Melting point and solid-liquid free energy computation using thermodynamic integration

Sai Jayaraman
1435 Multiscale Dynamic Materials Modeling
Sandia National Laboratories

LAMMPS Users' Workshop @ CSRI
February 24-26, 2010

Free energy calculations in LAMMPS

Frenkel & Ladd's method:
H. Zhao, and N. R. Aluru, ``Molecular Dynamics Simulation of Bulk Silicon Under Strain", Journal of Interaction and Multiscale Mechanics, **1** (2), 303-315, 2008.

Umbrella sampling

Atomistic computation of liquid diffusivity, solid-liquid interfacial free energy and kinetic coefficient in Au and Ag, J. J. Hoyt, M. Asta, Phys Rev B, **65**, 214106 (2002).

Method for Computing the Anisotropy of the Solid-Liquid Interfacial Free Energy, J. J. Hoyt, M. Asta, A. Karma, Phys Rev Lett, **86**, 5530 (2001).

Free energy calculation in MD:

Free energy perturbation (FEP)

Potential of mean force (PMF)

Thermodynamic Integration (TI)

Computing melting points:

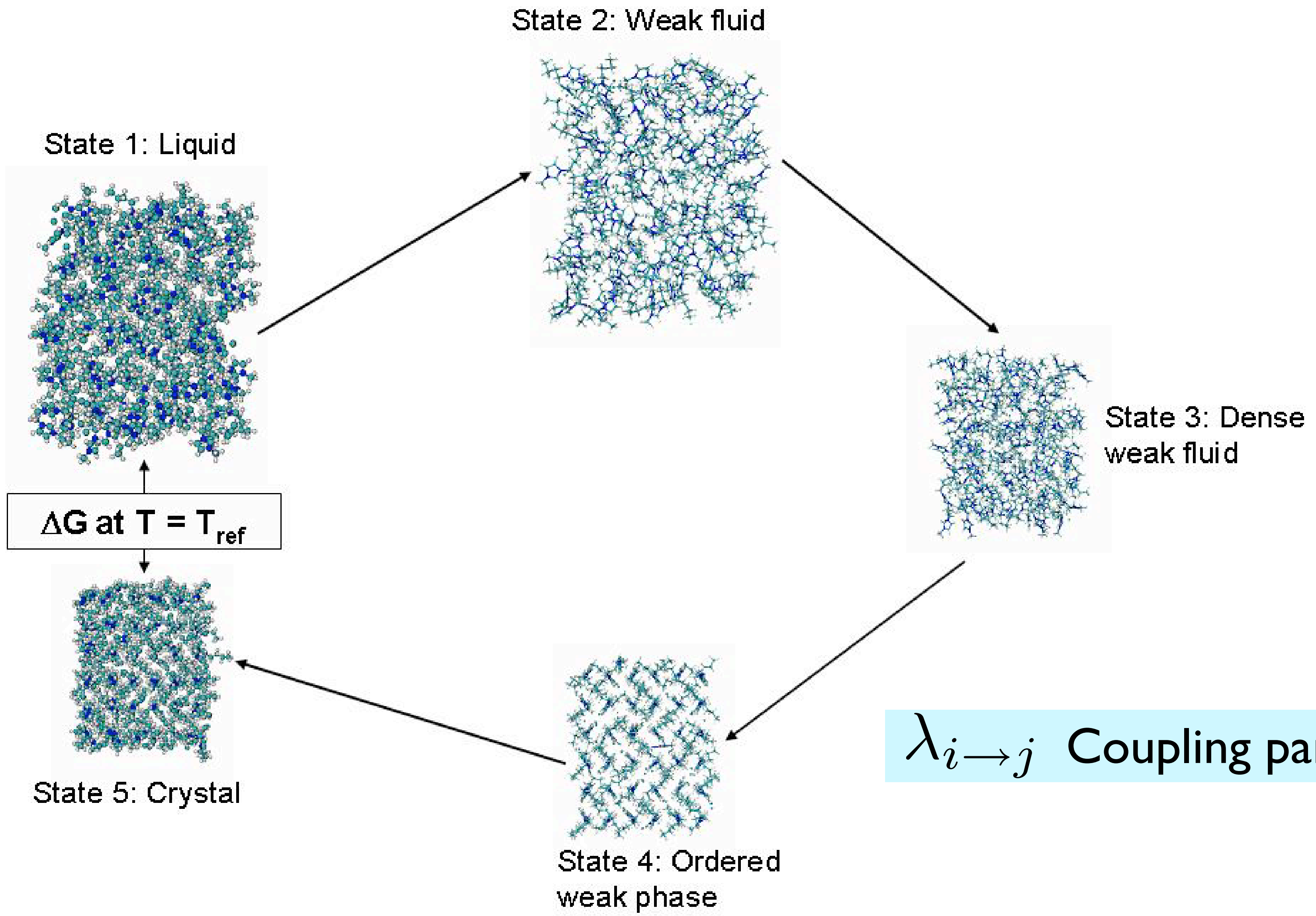
Direct methods: defect induced melting, simulation of solid-liquid interface

Free energy-based methods: Frenkel's Einstein crystal, Hoover & Ree's single occupancy cell

Pseudosupercritical path sampling method[1-3]

[1]D. M. Eike, J. F. Brennecke, and E. J. Maginn, J. Chem. Phys. 122, 014115 (2005)
[2]D. M. Eike and E. J. Maginn, J. Chem. Phys. 124, 164503 (2006)
[3]S. Jayaraman and E. J. Maginn, J. Chem. Phys. 127, 214504 (2007)

Pseudosupercritical path method

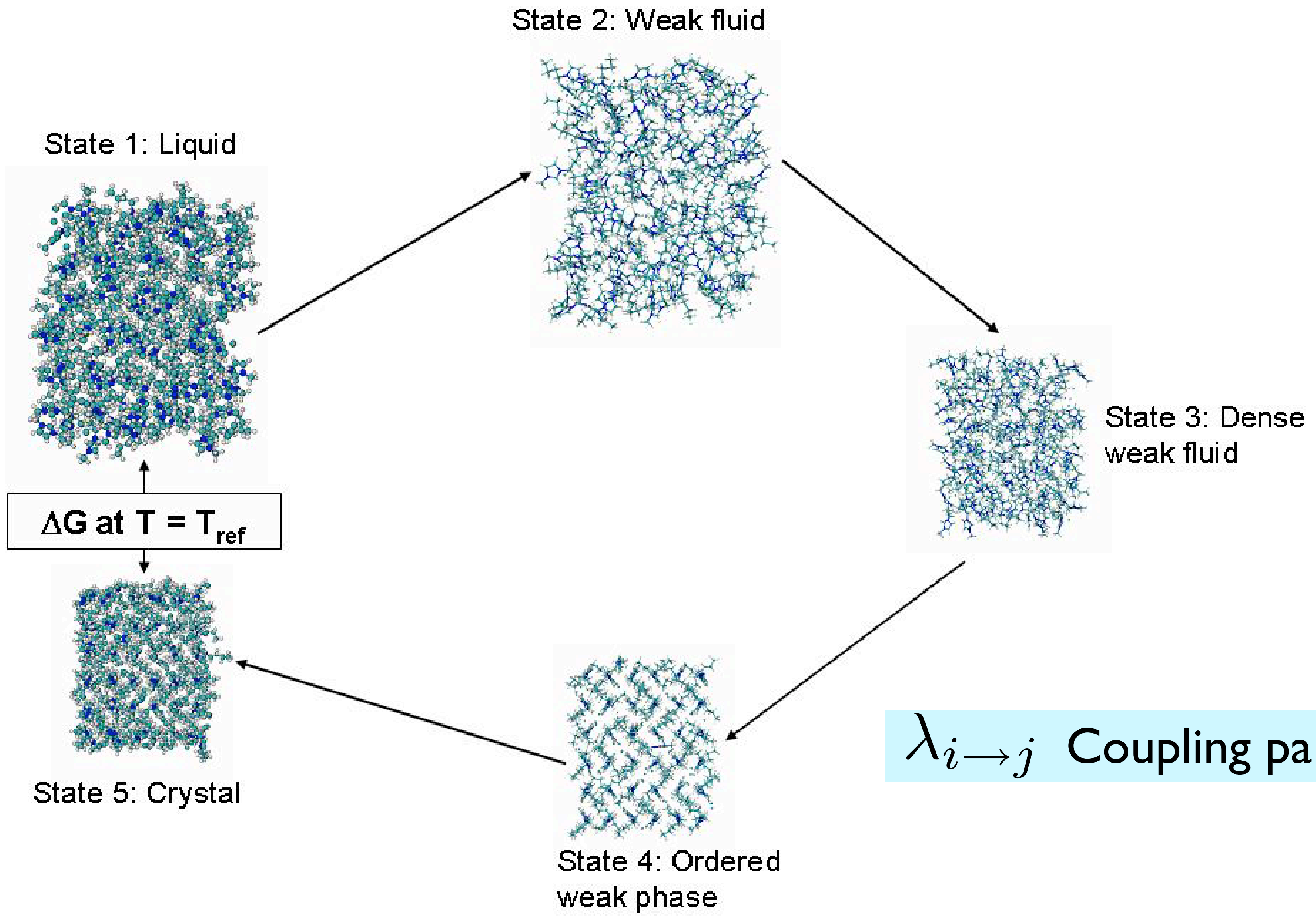


$\lambda_{i \to j}$ Coupling parameter from state $i \to j$

fix/alchemy, lj/cut/alchemy, coul/long/alchemy, pppm/alchemy

$$\Delta A_{i \to j} = \int_0^1 \left\langle \frac{\partial U}{\partial \lambda} \right\rangle_\lambda d\lambda \qquad \Delta A_{2 \to 3} = \int_{V^\ell}^{V^S} - \langle P \rangle \, dV \qquad \Delta G_{s-\ell} = \sum_{i,j} \Delta A_{i \to j}$$

