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Conference on Modern Concepts and New Materials for Thermoelectricity

ICTP

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Enhancement of the thermopower signal in ferrofluid based thermocells

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Introduction

- Currently, the liquid thermo-electrochemical cells receive increasing attention as an inexpensive alternative to conventional solid-state thermo-electrics for application in low-grade, waste heat harvesting.

- Enhanced Seebeck effect has been reported * by using ionically stabilized magnetic nanoparticles dispersed in electrolytes, opening in this way new perspectives to the design of a liquid-based thermoelectric device with relatively high efficiency and cost effectiveness.

*B.T. Huang, M. Roger, M. Bonetti, T.J. Salez, C. Wiertel-Gasquet, E. Dubois, R. Cabreira Gomes, G. Demouchy, G. Mériguet, V. Peyre, M. Kouyaté, C.L. Filomeno, J. Depeyrot, F.A. Tourinho, R. Perzynski, S. Nakamae, Thermoelectricity and thermodiffusion in charged colloids, J. Chem. Phys. 143 (2015).
T.J. Salez, B.T. Huang, M. Rietjens, M. Bonetti, C. Wiertel-Gasquet, M. Roger, C.L. Filomeno, E. Dubois, R. Perzynski, S. Nakamae, Can charged colloidal particles increase the thermoelectric energy conversion efficiency?, Phys. Chem. Chem. Phys. 19 (2017) 9409–9416.
T. Salez, S. Nakamae, R. Perzynski, G. Mériguet, A. Cebers, M. Roger, Thermoelectricity and Thermodiffusion in Magnetic Nanofluids: Entropic Analysis, Entropy. 20 (2018) 405.

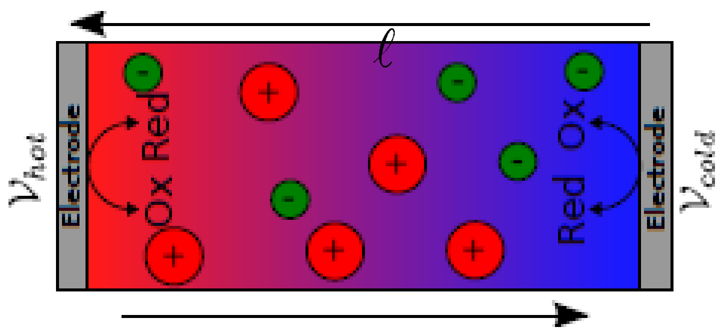
Seebeck effect

- Under a temperature gradient the charged species (ions/particles) migrate acting as charge carriers, analogous to electrons in solids.

- An internal electric field is induced proportional to the temperature gradient , known as Seebeck effect

- The resulting thermoelectric effect is a contribution from both electrolytes and charged colloidal particles

$$\vec{E} = S_{tot}\vec{\nabla}T$$



$$|\vec{E}| = \left|\frac{\nu_{hot} - \nu_{cold}}{\ell}\right|$$

What about magnetic particle Seebeck coefficient?
Aim of our work

- Total Seebeck coefficient of the complex fluid with nanoparticles consists of the liquid background and interacting nanoparticle system's contributions

$$S_{\mathrm{tot}}(T, N_{\mathrm{np}}) = S_{\mathrm{background}}(T) + S_{\mathrm{np}}(T, N_{\mathrm{np}})$$

charged environment

What about the magnetic particle contribution?

→ Study the role of the magnetic nanoparticles characteristics, the inter-particle interactions, applied magnetic field and particle charge in the formation of the enhanced thermoelectric signal based on the thermodynamic approach and Kelvin formula.

Outline of the talk

- **Theoretical calculation of the Magnetic Particle Seebeck coefficient**
- Modelling and Monte Carlo simulations
- Effect of the magnetic particle anisotropy
- Effect of the applied magnetic field
- Comparison with the experimental data
- Perspectives

Calculation of the Magnetic Particle Seebeck coefficient

Total Seebeck coefficient of the system that consists of all the subsystems of the carriers (electrolytes, interacting magnetic nanoparticles, electrodes) is

$$S_{tot} = \beta_{tot} / \sigma_{tot}$$

thermoelectric coefficient and the conductivity

$$\beta_{tot} = \sum_{\ell} \beta_{\ell} \qquad \sigma_{tot} = \sum_{\ell} \sigma_{\ell} = \sum_{\ell} \eta_{\ell} N_{\ell} Q_{\ell}$$

η_{ℓ}, mobility, Q_{ℓ} the charge and the N_{ℓ} number of particles of the ℓ^{th} subsystem

Calculation of the Magnetic Particle Seebeck coefficient

In the case of a broken external circuit (no current, the voltmeter of infinite resistance) the S_{tot} is related to the temperature derivative of the chemical potential by the Kelvin relation [4] for constant particle number N_ℓ and charge Q_ℓ of each ℓ^{th} subsystem as :

$$S_{tot} = \sum_\ell S_\ell = \sum_\ell \frac{1}{Q_\ell}\left(\frac{d\mu}{dT}\right)_{N_\ell}$$

Varlamov, A. A., Kavokin, A. V., Prediction of thermomagnetic and thermoelectric properties for novel materials and systems. *EPL* **103**, 47005 (2013)
Peterson, M. R. & Shastry, B. S. Kelvin formula for thermopower. *Phys. Rev. B* **82,** 195105(5) (2010)

Calculation of the Magnetic Particle Seebeck coefficient

Thus, combining previous equations, the thermoelectric conductivity reads:

$$\beta_{tot} = -\sum_{\ell} S_{\ell}\sigma_{\ell} = -\sum_{\ell} \eta_{\ell} N_{\ell} \left(\frac{d\mu_{\ell}}{dT} \right)_{N_{\ell}}$$

Thus we can rewrite eq. for the total Seebeck coefficient as:

$$S_{tot} = \frac{\beta_{tot}}{\sigma_{tot}} = \frac{\sum_{\ell} \eta_{\ell} N_{\ell} \left(\frac{d\mu_{\ell}}{dT} \right)_{N_{\ell}}}{\sum_{\ell} \eta_{\ell} N_{\ell} Q_{\ell}}$$

Calculation of the Magnetic Particle Seebeck coefficient

Focus on the new term included in S_{tot} namely the contribution to Seebeck coefficient S_{np} coming from the subsystem of interacting magnetic nanoparticles ($\ell = np$) added to the ionic liquid. This term for a given total conductivity and number of magnetic nanoparticles N_{np} is determined by the expression

$$S_{np} = -\frac{\beta_{np}}{\sigma_{tot}} = \frac{\eta_{np} N_{np} \left(\frac{d\mu_{np}}{dT} \right)_{N_{np}}}{\sum_{\ell} \eta_{\ell} N_{\ell} Q_{\ell}}$$

Temperature derivative of chemical potential

Calculation of the Magnetic Particle Seebeck coefficient

Chemical potential is defined as the energy which is in average necessary to pay to add one particle to the system, $\mu_{np} = <E_i>$ thus for given n_{np} N_{np} and σ_{tot}

$$S_{np} \sim \frac{d\mu_{np}}{dT} = \frac{d <E_i>}{dT}$$

Statistical average of the energy per particle over the temperature is calculated **by means of the Monte Carlo simulation technique with the implementation of Metropolis algorithm**

$$<E_i> = \frac{\sum_p E_p \exp(-\frac{E_p}{T})}{\sum_p \exp(-\frac{E_p}{T})}$$

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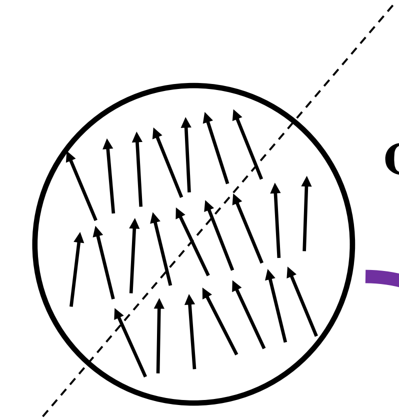
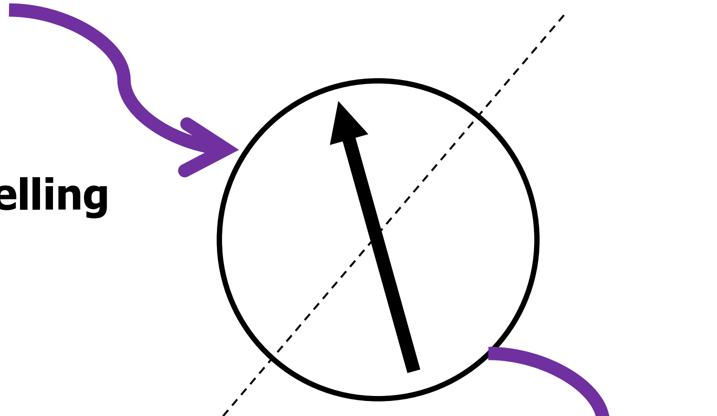
Mesoscopic Scale Modelling of random assemblies of Nanoparticles



