Molten salt eutectics from atomistic alchemical simulations

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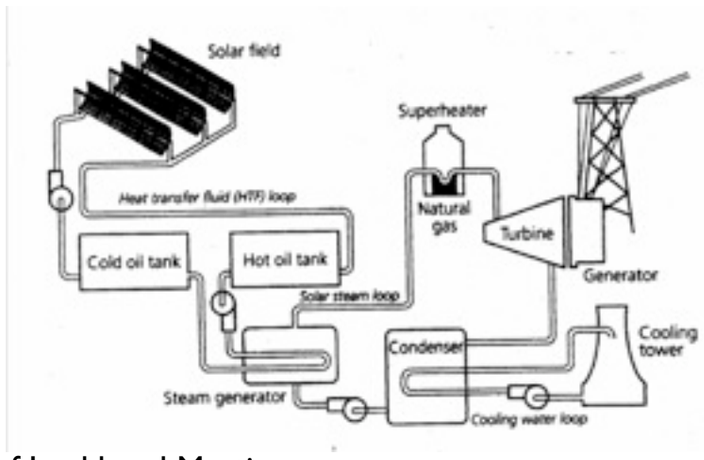
Lammps workshop
August 11, 2011



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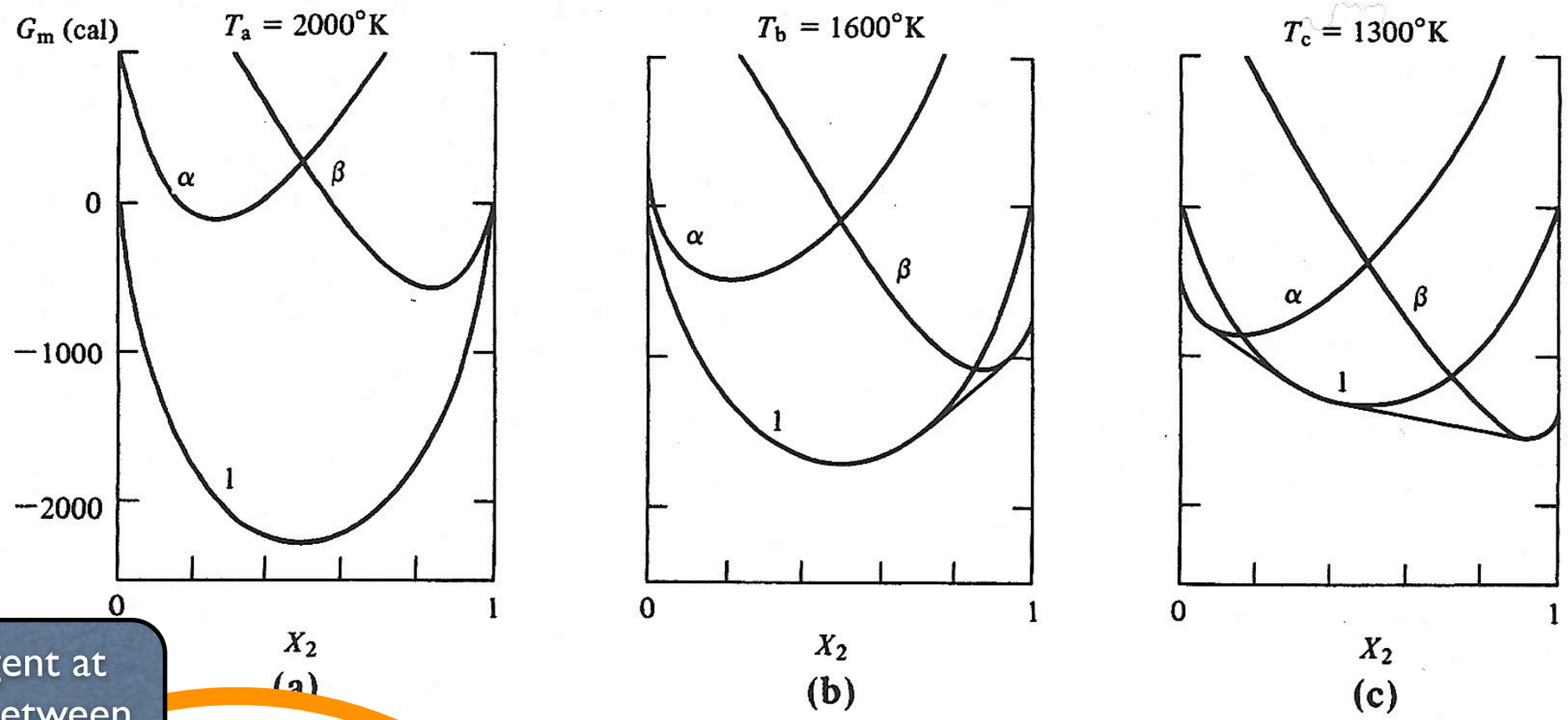
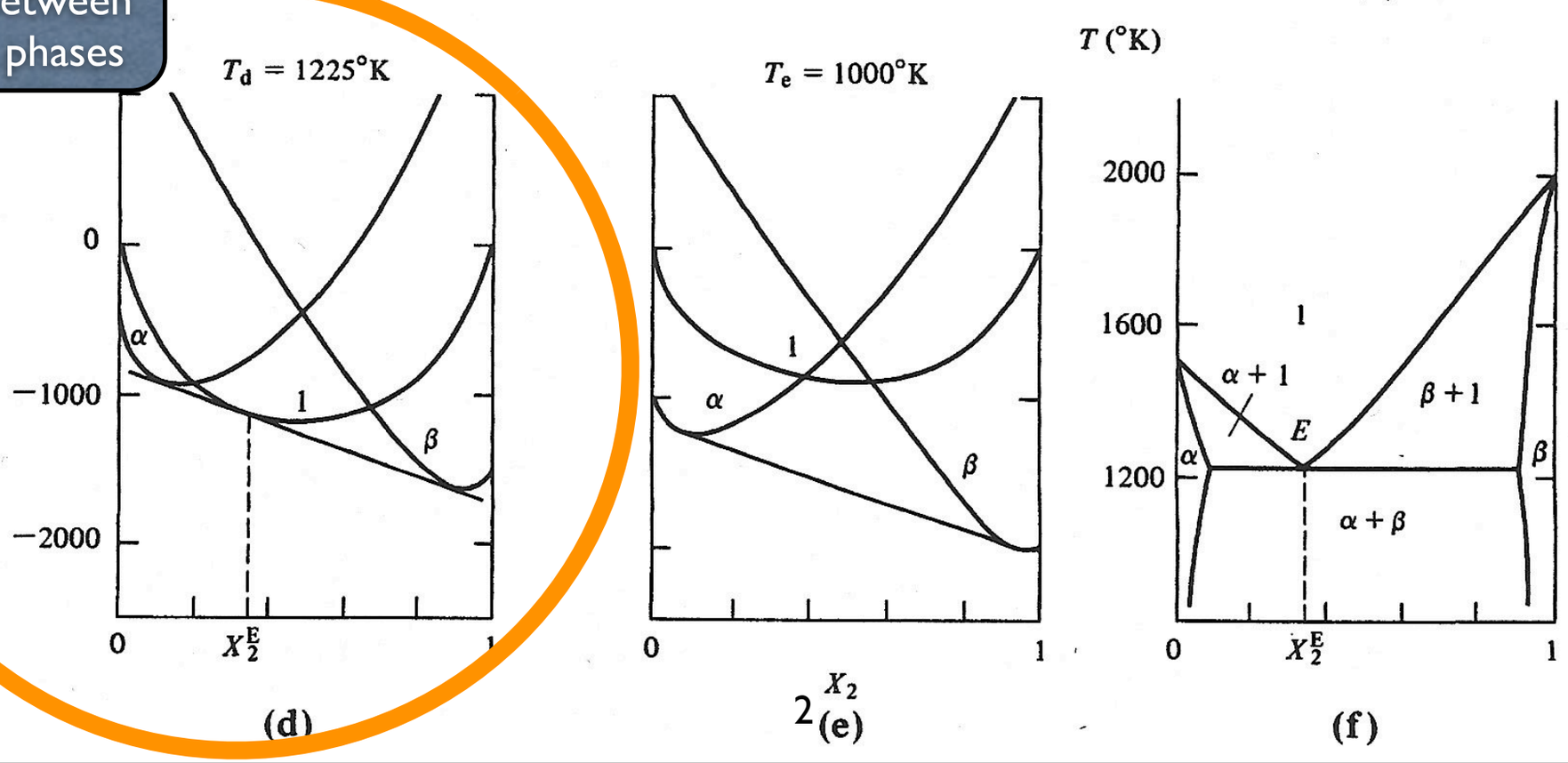
Chemical thermodynamics of Materials - C. H. P. Lupis
North-Holland, 1983