Pseudosupercritical path method



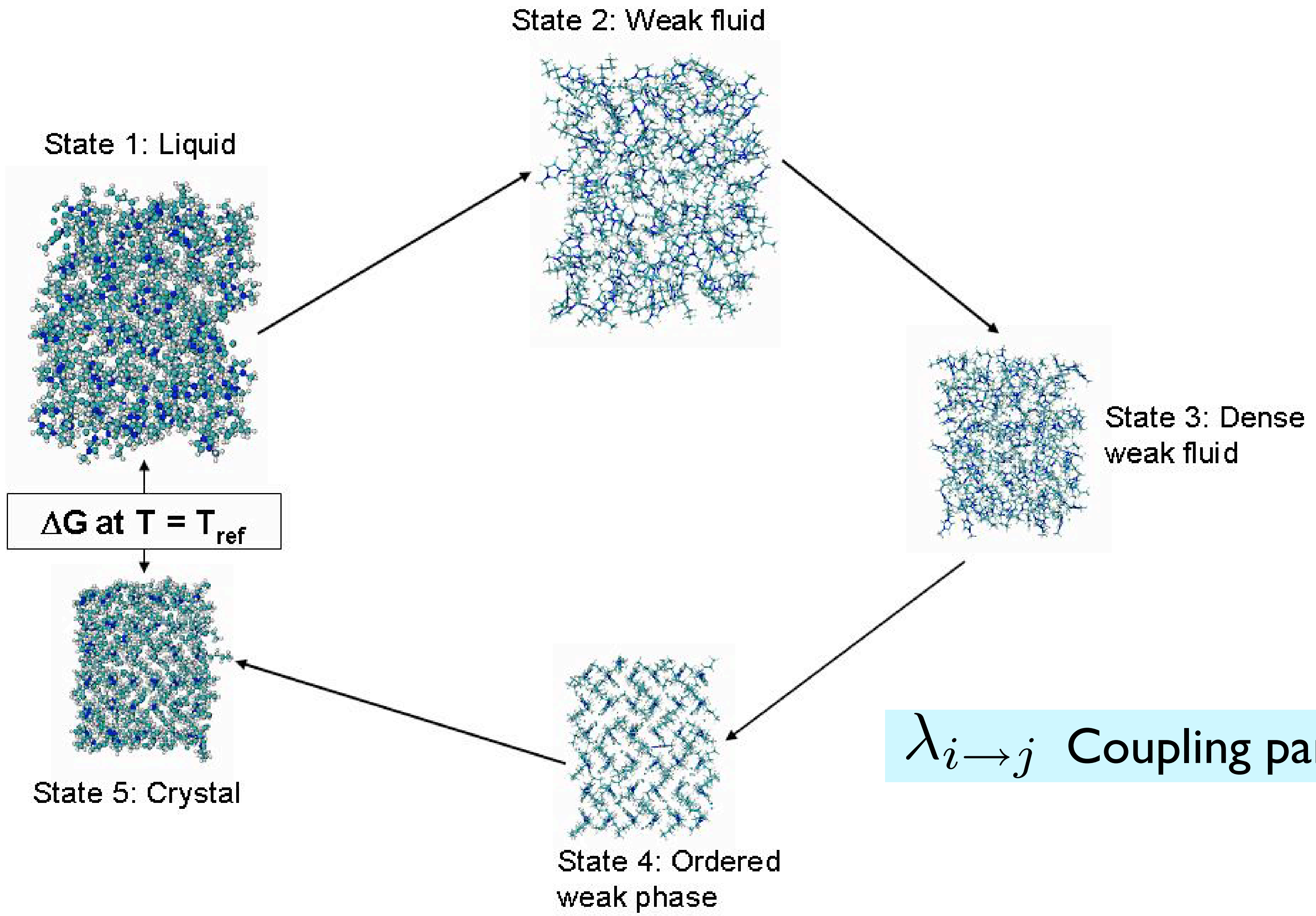
$\lambda_{i \to j}$ Coupling parameter from state $i \to j$

fix/alchemy, lj/cut/alchemy, coul/long/alchemy, pppm/alchemy

$$U_{1\to 2}(\lambda) = [1 + \lambda(\eta - 1)]^m U^{VDW} + [1 + \lambda(\eta - 1)]^n U^{ELEC} + U^{NS}$$

$$\Delta A_{i\to j} = \int_0^1 \left\langle \frac{\partial U}{\partial \lambda} \right\rangle_\lambda d\lambda \qquad \Delta A_{2\to 3} = \int_{V^\ell}^{V^S} -\langle P \rangle \, dV \qquad \Delta G_{s-\ell} = \sum_{i,j} \Delta A_{i\to j}$$

Pseudosupercritical path method

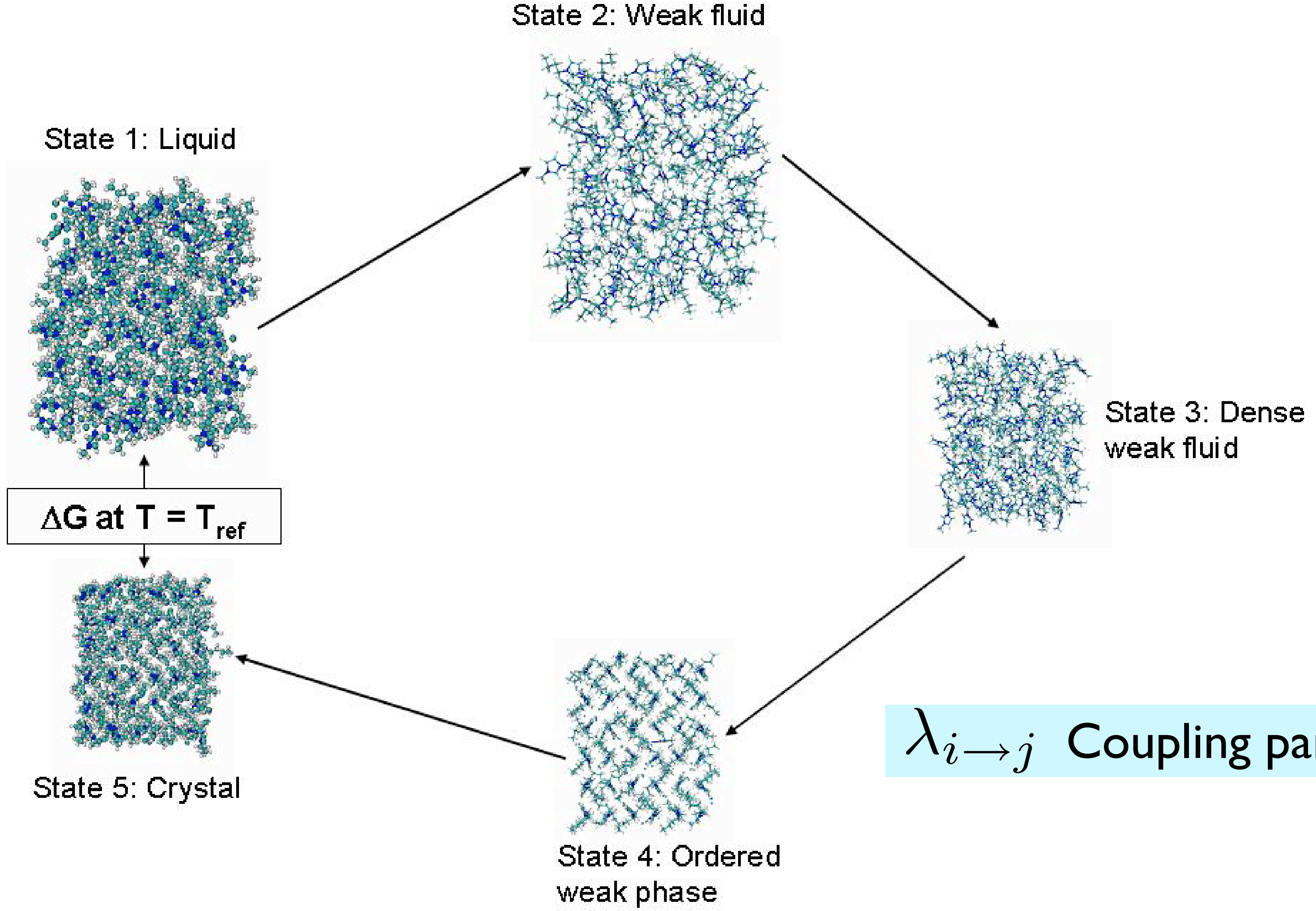


$\lambda_{i \rightarrow j}$ Coupling parameter from state $i \rightarrow j$

fix/alchemy, lj/cut/alchemy, coul/long/alchemy, pppm/alchemy

$$\Delta A_{i \rightarrow j} = \int_0^1 \left\langle \frac{\partial U}{\partial \lambda} \right\rangle_\lambda d\lambda \qquad \Delta A_{2 \rightarrow 3} = \int_{V^\ell}^{V^S} - \langle P \rangle \, dV \qquad \Delta G_{s-\ell} = \sum_{i,j} \Delta A_{i \rightarrow j}$$

Pseudosupercritical path method



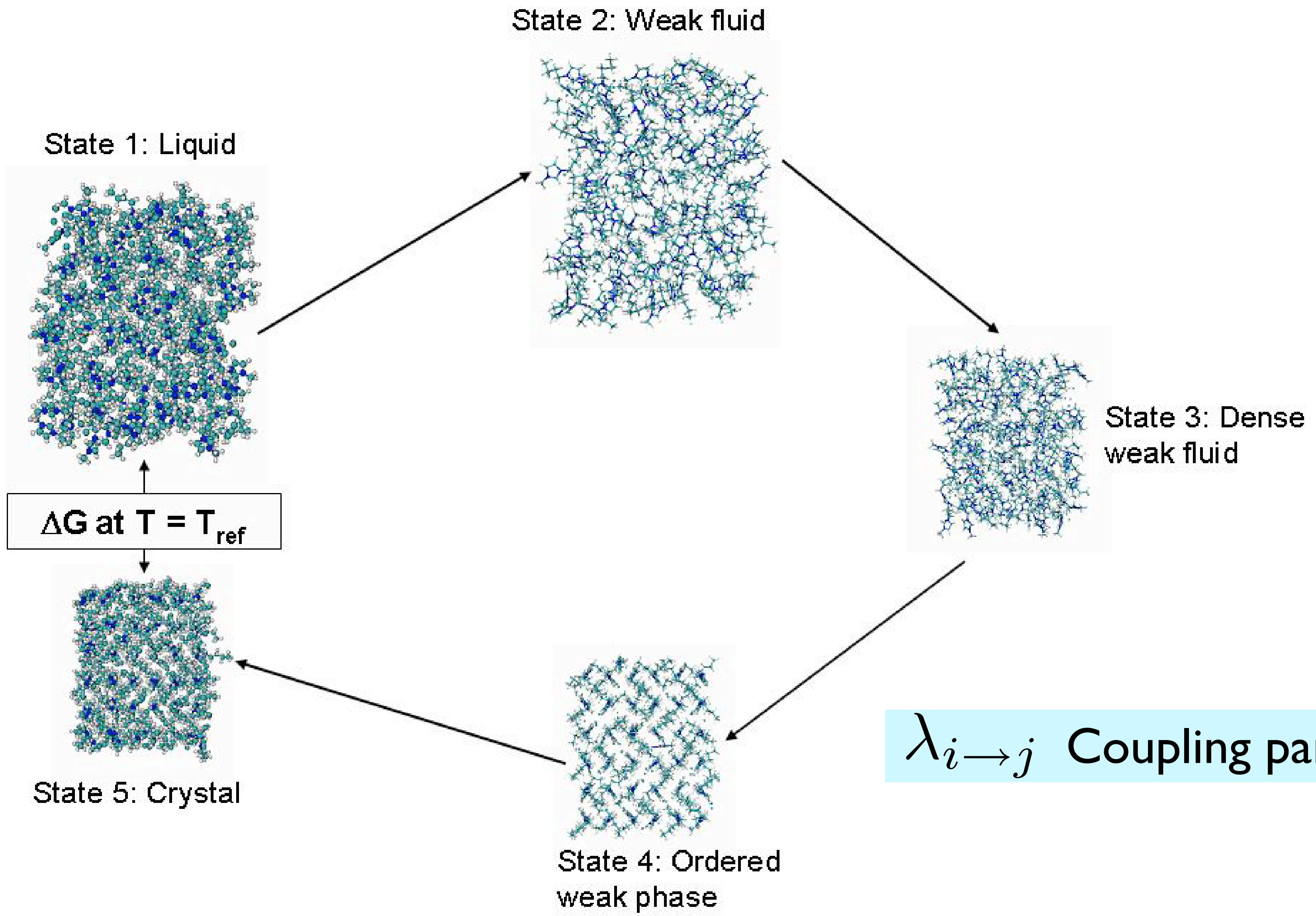
$\lambda_{i\to j}$ Coupling parameter from state $i \to j$

fix/alchemy, lj/cut/alchemy, coul/long/alchemy, pppm/alchemy

$$U_{3\to4}(\lambda) = \eta^m U^{VDW} + \eta^n U^{ELEC} + U^{NS} - \lambda \sum_i \sum_j a_{ij} \exp(-b_{ij} r_{ij}^2)$$

$$\Delta A_{i\to j} = \int_0^1 \left\langle \frac{\partial U}{\partial \lambda} \right\rangle_\lambda d\lambda \qquad \Delta A_{2\to3} = \int_{V^\ell}^{V^S} -\langle P \rangle \, dV \qquad \Delta G_{s-\ell} = \sum_{i,j} \Delta A_{i\to j}$$