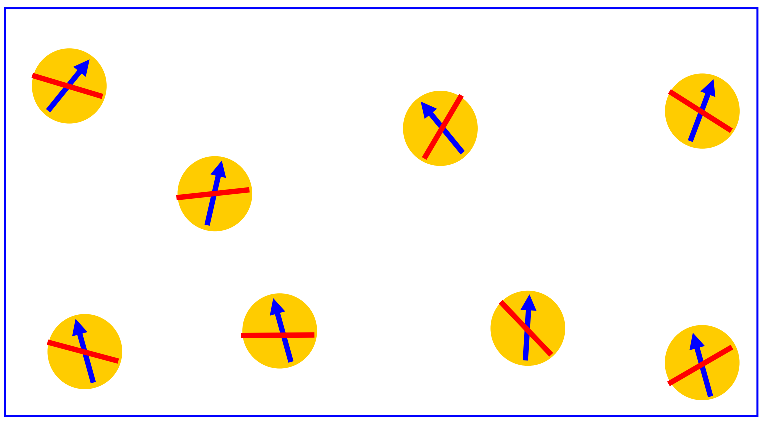
Atomic Scale Modelling



Mesoscopic Scale Modelling

Model of Coherent Rotation

Stoner-Wohlfarth

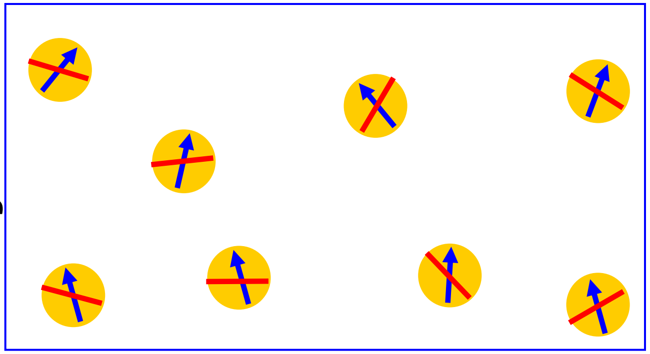


Surf. Sci. Rep. **56** (2005) 189
Phys. Rev. B **58** (1998) 12169

Mesoscopic Scale Modelling of random assemblies of Nanoparticles

$$E = g_{np} \sum_{i>j}^{N_{np}} \frac{(\hat{s}_i \cdot \hat{s}_j) - 3(\hat{s}_i \cdot \hat{r}_{ij}) \cdot (\hat{s}_j \cdot \hat{r}_{ij})}{\hat{r}_{ij}^3} - \sum_{i=1}^{N_{np}} K_{np} (\hat{s}_i \cdot \hat{e}_i)^2$$

- *Dipolar strength* $g_{np} = \mu_0 (M_s V)^2 / 4\pi d^3$
- *Effective Anisotropy constant* $K_{np} = K_{eff} V$



K_{eff}: effective anisotropy constant including the surface,magneto-crystalline,shape anisotropy

Uniaxial anisotropy for nanoparticles

Gazeau et al., JMMM 186 (1998) 175
Moumen et al.,J.Phys.Chem. 100 (1996) 14410

Temperature dependent model parameters

- ***γ-Fe_2O_3 Nanoparticles*** *(9 nm size)*

➢ *Saturation magnetization* **$M_s(T)=M_s(5K) - b_1 * T^{2.3}$**

b_1 is such that $M_S(300K)/M_S(5K)=85\%$

(modified Bloch law (Hendriksen et al. PRB 48 1993), Ms(T)experimental results Safronov et al, 2013* γ-Fe_2O_3 nanofluid with electrostatic stabilizer)

➢ *Dipolar strength* $g_{np}=\mu_0(M_sV)^2/4\pi d^3$ ~ **$g_{np}(T)=g_{np}(5K) - b_2 * T^{2.3}$**

$(g_{np}(300K)/ g_{np}(5K)=85\%)$

➢ *Effective Anisotropy constant* $K_{np}=\mu_0 H_a M_s/2$ ~ **$K_{np}(T)= K_{np}(5K) - b_3 * T^{2.3}$**

$(K_{np}(300K)/ K_{np}(5K)=85\%)$

*A.P. Safronov, I. V. Beketov, S. V. Komogortsev, G. V. Kurlyandskaya, A.I. Medvedev, D. V. Leiman, A. Larrañaga, S.M. Bhagat, Spherical magnetic nanoparticles fabricated by laser target evaporation, AIP Adv. 3 (2013).

Reduced Dimensionless parameters used in Monte Carlo simulations

- In our calculations the energy parameters are normalised to the thermal energy $5k_B$ so they are dimensionless. The reduced temperature is defined as $t = T(K) / 5K$, the reduced dipolar strength as g and the reduced magnetic anisotropy k
- S_{np} is divided with the factor $\sigma_{tot} / \eta_{np}\ k_B$ so we calculate the reduced Seebeck coefficient at average temperature t

Monte Carlo calculation of the S_{np} for γ-Fe_2O_3 NPs

- **M_s**=249 kA/m at 5K

→ typical value for a range of sizes of these nanoparticles used in stable ionic ferrofluids C. Filomeno et al., *J. Phys. Chem. C*, 2017, Priyananda et al, Langmuir , 2018, Nourafkan et al., J. Ind. Eng. Chem. 2017, D. Cao et al, Sc.Rep.,2016)

- Effective anisotropy values $K_{eff} > K_{bulk\ eff}$
- $K_{bulk\ eff}$: bulk value of effective magnetocrystalline anisotropy γ-Fe_2O_3

($K_{bulk\ eff} = K_{cub\ bulk}/12$)= 0.04 $10^4 J/m^3$

γ-Fe_2O_3	M_s(5K) kA/m	M_s(300K) kA/m	K_{eff} ($\cdot 10^5 J/m^3$)	$g(t)=g_{np}(t)/5k_B$	$k(t) = K_{eff} V/ 5k_B$
1	249	215	0.06	$17-0.00019\cdot t^{2.3}$	$33.7-0.00038\cdot t^{2.3}$
2			0.12	$17-0.00019\cdot t^{2.3}$	$67.4-0.00076\cdot t^{2.3}$
3			0.3	$17-0.00019\cdot t^{2.3}$	$168.5-0.0019\cdot t^{2.3}$
4			1.2	$17-0.00019\cdot t^{2.3}$	$673.8-0.0076\cdot t^{2.3}$

K_{eff} corresponds to

1. D = 7 nm dispersed in a polymer matrix (Figueroa et al., Physics Procedia, 75 (2015) 1050–7)
2. D =7 nm colloidal attributed to the surface effects (Gazeau et al., J.M.M.M.186 (1998) 175)
3. D= 9 nm attributed to surface effects (Fiorani et al., Physica B 320 (2002) 122)
4. D= 9 nm produced by laser target evaporation technique (Safronov et al., *AIP Adv.* 3 (2013) 052135)

Calculation of the S_{np} for NPs

- Monte Carlo calculations of $<E>$ are performed for various frozen ferrofluids configurations at different temperatures (e.g.T_1,T_2,T_3…)
- Constant temperature step $\Delta T=10K$ that is commonly used in experiments for measuring Seebeck coefficient.
- Calculation of the $d<E>/dT \sim S_{np}$ at average temperature T_i ($T_{i-1} < T_i < T_{i+1}$) as the average of the slopes between the energy at T_i and at T_{i-1}, T_{i+1} respectively

$$\frac{d<E(T_i)>}{dT}=\frac{1}{2}\left(\frac{<E(T_{i+1})>-<E(T_i)>}{T_{i+1}-T_i}+\frac{<E(T_i)>-<E(T_{i-1})>}{T_i-T_{i-1}}\right)$$

Outline of the talk

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Theoretical calculation of S_{np} for nanoparticles with k=0

Analytical approach for an assembly of dipoles without anisotropy gives

$$\mu_{np} = \langle E_i \rangle$$

$$\langle E_i \rangle = \frac{\sum_p E_p \exp(-\frac{E_p}{T})}{\sum_p \exp(-\frac{E_p}{T})}$$

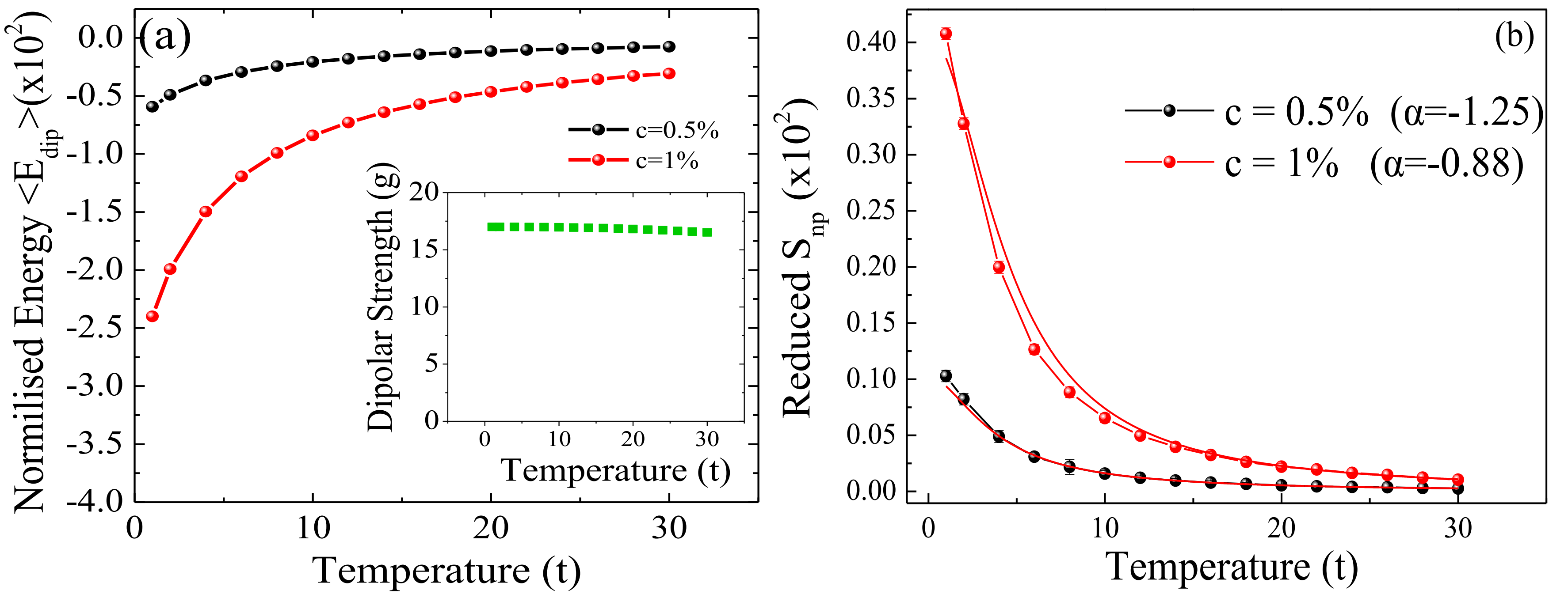
$$\frac{d\mu_{np}}{dT} = \frac{d\langle E_{i,dip} \rangle}{dT} = (\frac{g}{T})^2 \phi(\frac{g}{T})$$

