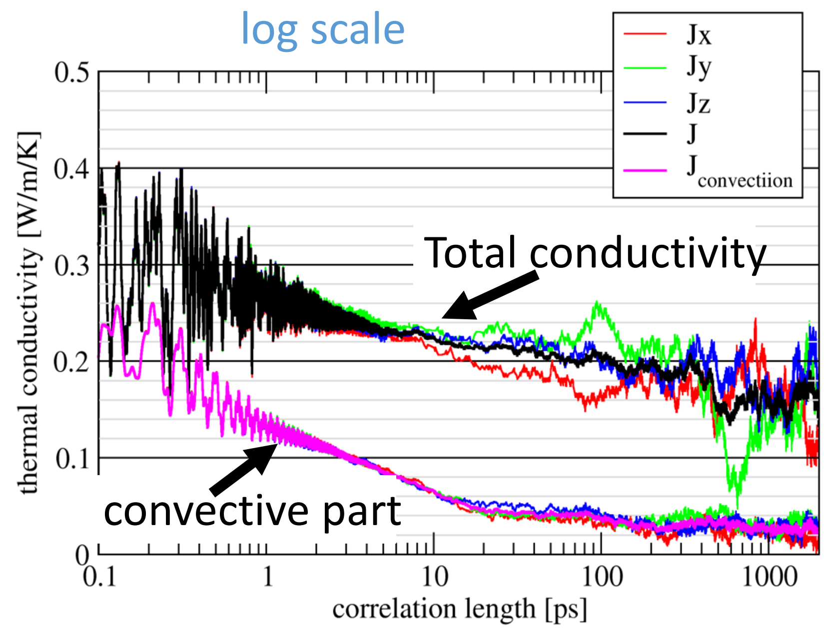
$$\begin{aligned}
\mathbf{J} &= \frac{1}{V}\left[\sum_i e_i \mathbf{v}_i - \sum_i \mathbf{S}_i \mathbf{v}_i\right] \\
&= \frac{1}{V}\left[\sum_i e_i \mathbf{v}_i + \sum_{i<j} \left(\mathbf{f}_{ij} \cdot \mathbf{v}_j\right) \mathbf{x}_{ij}\right] \\
&= \frac{1}{V}\left[\sum_i e_i \mathbf{v}_i + \frac{1}{2} \sum_{i<j} \left(\mathbf{f}_{ij} \cdot (\mathbf{v}_i + \mathbf{v}_j)\right) \mathbf{x}_{ij}\right]
\end{aligned}$$

convective contribution

vibrational/phononic contribution

Thermal Conductivity





Issues:

- Achieving converged results from short simulations (Ercole, Marcolongo & Baroni)
- Computing the heat flux and conductivity from ab-initio (Marcolongo, Umari, Baroni)

Outlook

- Created a workflow for the automatization of the simulations of the thermal properties of nanofluids
- Validation with experimental measurements in GNF in DMF (measured at ICN2) – extreme case: very large changes for very small concentrations of NPs
- Identify microscopic mechanisms
- Adopt the new developments by Baroni and co-workers on the thermal conductivity

MAX DRIVING THE EXASCALE TRANSITION

ICN2 Institut Català de Nanociència i Nanotecnologia

EXCELENCIA SEVERO OCHOA