Pseudosupercritical path method

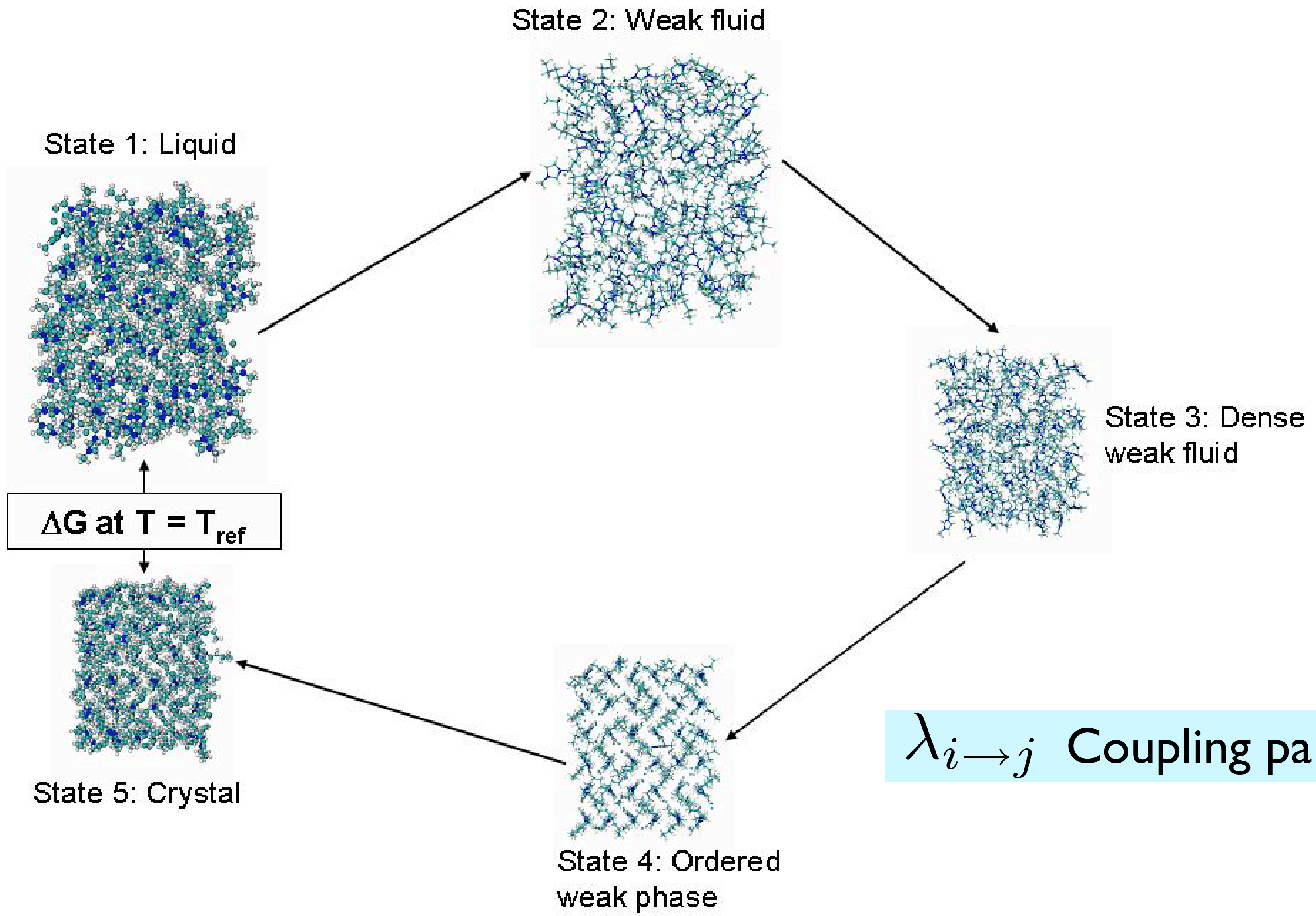


$\lambda_{i \to j}$ Coupling parameter from state $i \to j$

fix/alchemy, lj/cut/alchemy, coul/long/alchemy, pppm/alchemy

$$\Delta A_{i \to j} = \int_0^1 \left\langle \frac{\partial U}{\partial \lambda} \right\rangle_\lambda d\lambda \qquad \Delta A_{2 \to 3} = \int_{V^\ell}^{V^S} - \langle P \rangle \, dV \qquad \Delta G_{s-\ell} = \sum_{i,j} \Delta A_{i \to j}$$

Pseudosupercritical path method



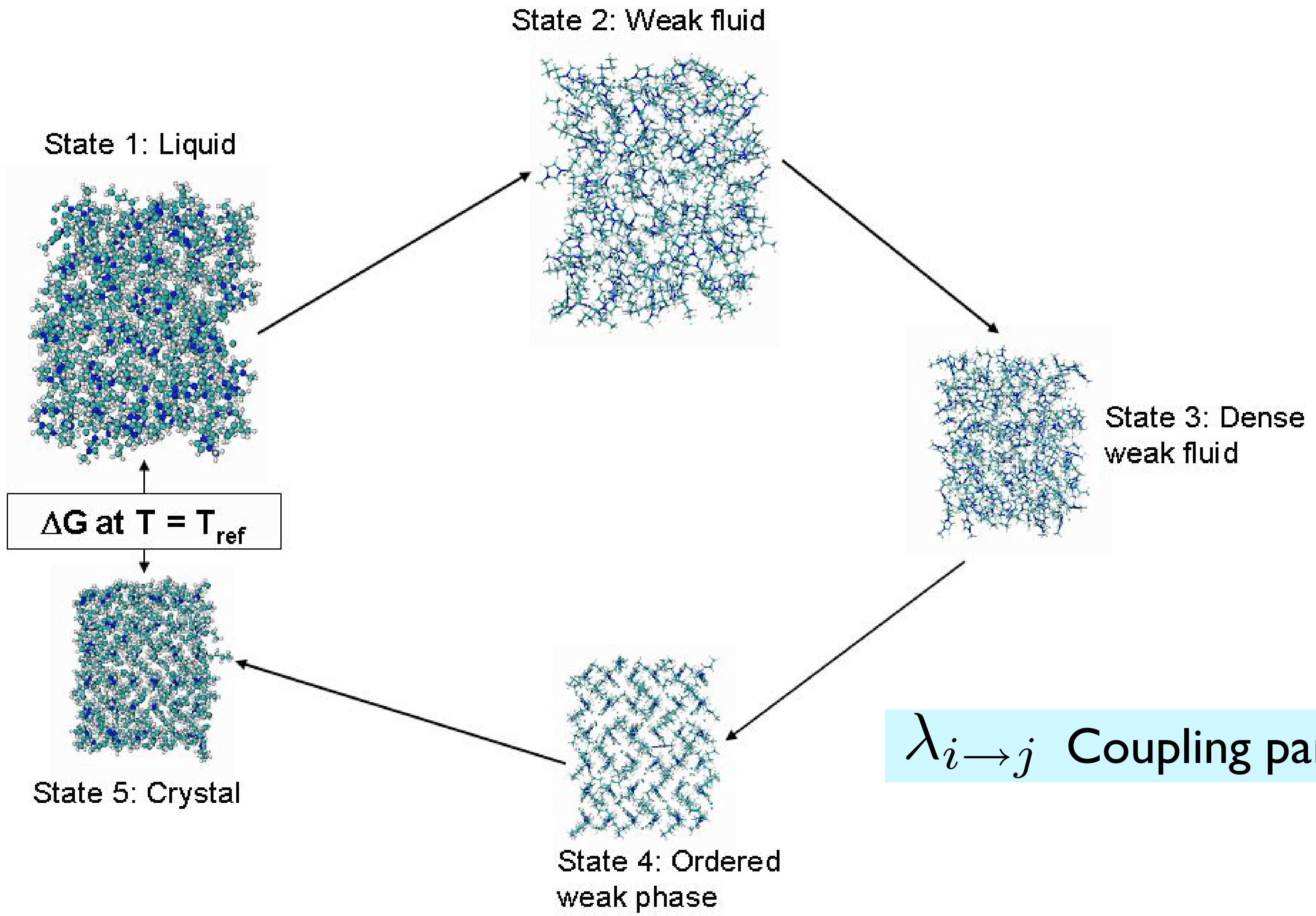
$\lambda_{i \to j}$ Coupling parameter from state $i \to j$

fix/alchemy, lj/cut/alchemy, coul/long/alchemy, pppm/alchemy

$$U_{4\to5}(\lambda) = [\eta + \lambda(1-\eta)]^m U^{VDW} + [\eta + \lambda(1-\eta)]^n U^{ELEC} + U^{NS} - (1-\lambda)\sum_i \sum_j a_{ij} \exp(-b_{ij} r_{ij}^2)$$

$$\Delta A_{i\to j} = \int_0^1 \left\langle \frac{\partial U}{\partial \lambda} \right\rangle_\lambda d\lambda \qquad \Delta A_{2\to3} = \int_{V^\ell}^{V^S} -\langle P \rangle\, dV \qquad \Delta G_{s-\ell} = \sum_{i,j} \Delta A_{i\to j}$$