$$\phi(\frac{g}{T}) \sim x^{\alpha}$$

$$S_{np} \sim \frac{d\mu_{np}}{dT} \sim (\frac{g}{T})^{\alpha}$$

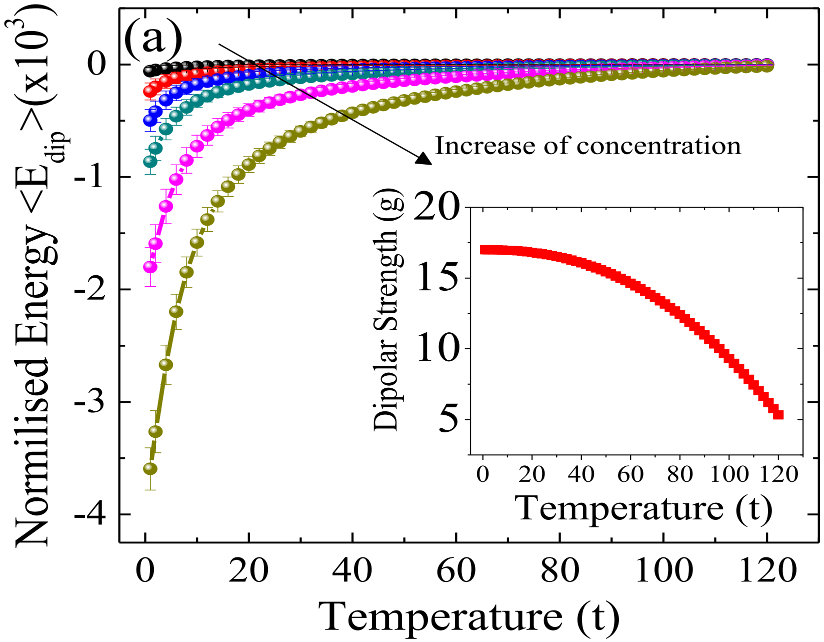
✓ Monotonic T dependence of the Seebeck coefficient for given g

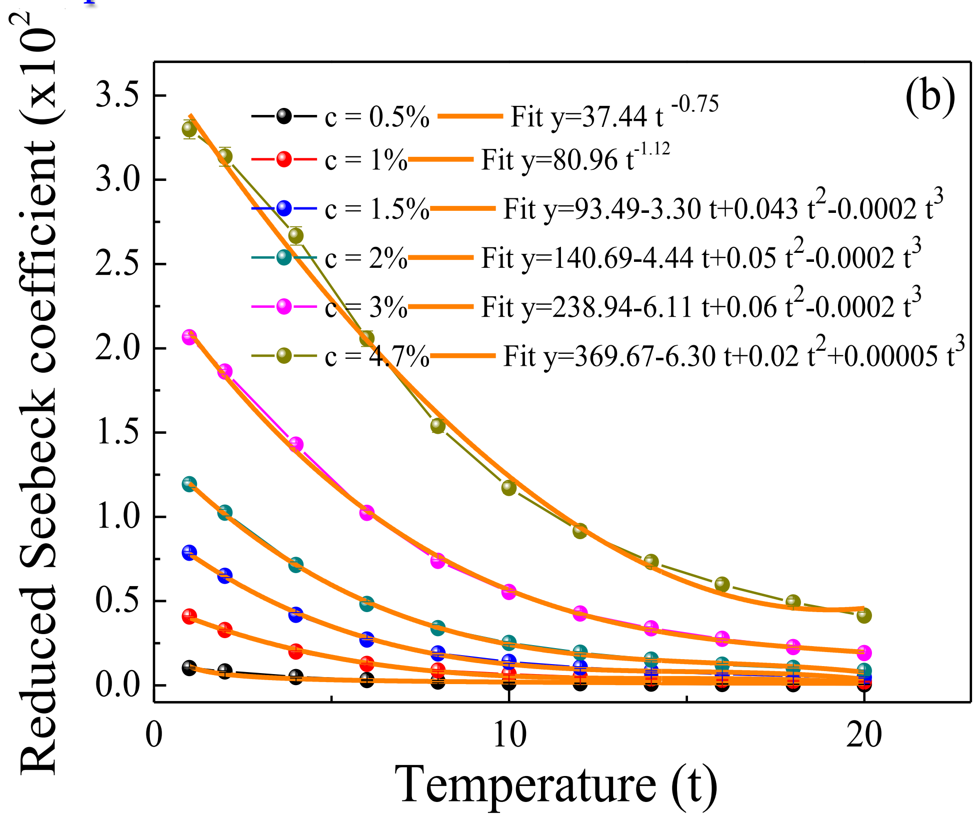
Monte Carlo calculation of S_{np} for nanoparticles with k=0

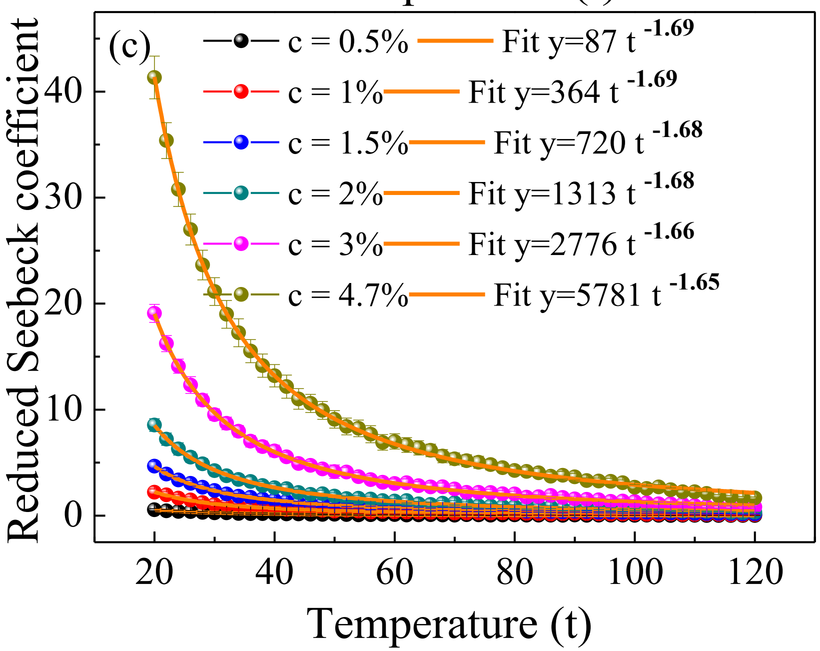


✓ Monotonic T dependence of the Seebeck coefficient

Monte Carlo calculation of S_{np} for nanoparticles with k=0

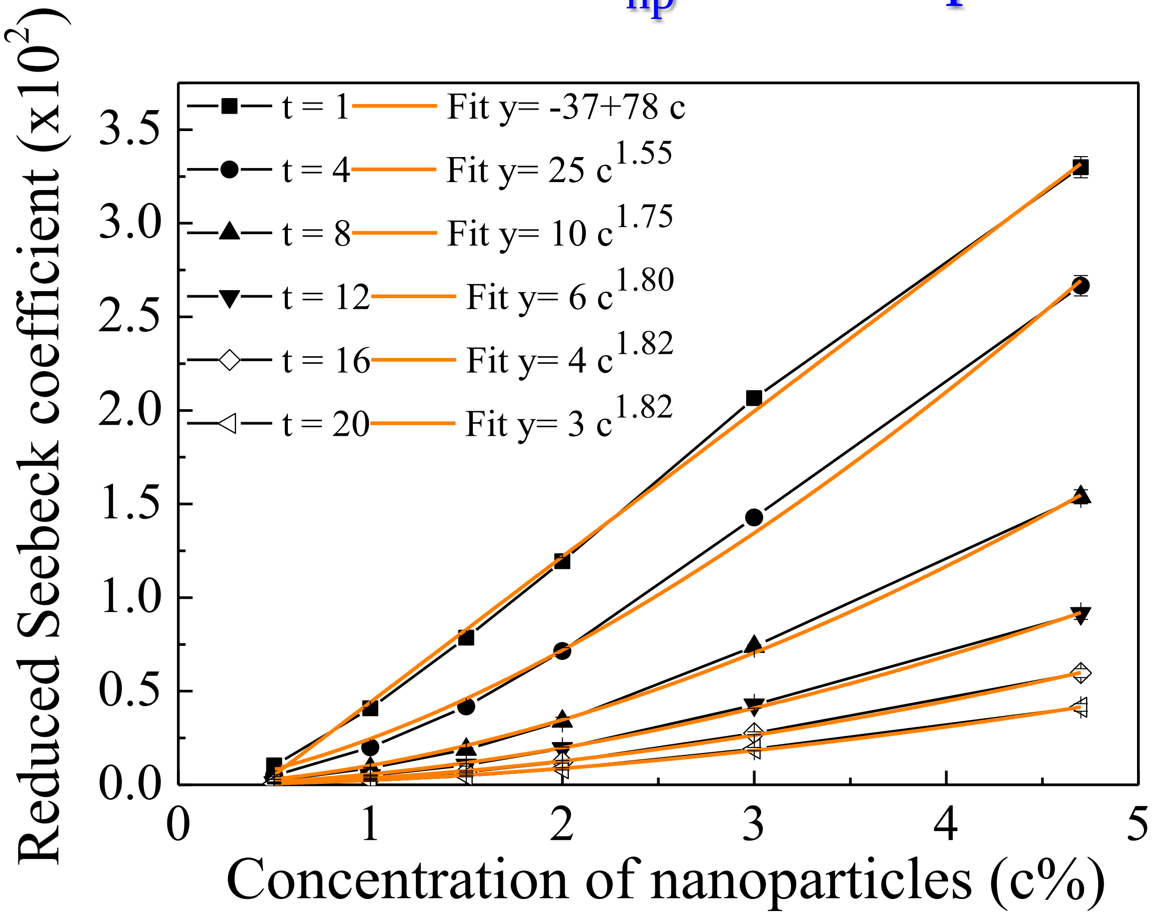






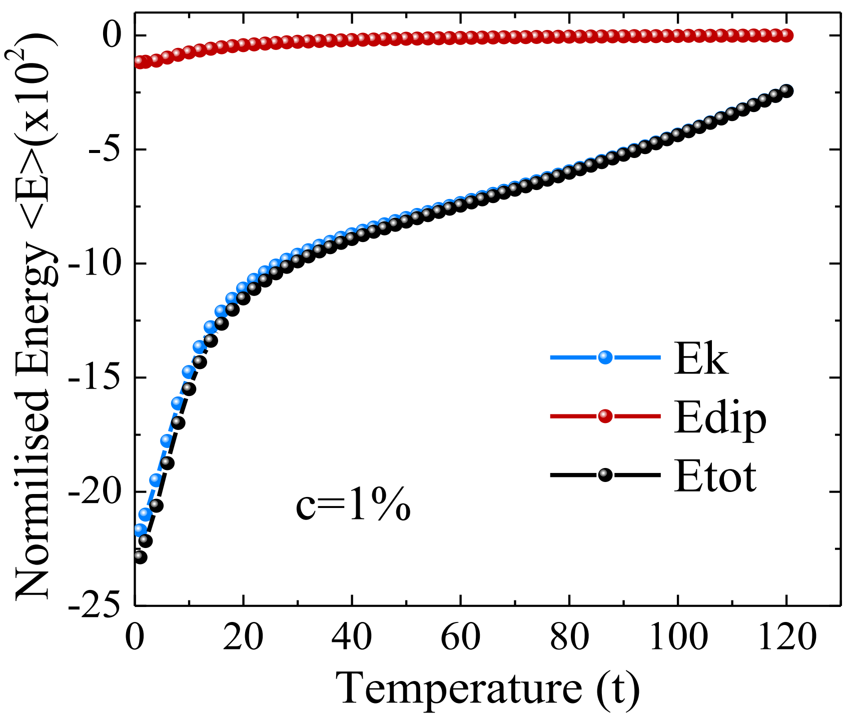
- ✓ Monotonic t dependence of Snp
- ✓ Power law coefficient α~-1.25 for c=0.5% and t<20 and α~-0.33 on average for all concentrations at t>20

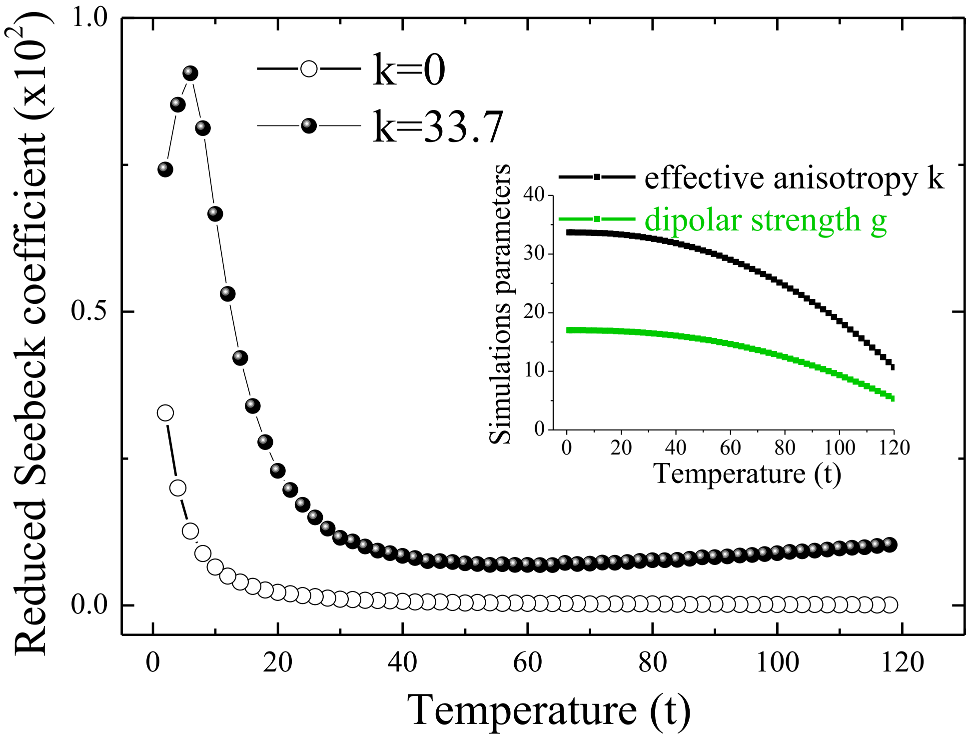
Monte Carlo calculation of S_{np} for nanoparticles with k=0



- ✓ Linear dependence of the Seebeck coeffficient on the nanoparticle concentration exists only at very low temperatures (t<4), for higher temperatures, this dependence follows a power law

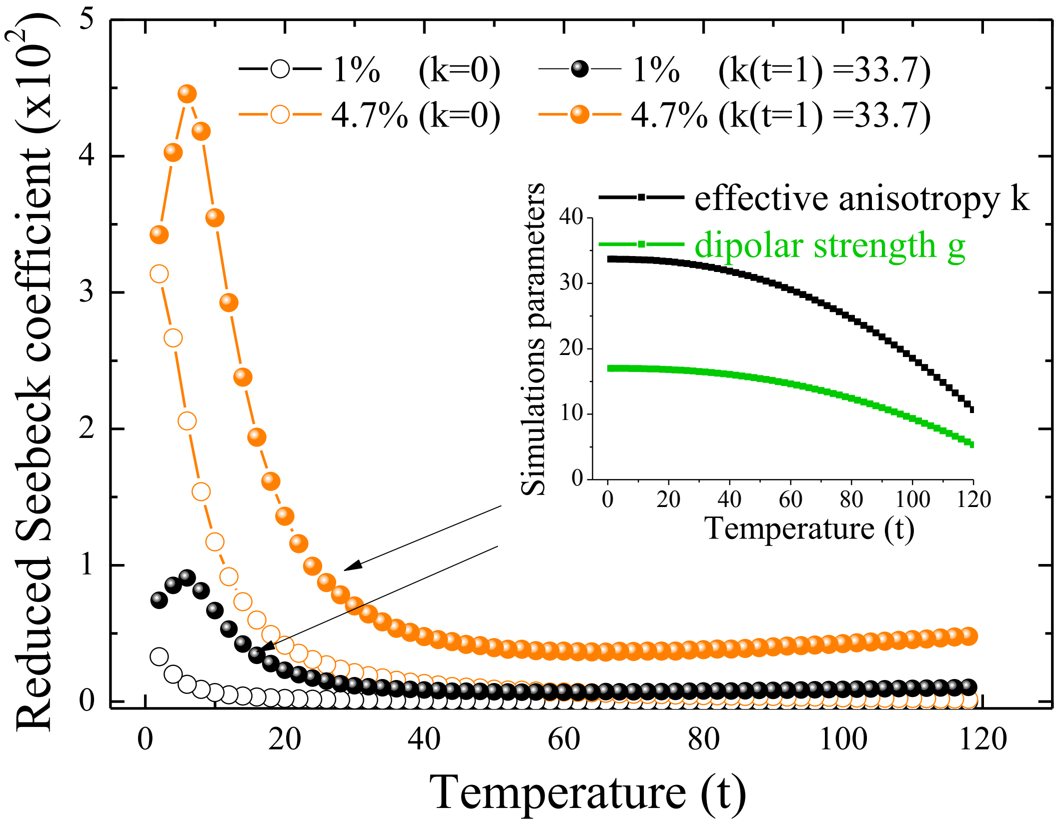
Monte Carlo calculation of the S_{np} for γ-Fe_2O_3 NPs





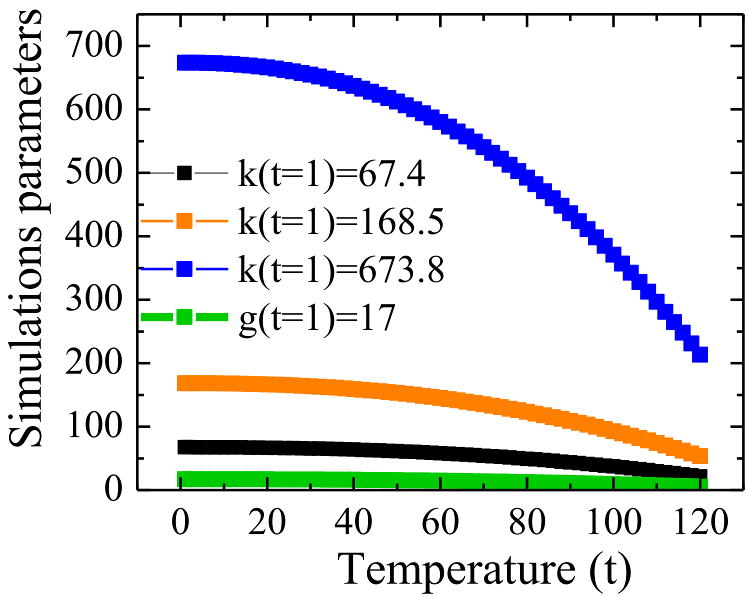
- ➢ $S_{np}(t)$ curve departs from the monotonic t dependence of the k=0 case
- ➢ Effect of the additional anisotropy energy barrier on the calculated Seebeck coefficient versus temperature