Pseudosupercritical path method

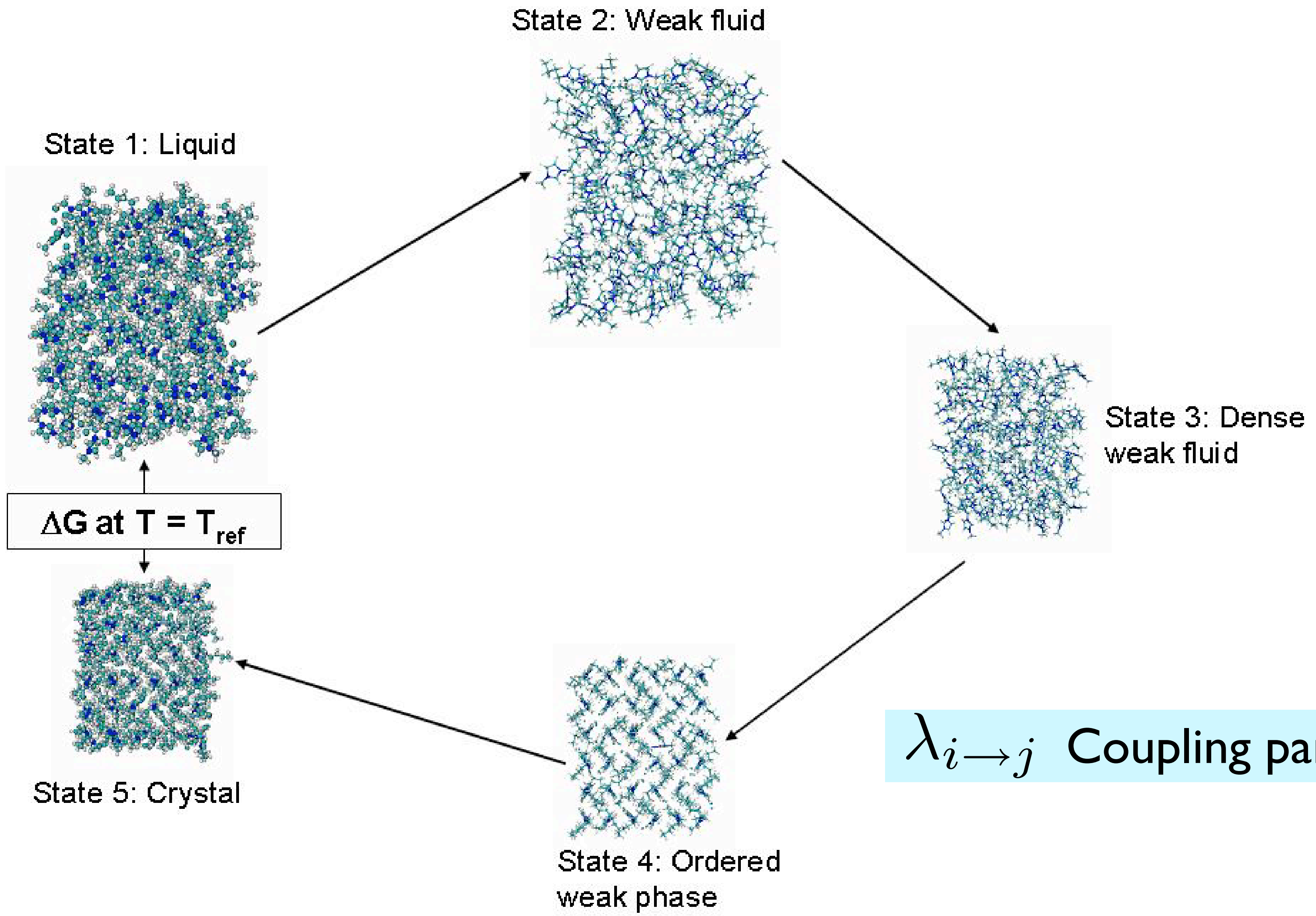


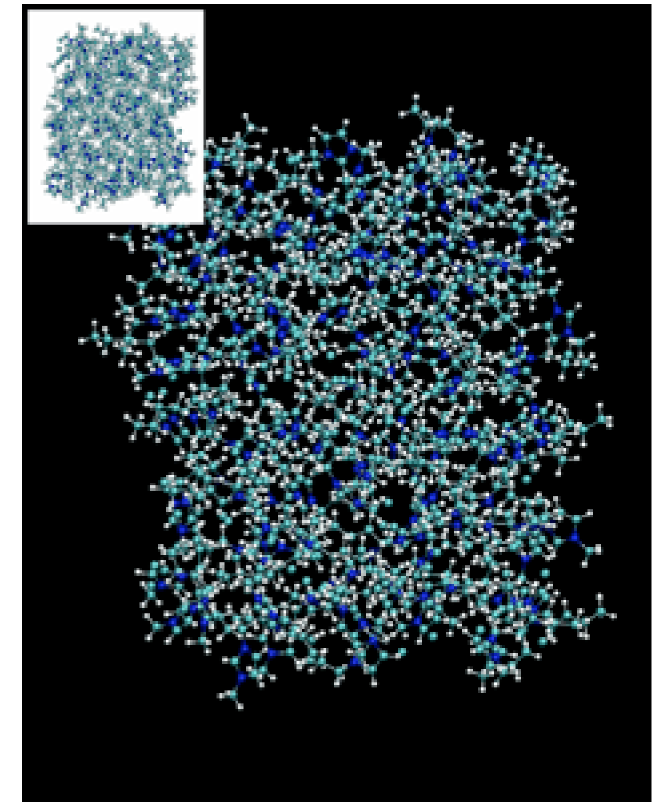
$\lambda_{i \to j}$ Coupling parameter from state $i \to j$

fix/alchemy, lj/cut/alchemy, coul/long/alchemy, pppm/alchemy

$$\Delta A_{i \to j} = \int_0^1 \left\langle \frac{\partial U}{\partial \lambda} \right\rangle_\lambda d\lambda \qquad \Delta A_{2 \to 3} = \int_{V^\ell}^{V^S} -\langle P \rangle \, dV \qquad \Delta G_{s-\ell} = \sum_{i,j} \Delta A_{i \to j}$$

Pseudosupercritical path method



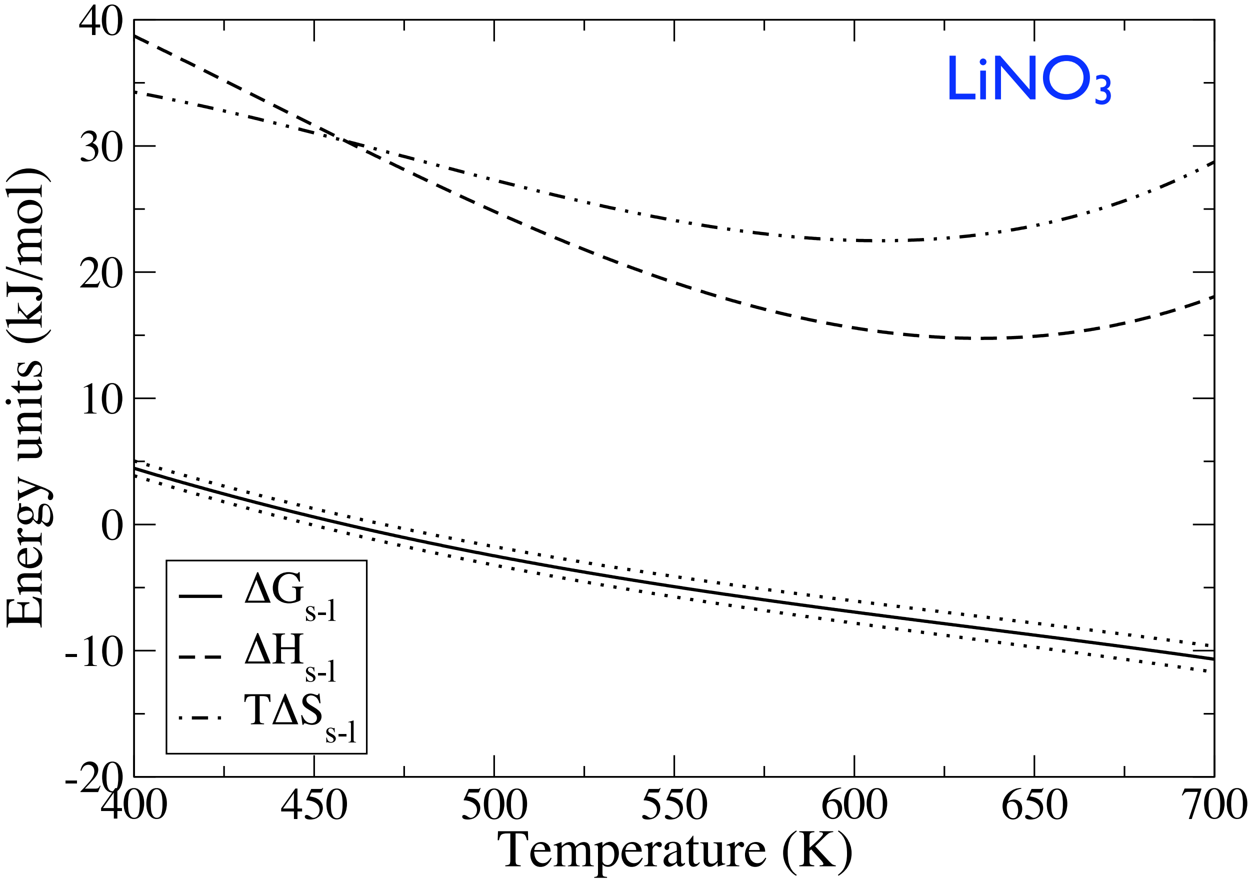


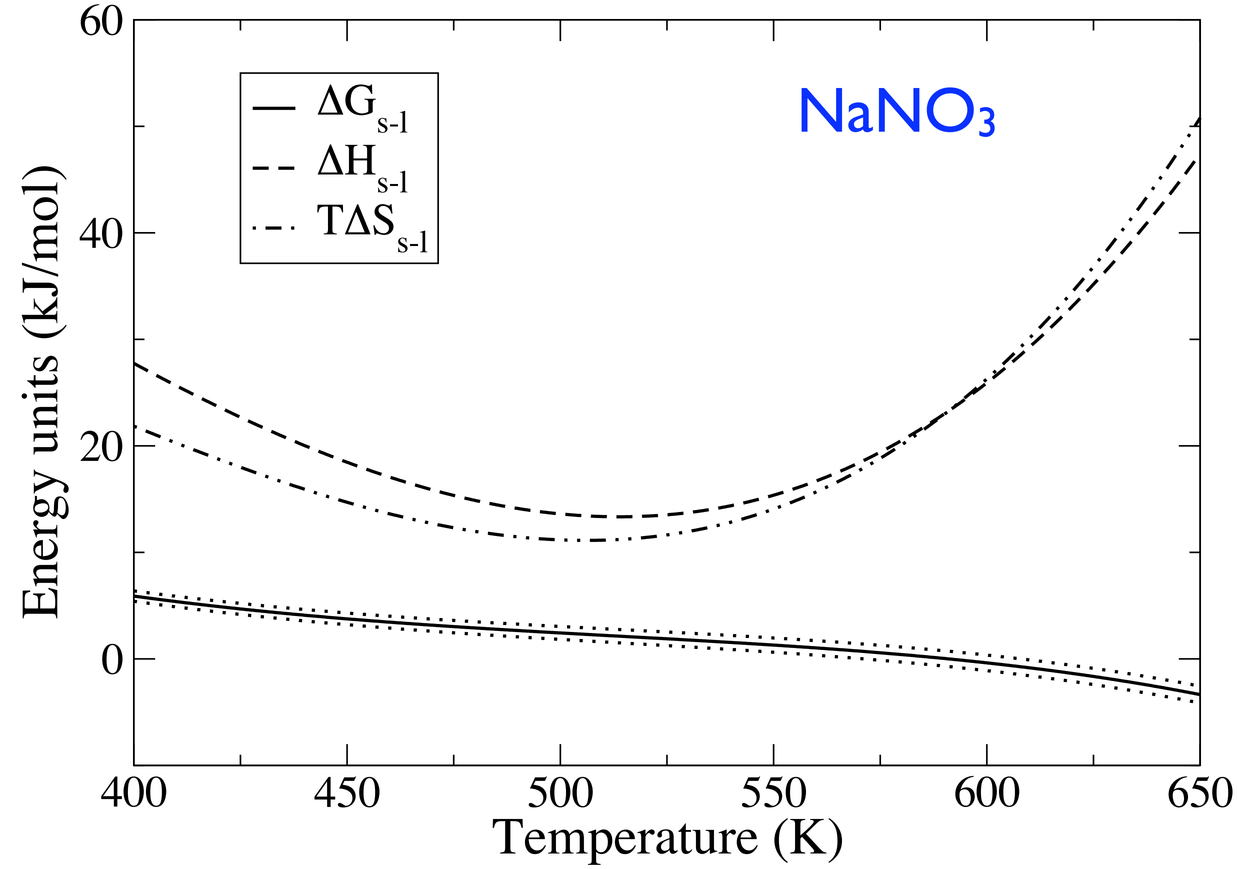
$\lambda_{i \to j}$ Coupling parameter from state $i \to j$