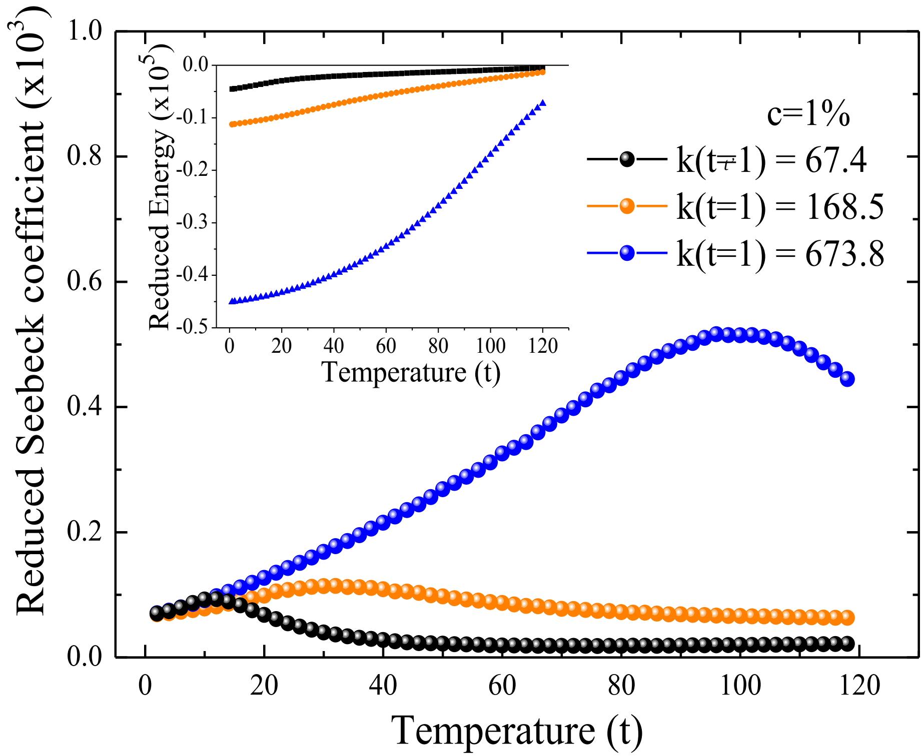
Monte Carlo calculation of the S_{np} for γ-Fe_2O_3 NPs



- Effect of the Interplay between interparticle interactions and effective magnetic anisotropy on the calculated Seebeck coefficient versus temperature
- $S_{np}(t)$ curve shows a maximum for both concentrations c=1% and 4.7% at t=6
- $S_{np}(t)$ increase with the increase of the particle concentration

Monte Carlo calculation of the S_{np} for γ-Fe_2O_3 NPs





- Strong particle magnetic anisotropy enhances Seebeck coefficient
- Shifting of the maximum S_{np} towards higher temperatures as the magnetic anisotropy increases

Monte Carlo calculation of the S_{np} for $CoFe_2O_4$ NPs

Temperature dependent Model Parameters

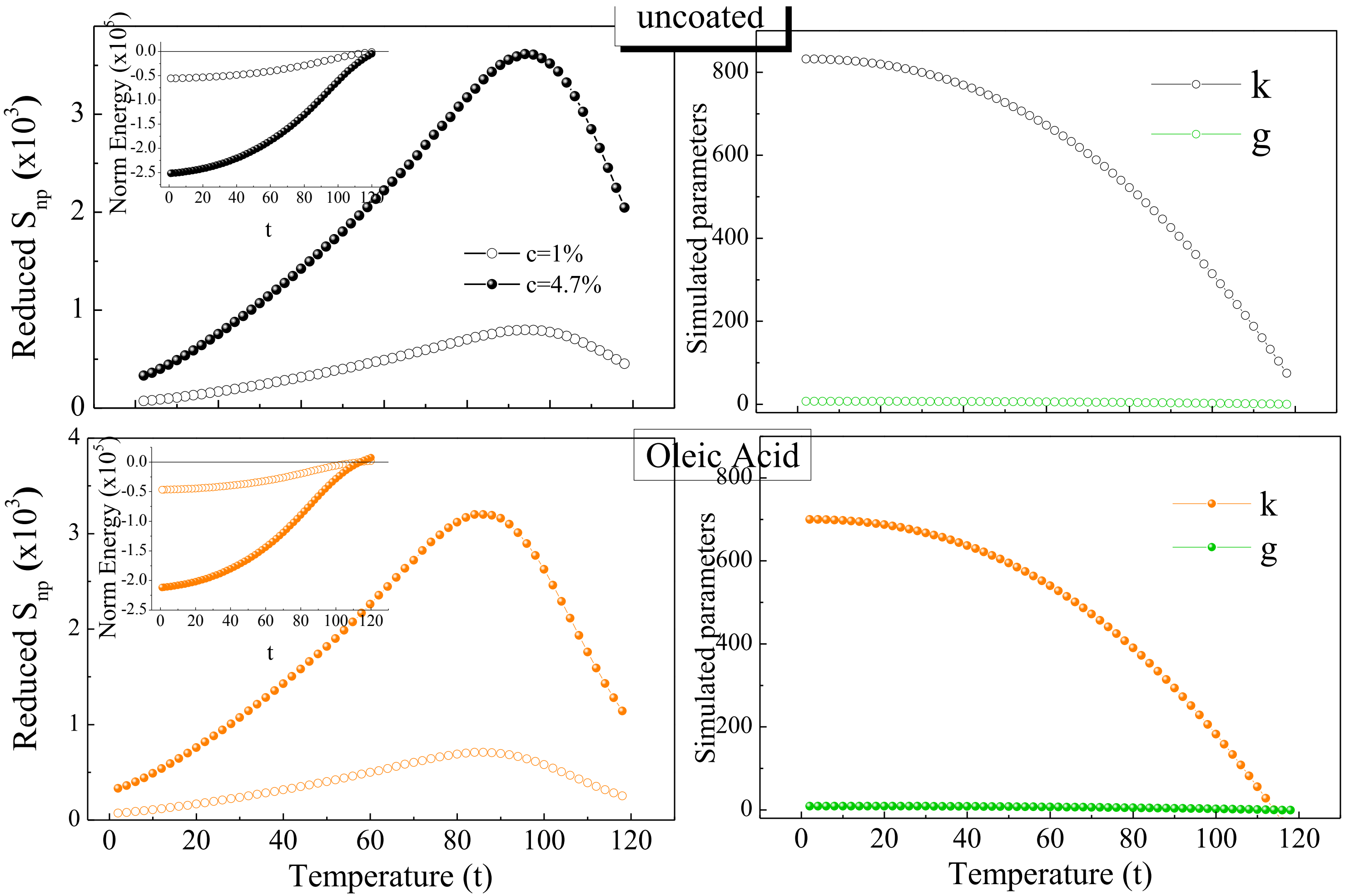
CoFerrite	M_s(5K) kA/m	M_s(300K) kA/m	K_{eff} ($\cdot 10^5 J/m^3$)	g(t)	k(t)
OA	432	333	7.4	$9.3-0.00017\cdot t^{2.3}$	$700-0.01300\cdot t^{2.3}$
DEG	624	572	4.8	$19.4-0.00012\cdot t^{2.3}$	$455-0.00300\cdot t^{2.3}$
Uncoated	381	305	8.8	$7.2-0.00012\cdot t^{2.3}$	$832-0.00130\cdot t^{2.3}$

- Calculations were made for D = 5 nm taking into account M_s and K_{eff} values reported in

Vasilakaki, M. et al. Nanoscale 10, 21244–21253 (2018)
Ntallis, N., Vasilakaki, M., Peddis, D. & Trohidou, K. N.(submitted)
Torres, T. E. et al. J. Phys. Conf. Ser. 200, 72101 (2010)

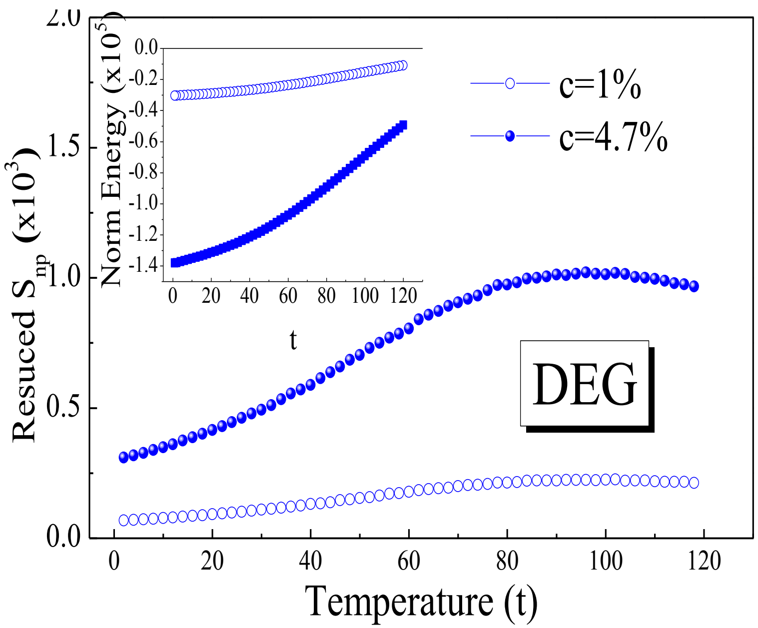
- Assume the same power low T dependence but different ratios **M_S,g,k**
- **OA M_S(300K)/M_S(5K)=77%**
- **DEG M_S(300K)/M_S(5K)=92%**
- **Uncoated M_S(300K)/M_S(5K)=80%**

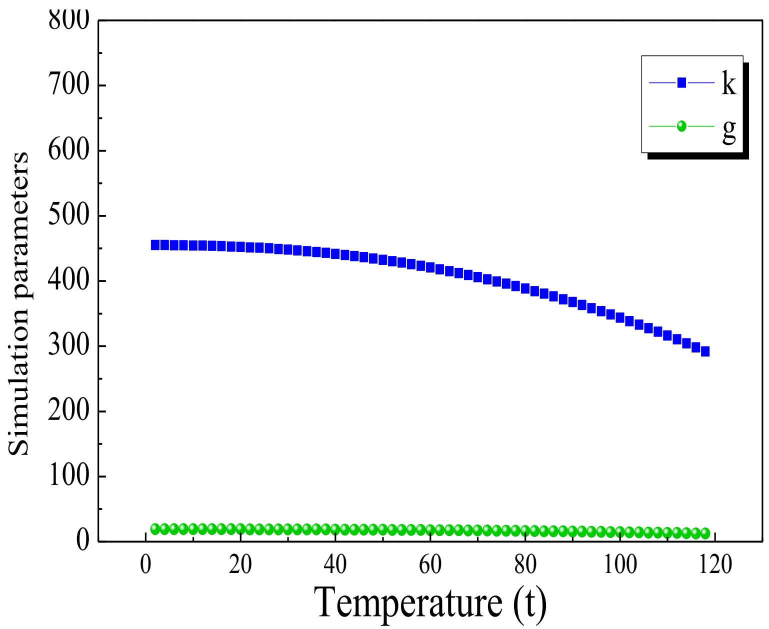
Monte Carlo calculation of the S_{np} for $CoFe_2O_4$ NPs