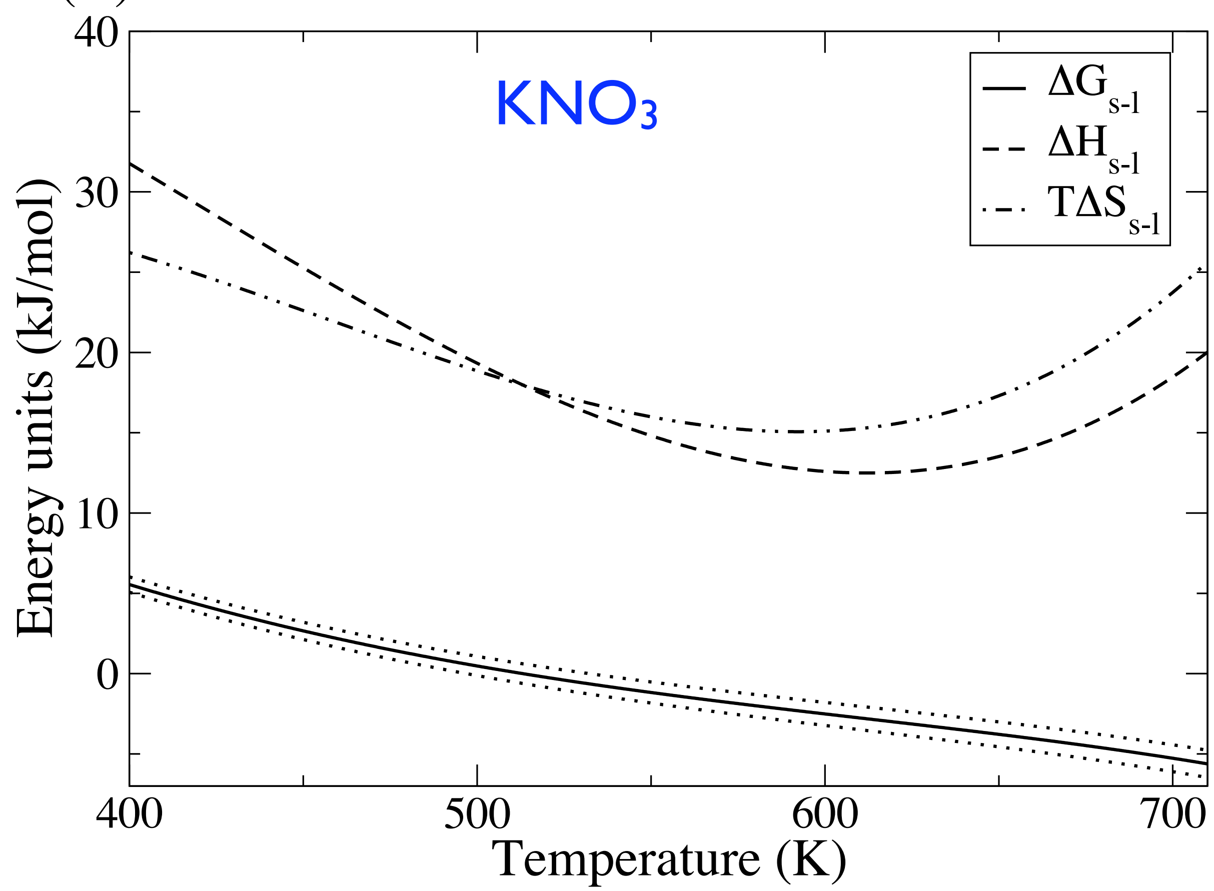
fix/alchemy, lj/cut/alchemy, coul/long/alchemy, pppm/alchemy

$$\Delta A_{i \to j} = \int_0^1 \left\langle \frac{\partial U}{\partial \lambda} \right\rangle_\lambda d\lambda \qquad \Delta A_{2 \to 3} = \int_{V^\ell}^{V^S} - \langle P \rangle \, dV \qquad \Delta G_{s-\ell} = \sum_{i,j} \Delta A_{i \to j}$$

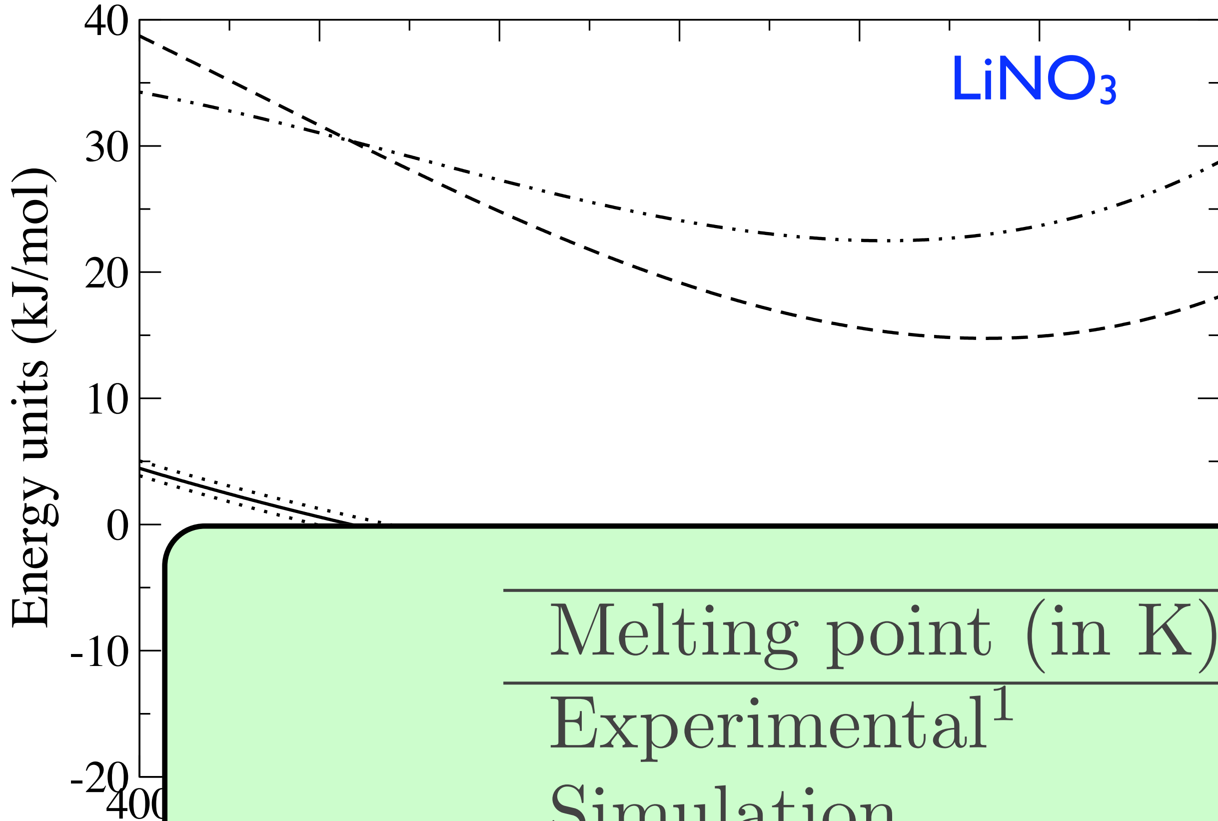
Contributions to $\Delta G_{s\text{-}l}$: nitrate salts

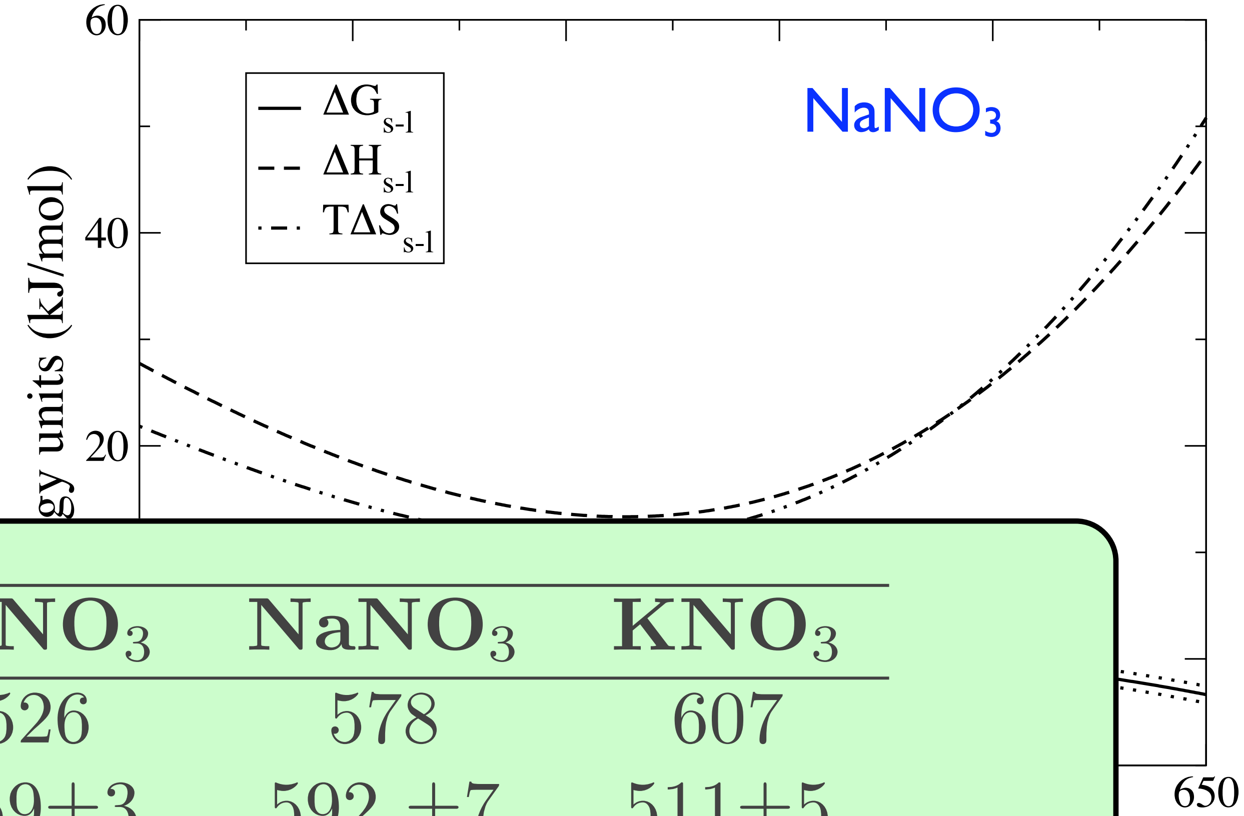






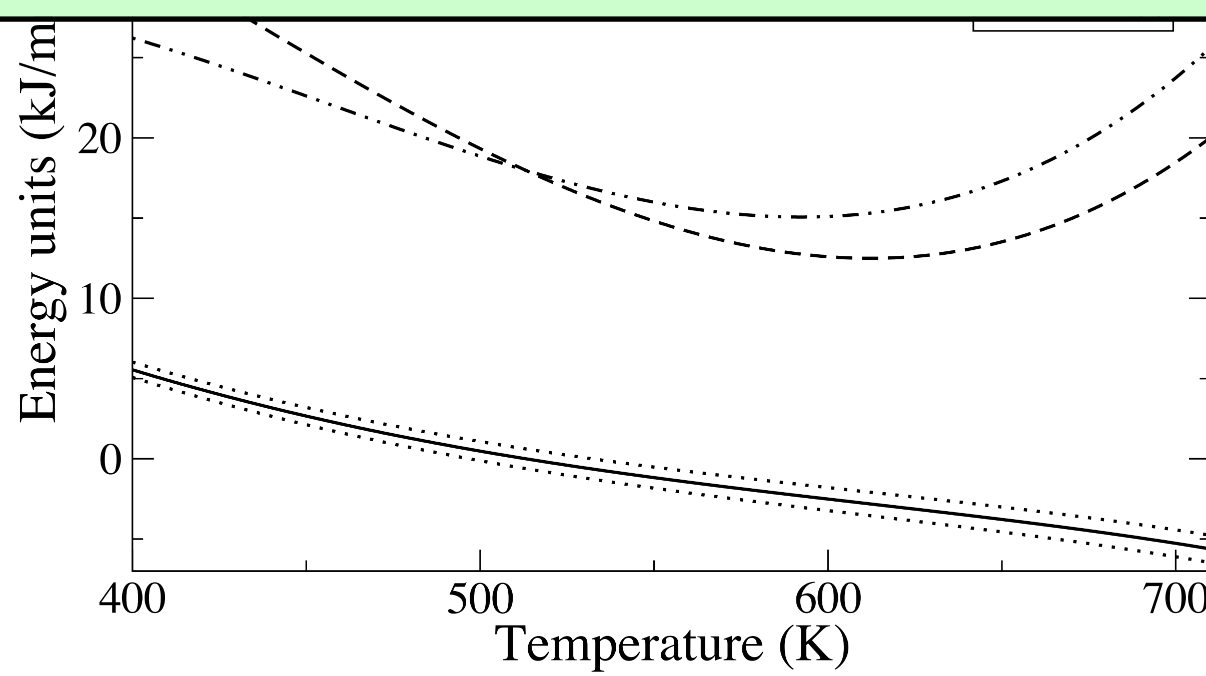
Contributions to $\Delta G_{s\text{-}l}$: nitrate salts