- Similar behaviour of $S_{np}(T)$

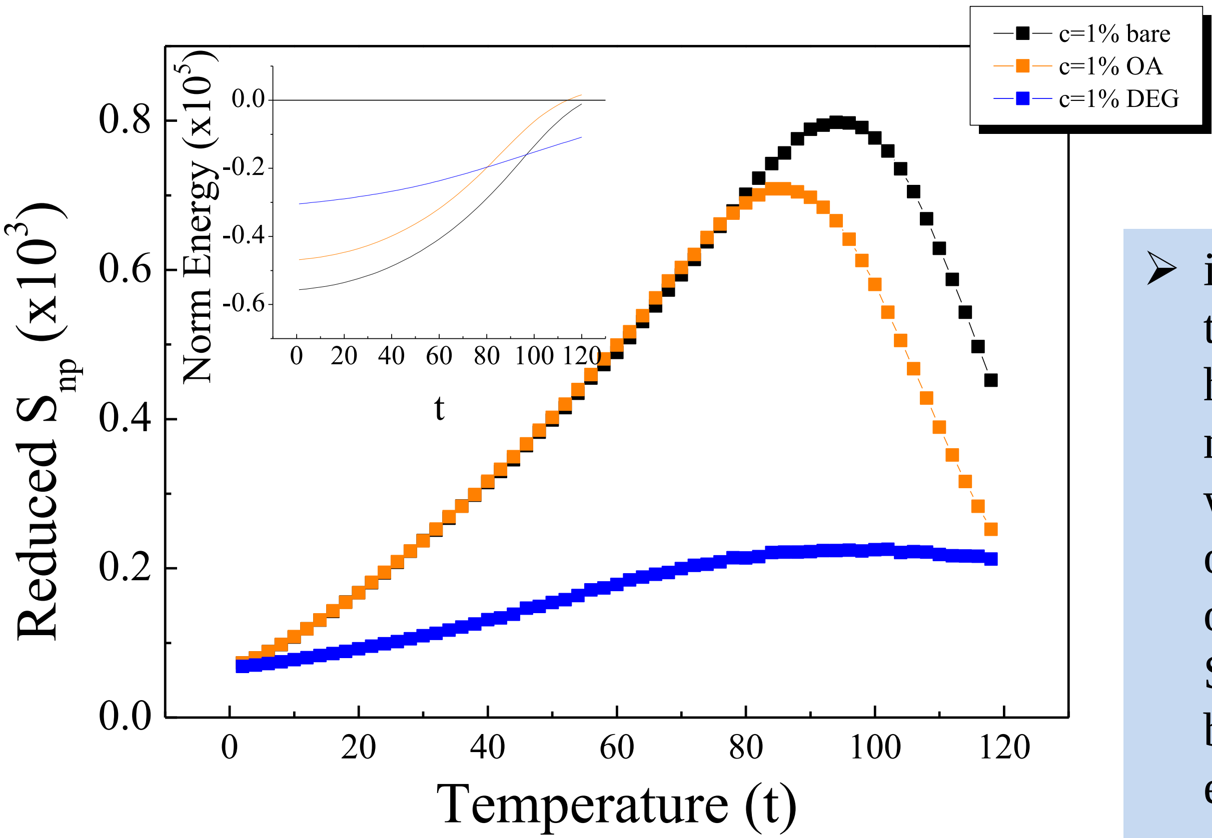
Monte Carlo calculation of the S_{np} for $CoFe_2O_4$ NPs





- Broader maximum of the S_{np}(t) curve in the case of diethylene glycol coating comparing to the other cases

Monte Carlo calculation of the S_{np} for $CoFe_2O_4$ NPs



- it is advantageous for thermoelectric applications to have MNPs with high magnetic anisotropy with weak temperature dependence of their anisotropy, in order to obtain maximum values of Seebeck coefficient for a broad temperature range, especially at temperatures above 300K.

Outline of the talk

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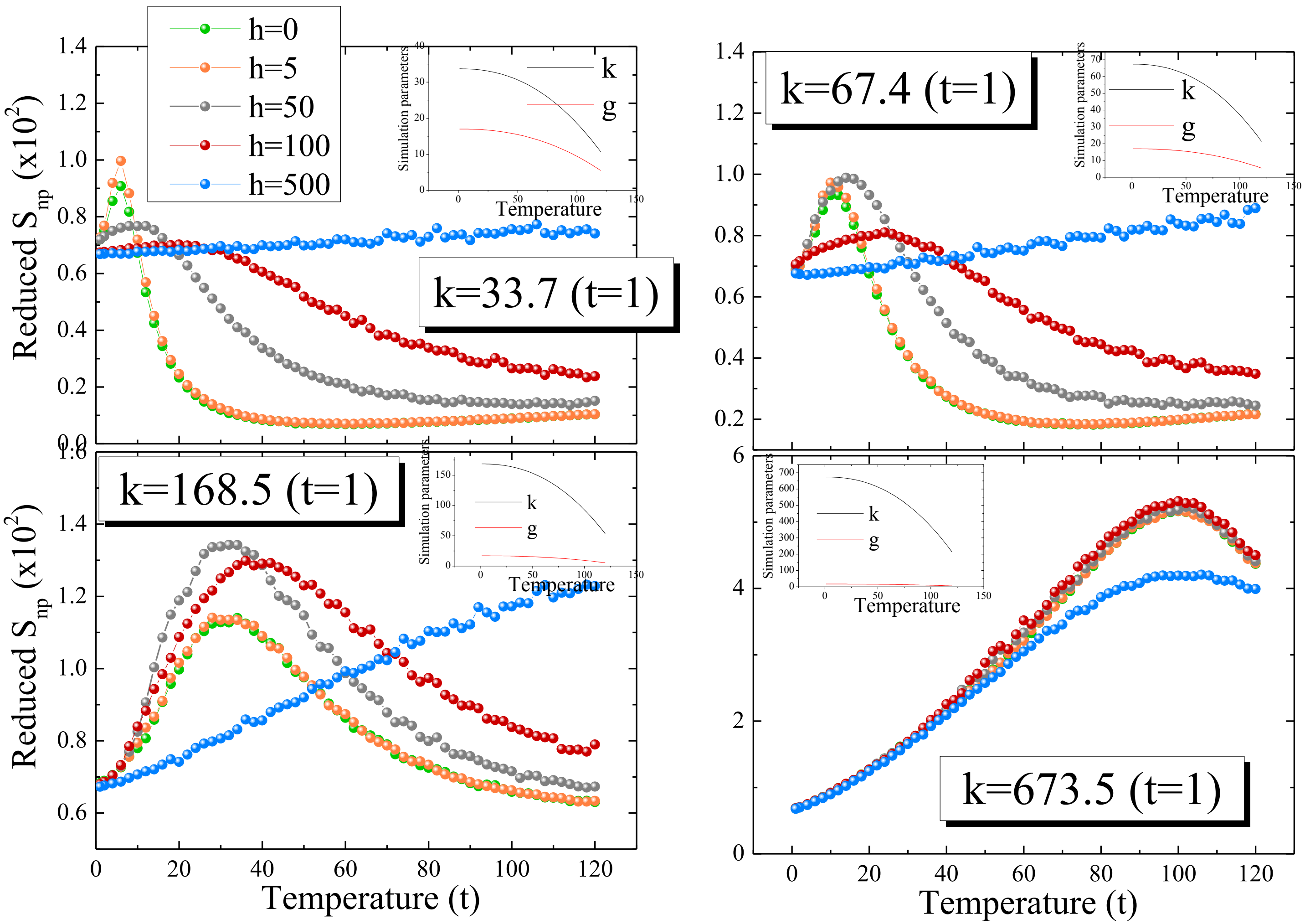
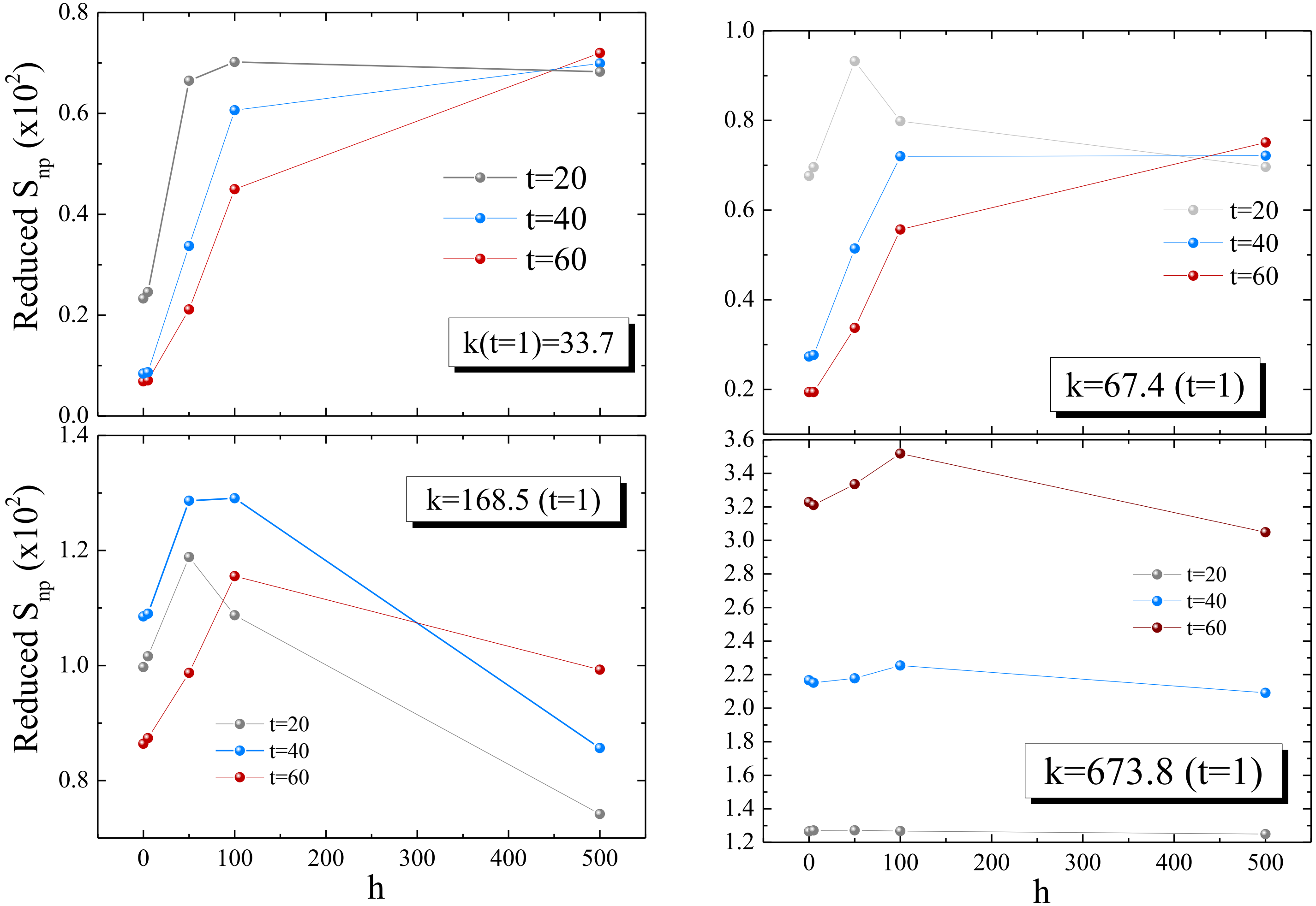
- Perspectives