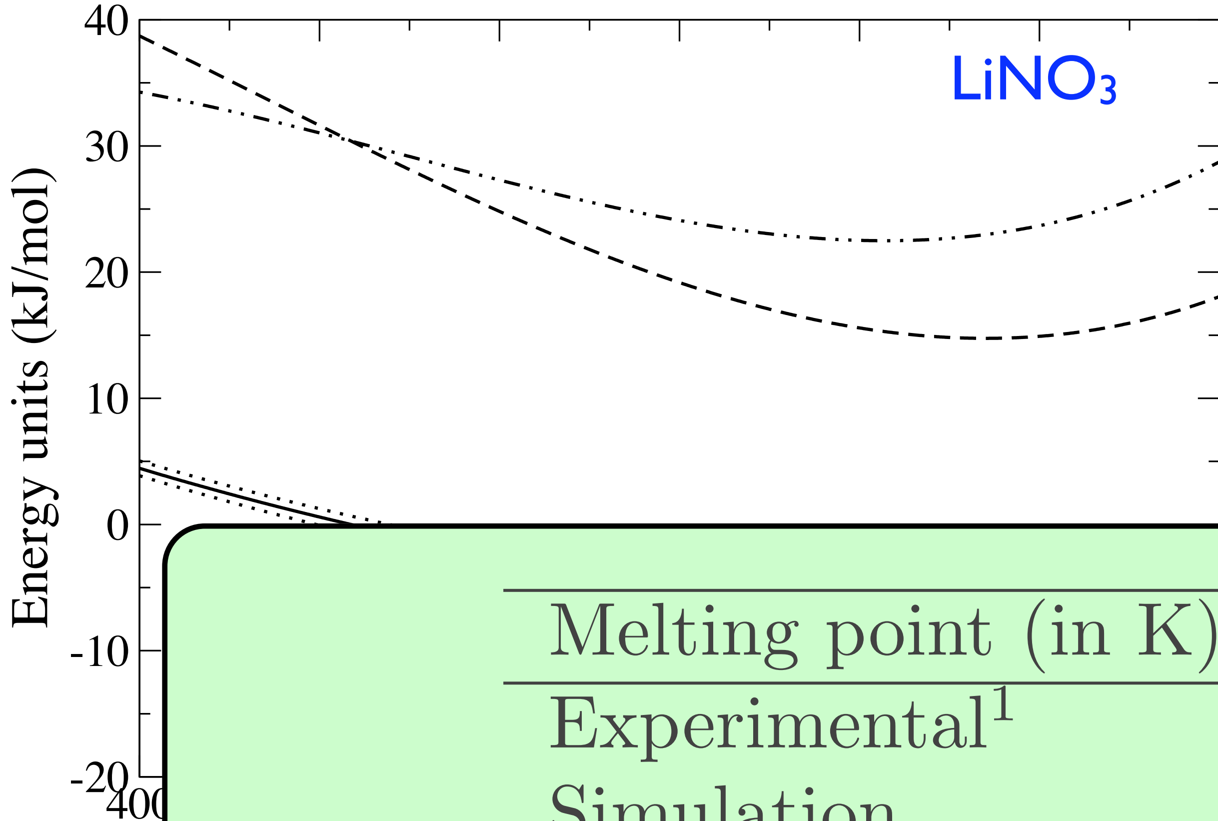


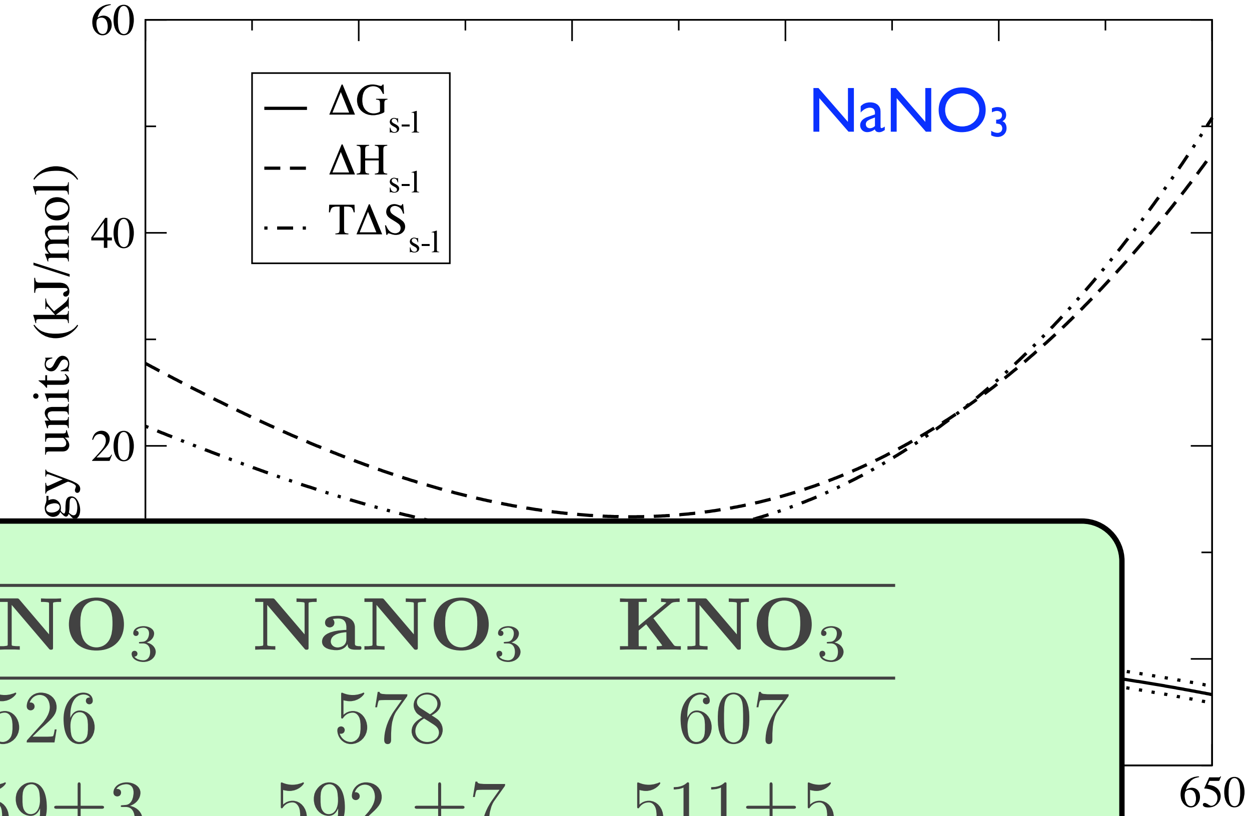
Melting point (in K)	**$LiNO_3$**	**$NaNO_3$**	**KNO_3**
Experimental[1]	526	578	607
Simulation	459±3	592 ±7	511±5

[1]: Experimental values were obtained from:
Takahashi Y, Sakamoto R, Kamimoto M, Int. J. Thermophys., **9**, No. 6, 1081-1090 (1988)



Contributions to $\Delta G_{s\text{-}l}$: nitrate salts



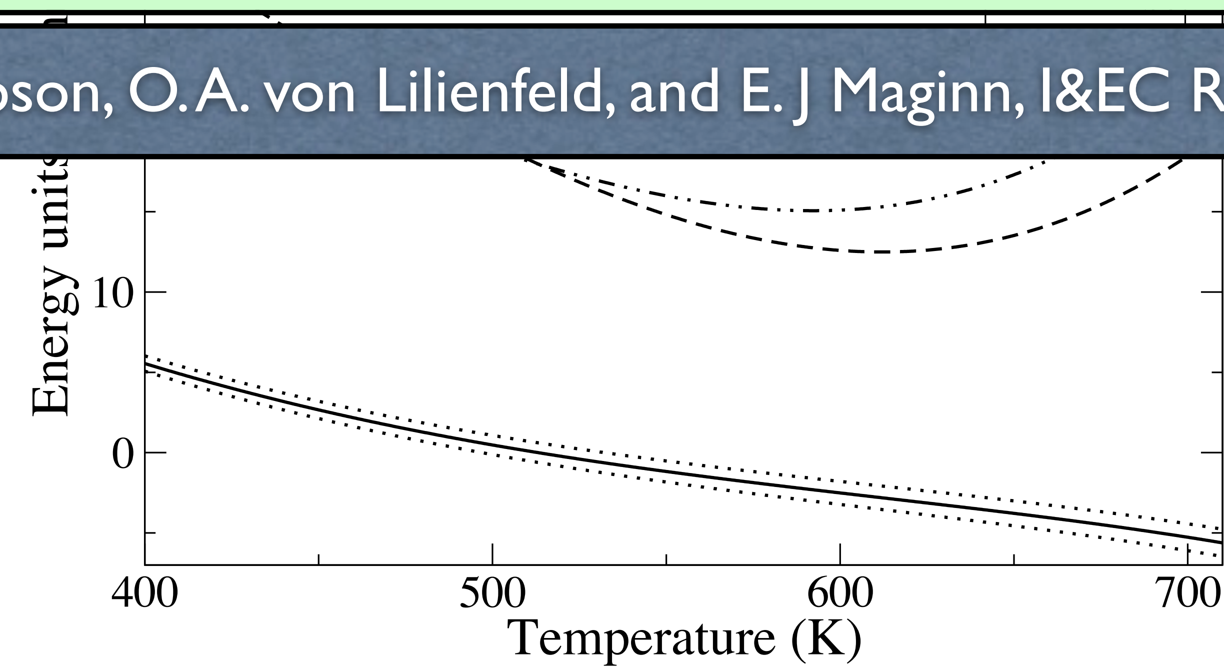


Melting point (in K)	$LiNO_3$	$NaNO_3$	KNO_3
Experimental[1]	526	578	607
Simulation	459±3	592 ±7	511±5

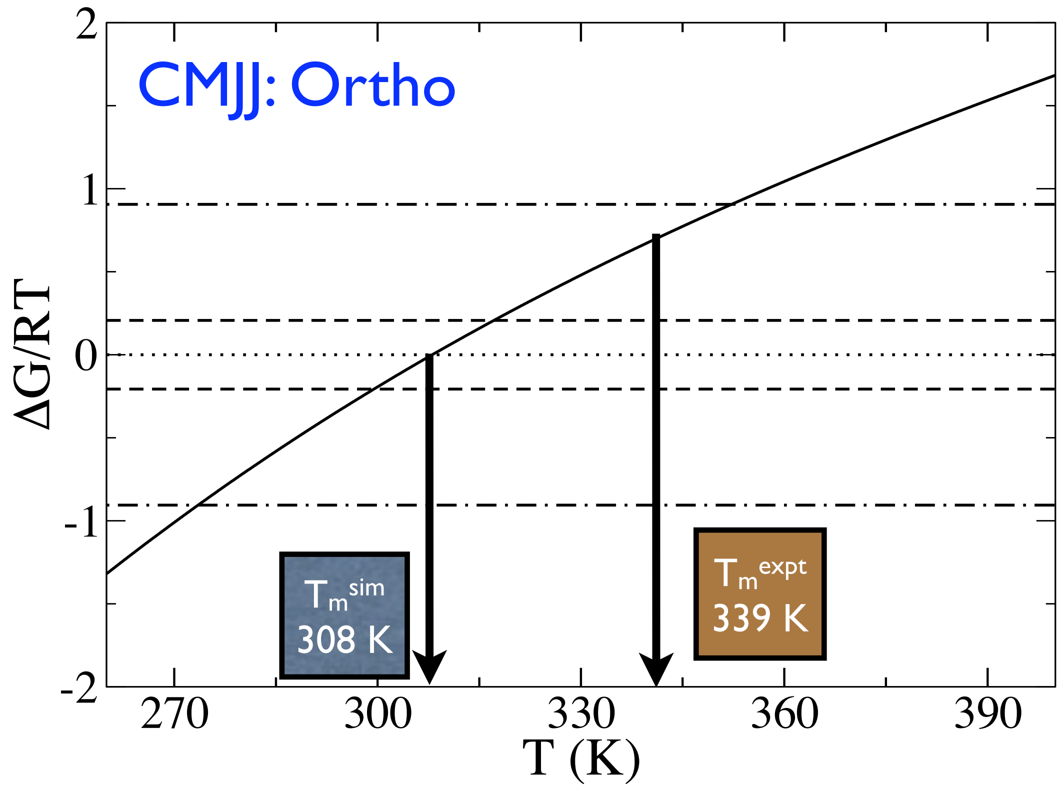
[1]: Experimental values were obtained from:

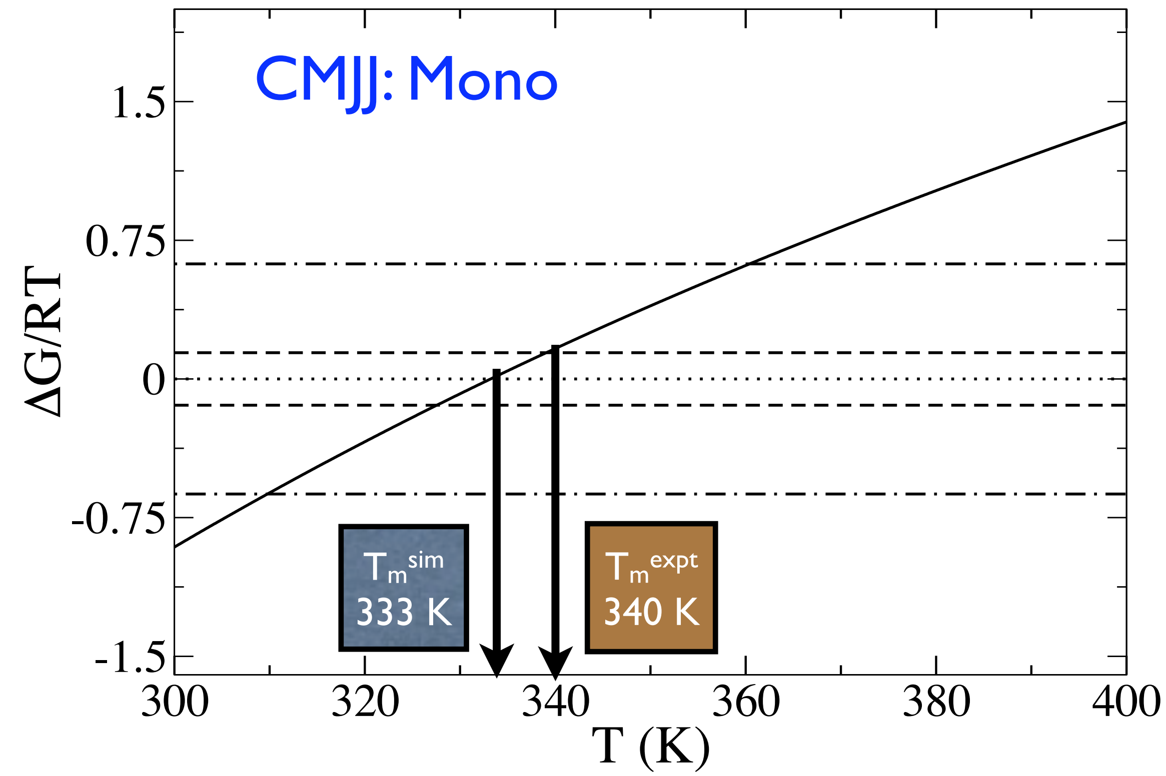
Takahashi Y, Sakamoto R, Kamimoto M, Int. J. Thermophys., **9**, No. 6, 1081-1090 (1988)

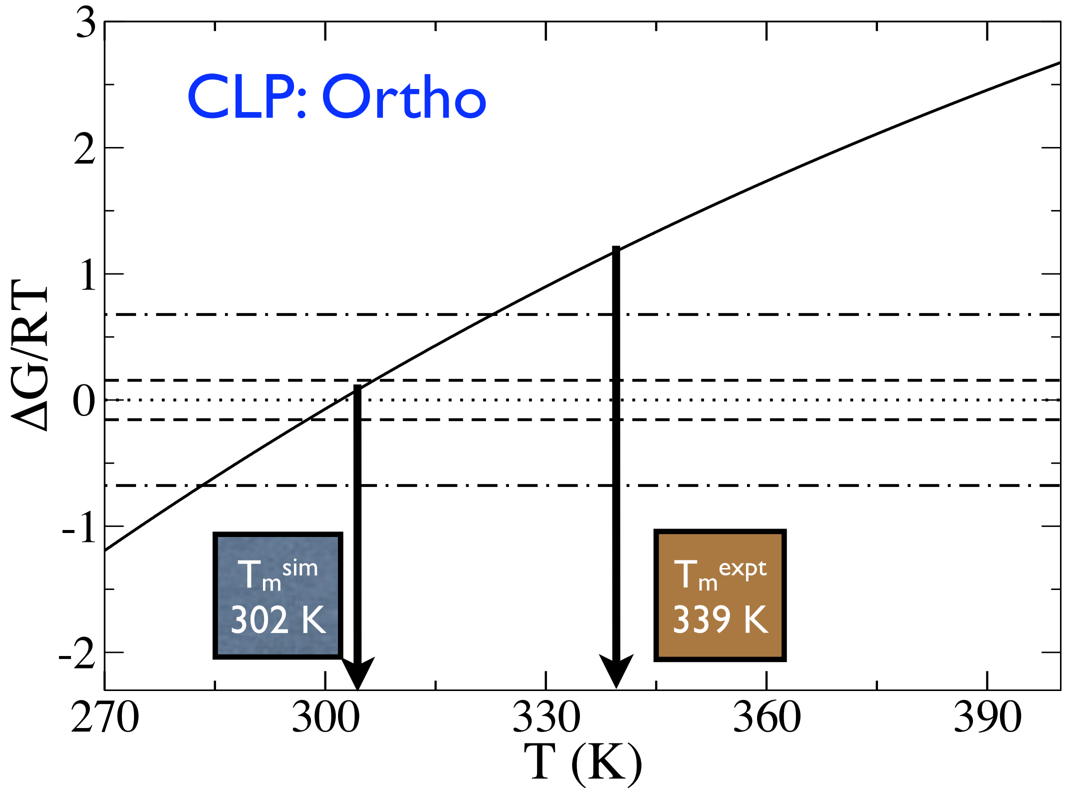
S. Jayaraman, A. Thompson, O. A. von Lilienfeld, and E. J Maginn, I&EC Res., **49**, 559-571 (2010)

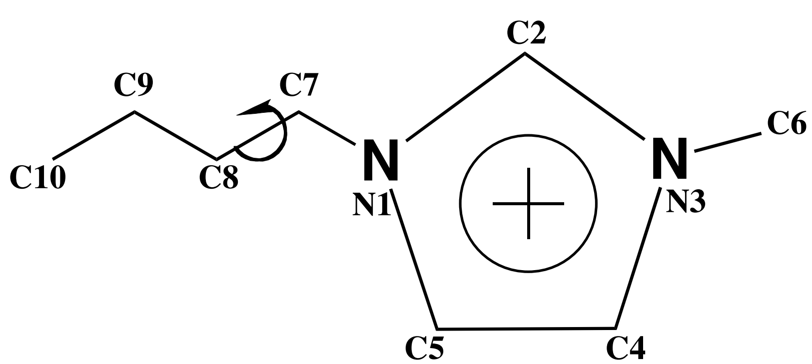


Melting point of [C$_4$mim][Cl]