Field effect on the S_{np} for γ-Fe_2O_3 NPs (c=1%)



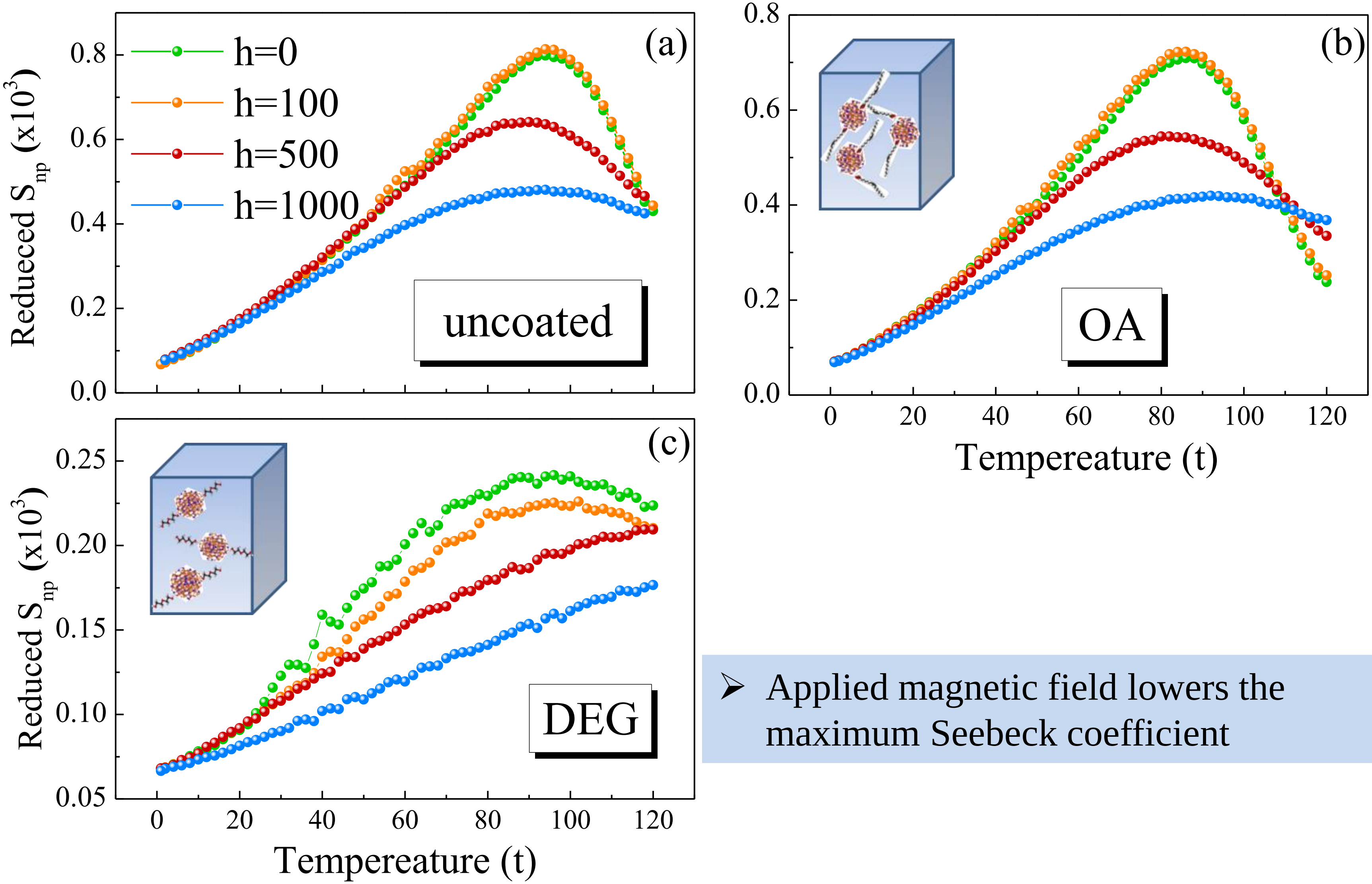
➢ Applied magnetic field shifts the maximum Seebeck coefficient towards higher T

Field effect on the S_{np} for γ-Fe_2O_3 NPs (c=1%)



- Field effect depends on temperature and magnetic particle anisotropy

Field effect on the S_{np} for $CoFe_2O_4$ NPs (c=1%)



- Applied magnetic field lowers the maximum Seebeck coefficient

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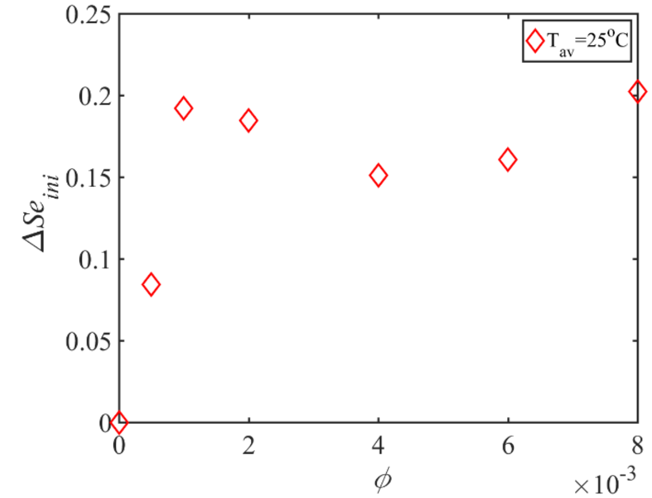
S_{np} versus particle concentration

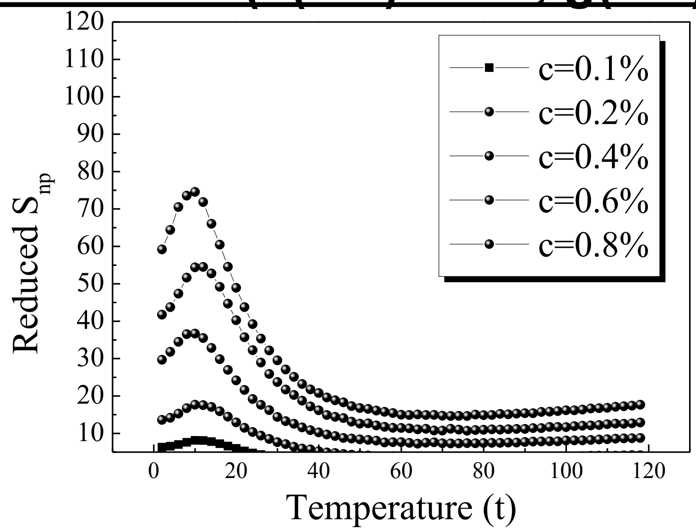
Experimental from CEA-CNRS

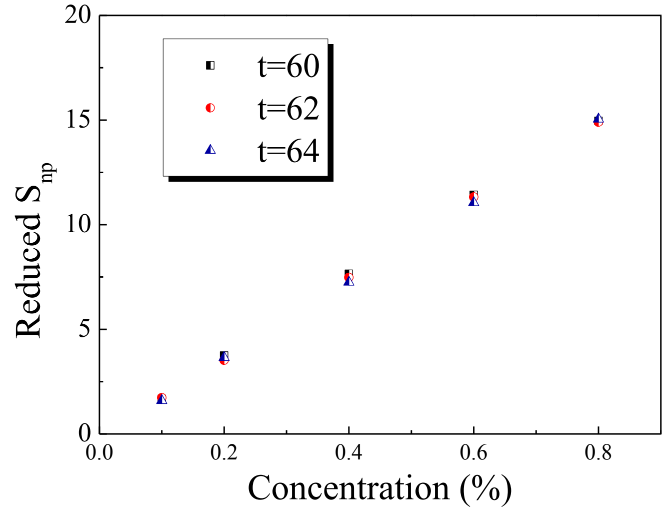
•EAN-FF(1%) :
  maghemite MNP d~9.3nm
•Na counterions + free citrate ions)
•I_2/LiI redox couples @ 10mM.