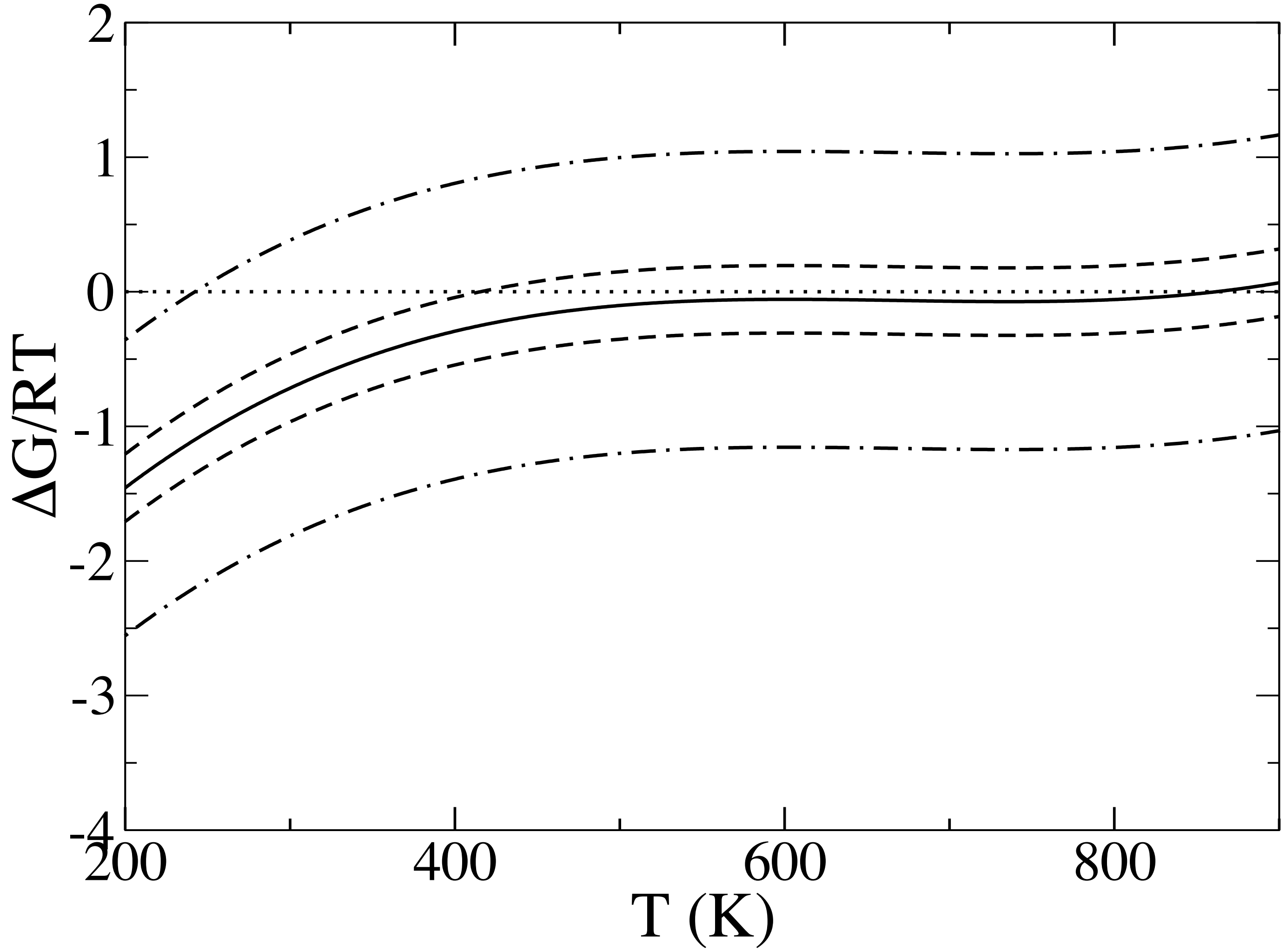






S. Jayaraman and E. J. Maginn, J. Chem. Phys. **127**, 214504 (2007)

Crystal polymorph stabilities [C_4mim][Cl]

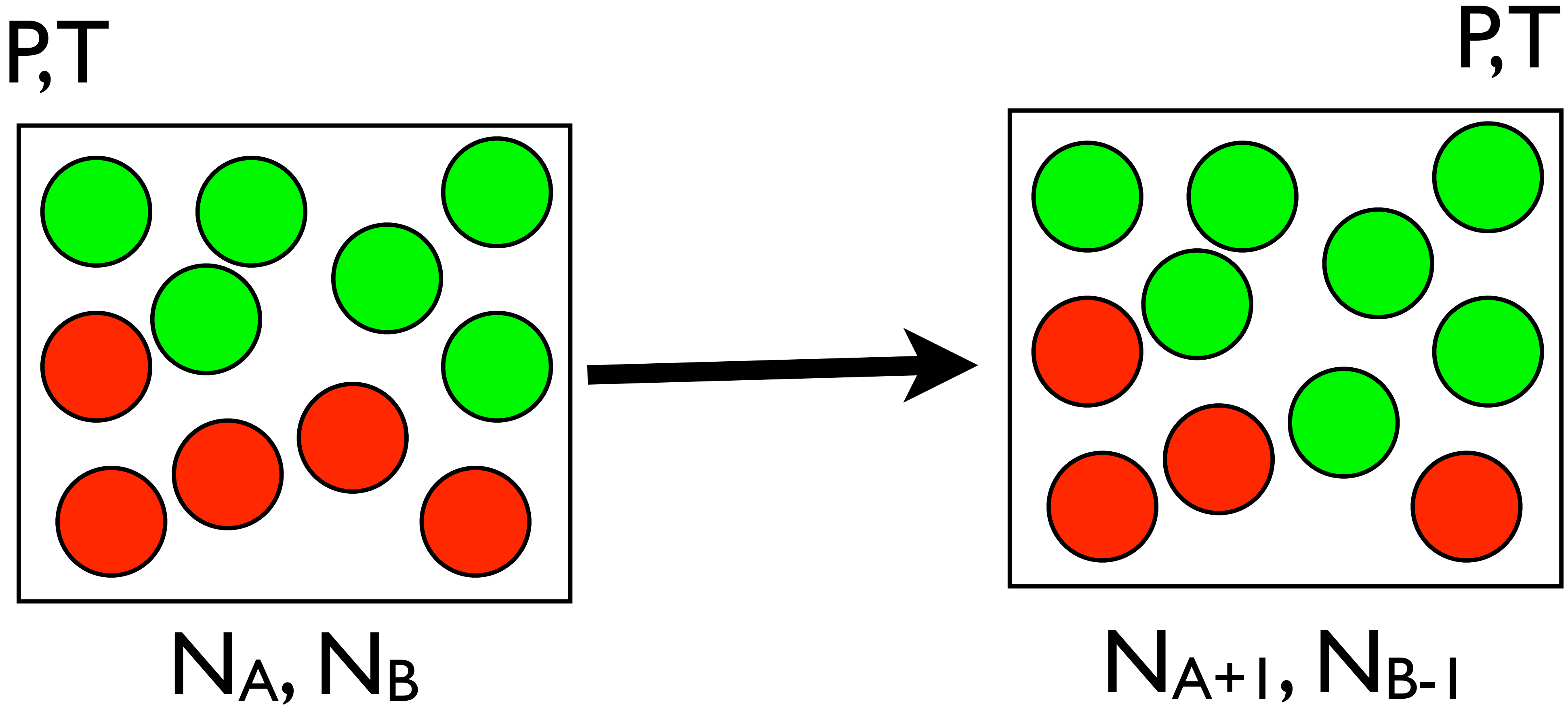


Computed Gibbs free energy difference between monoclinic and orthorhombic polymorphs of [C_4mim][Cl] using the CMJJ potential

- Monoclinic thermodynamically stable relative to orthorhombic form at all temperatures below melting points of either polymorph.
- Free energy differences within accuracy of simulations

S. Jayaraman and E. J. Maginn, J. Chem. Phys. **127**, 214504 (2007)

Free energy of binary mixtures



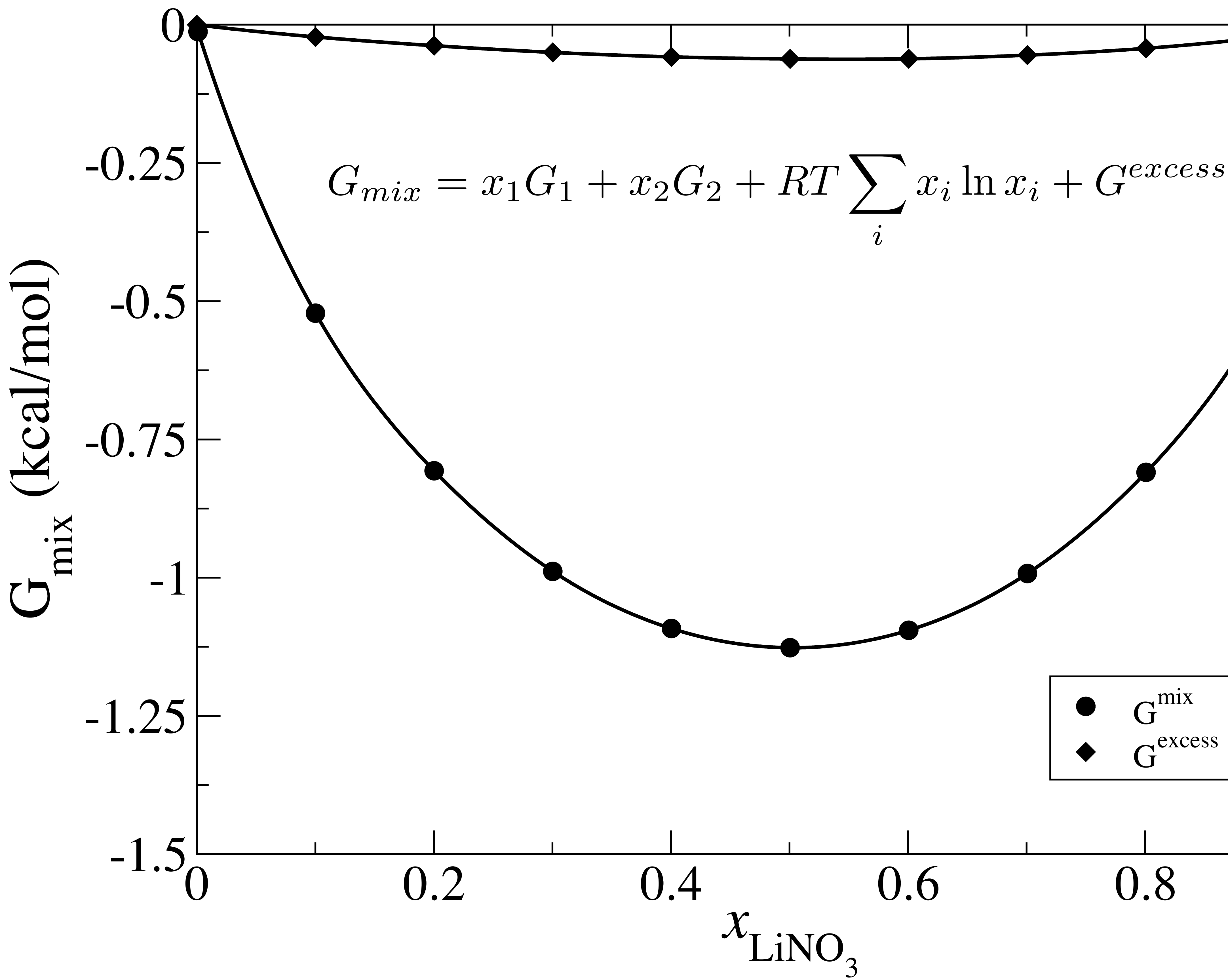
$$Z_{N_A,N_B,T,P} = Z^{id}_{N_A,N_B,T,P} \int_0^\infty dV \exp(-\beta PV) \int_V \dots \int_V d\mathbf{r}^N \exp(-\beta U(N_A, N_B))$$

$$Z^{id}_{N_A,N_B,T,P} = \frac{1}{N_A! N_B!} q_A^{N_A} q_B^{N_B}$$

$$\frac{Z_{N_{A+1},N_{B-1},T,P}}{Z_{N_A,N_B,T,P}} = \frac{Z^{id}_{N_{A+1},N_{B-1},T,P}}{Z^{id}_{N_A,N_B,T,P}} \langle \exp(-\beta\Delta U)^{A+B-} \rangle_{N_A,N_B,P,T}$$

$$\frac{\partial g}{\partial x_A} = -k_B T \ln\left(\frac{q_A}{q_B}\right) + k_B T \ln\left(\frac{x_A}{1-x_A}\right) - k_B T \ln\langle \exp(-\beta\Delta U)\rangle_{N_A,N_B}$$

Free energy of binary mixtures



Summary

- Implemented a rigorous method for computing the melting point and crystal phase stability in LAMMPS.
- Verified implementation and computed melting points of alkali nitrate salts using LAMMPS.
- Thermodynamic Integration can be used in alchemical transformations - free energies of mixtures.

Acknowledgements

- University of Notre Dame: Prof. Ed Maginn
    - Maginn group members
    - Center for Research Computing
    - Air Force Office of Scientific Research
- Sandia National Labs: Steve Plimpton, Aidan Thompson, Anatole Lilienfeld, Nate Siegel, Bob Bradshaw, John Aidun

•S. Jayaraman and E. J. Maginn, J. Chem. Phys. **127**, 214504 (2007)

•S. Jayaraman, A. Thompson, O. A. von Lilienfeld, and E. J Maginn, I&EC Res., **49**, 559-571 (2010)

NaCl melting point calculations