$\Delta Se \sim S_{np}$ for ϕ = 0-0.8%,ΔT=10K



Monte Carlo (k(t=1)=67.4, g(t=1)=17)





➢ There are differences between experiment and simulations results attributed to the additional charge effect of the MNPs

S_{np} versus applied magnetic field

Experimental from CEA-CNRS

- FF(0.05%) : maghemite MNP d~9.3nm
- SMIM counterions
- $Co^{II/III}$(ppy)TFSI and $Co^{III/III}$(ppy)TFSI @ 5mM.

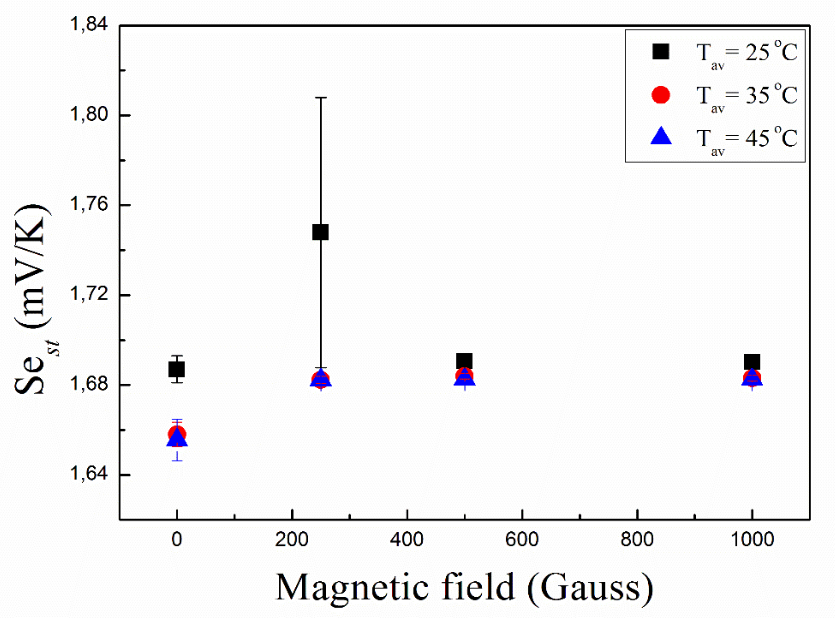
$\Delta Se \sim S_{np}$ for ϕ = 0-0.8%,ΔT=10K

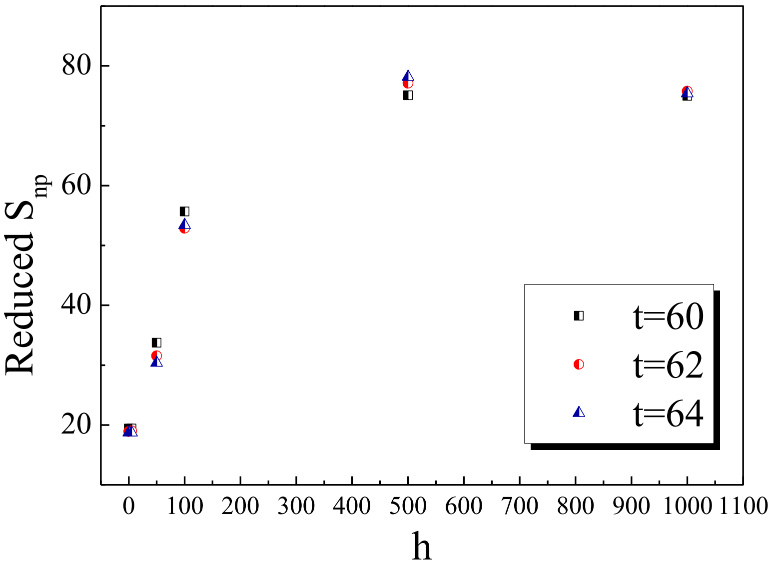
Monte Carlo simulations

k(t=1)=67.4

g(t=1)=17

c=1%





- There is a qualitative agreement between experimental and MC results probably because the Zeeman energy dominates over the other energies

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- Comparison with the experimental data
- **Perspectives**

Effect of electrostatic energy term of charged γ-Fe_2O_3

$$E_{tot} = E_{dip} - E_k + E_{ele}$$

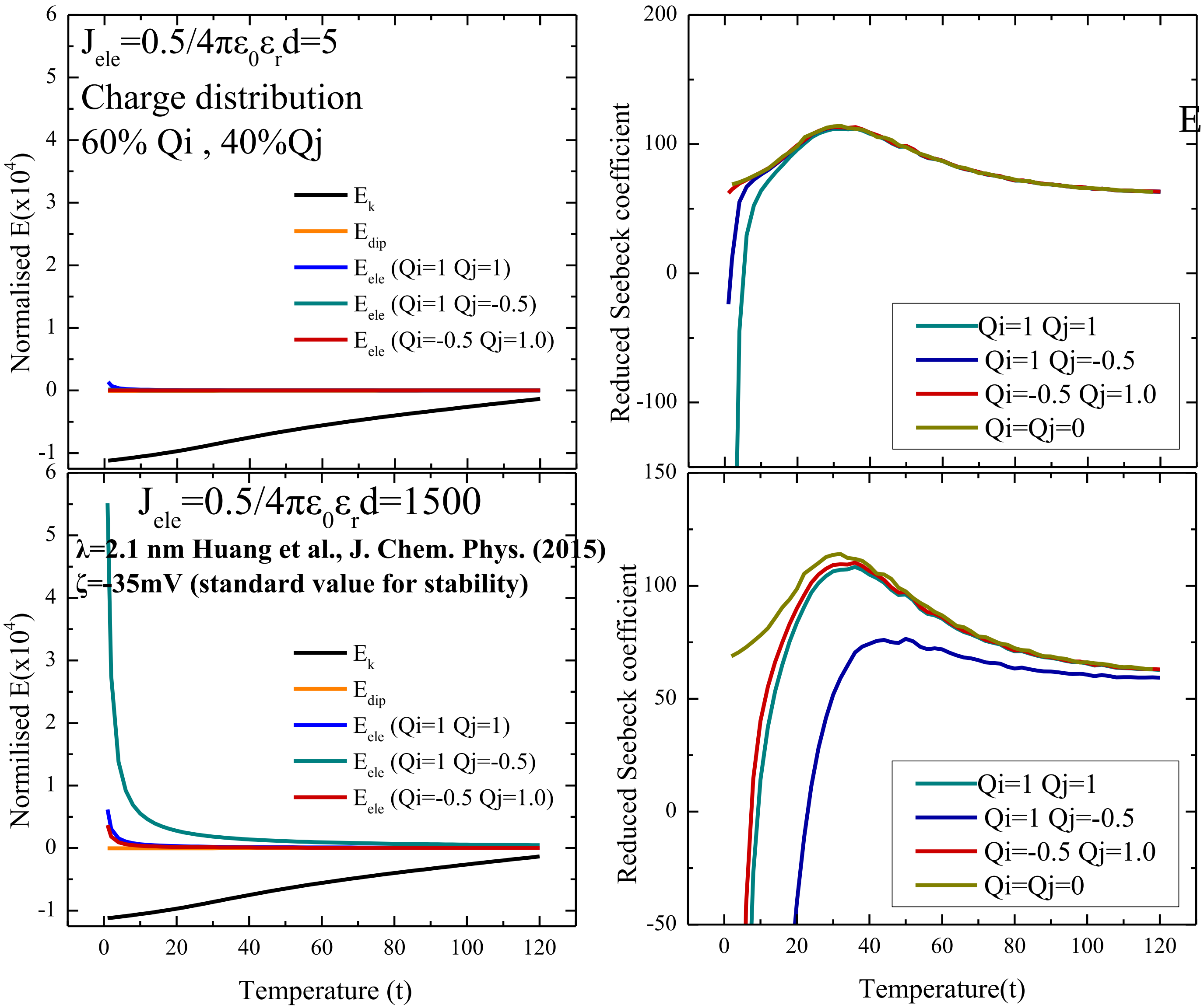
$$E_{ele} = \frac{1}{2}\sum_{i=1}\frac{Q_i}{4\pi\varepsilon_r\varepsilon_0 d}\sum_{j=1,i\neq j}\frac{Q_j}{r_{ij}} = J_{ele}\sum_{i,j=1,i\neq j}\frac{Q_i Q_j}{r_{ij}}$$

Experiments show that the nanoparticles possess the charge Q, which is due to the polaron effect of ions in the electrolyte.

J_{ele}: Electrostatic strength between two particles with effective charge **Q=σA**
where $\boldsymbol{\sigma=\varepsilon_o\varepsilon_r\zeta/\lambda}$ **:**surf charge density and **A**: surface area
ζ: zeta potential, λ:Debye length(~1/T),
r: pair distance taken from MC particle configurations

- J_{ele} depends on charge value & temperature $J_{ele} = \frac{\varepsilon_0\varepsilon_r A^2\zeta^2}{4\pi d\lambda^2} \sim \frac{1}{k_B T^2}$

Effect of electrostatic energy term of charged γ-Fe_2O_3 for g=17 , k=168.5 (t=1) (c=1%)



$$E_{ele} = J_{ele} \sum_{i,j=1,i\neq j} \frac{Q_i Q_j}{r_{ij}}$$

- ✓ dE/dT depends on J_{ele} that depends on :
- ✓ Charge value
- ✓ Charge distribution
- ✓ λ, ζ

Concluding Remarks

- We study for the first time the role of the magnetic particle anisotropy in the formation of the enhanced thermoelectric signal based on a thermodynamic approach and Kelvin formula and Monte Carlo simulations.

- Our results show that Seebeck coefficient (through dE/dT) is enhanced with the increase in the magnetic particle anisotropy following a non-monotonic temperature dependence.

- Optimum values of Snp can be achieved with MNPs of high magnetic anisotropy with weak temperature dependence of their anisotropy for a broad temperature range, especially at temperatures above 300K.

- Seebeck coefficient value increases with the particle concentration, the magnetic applied field, the magnetic particle charge distribution

➢ Next steps : Introducing DFT charge parameters
Inclusion of Van der Waals interactions

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THANK YOU