Common tangent at eutectic point between liquid and solid phases



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Computing the free energy of a liquid mixture

$$G_{mix} = x_A G_A + x_B G_B + RT \sum_{i=A,B} x_i \ln x_i + G^{excess}$$

Free energy of binary mixture at T, P, x_A, x_B

Free energy of Pure species A at T,P

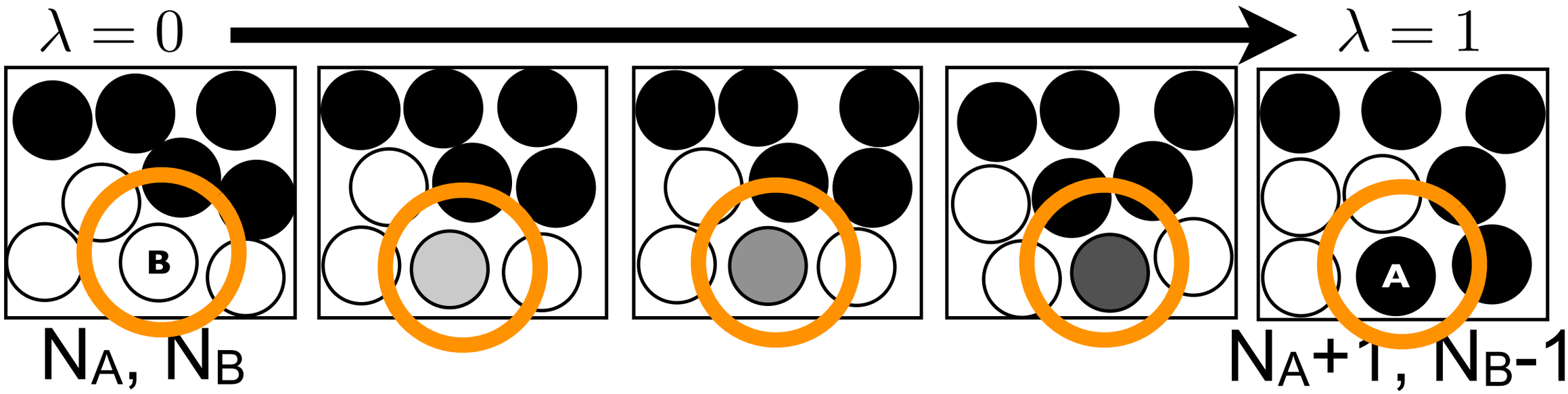
Free energy of Pure species B at T,P

Free energy contribution arising from entropy of mixing

Residual contribution from energetic interaction between molecules of A and B.

Alchemical Transformation

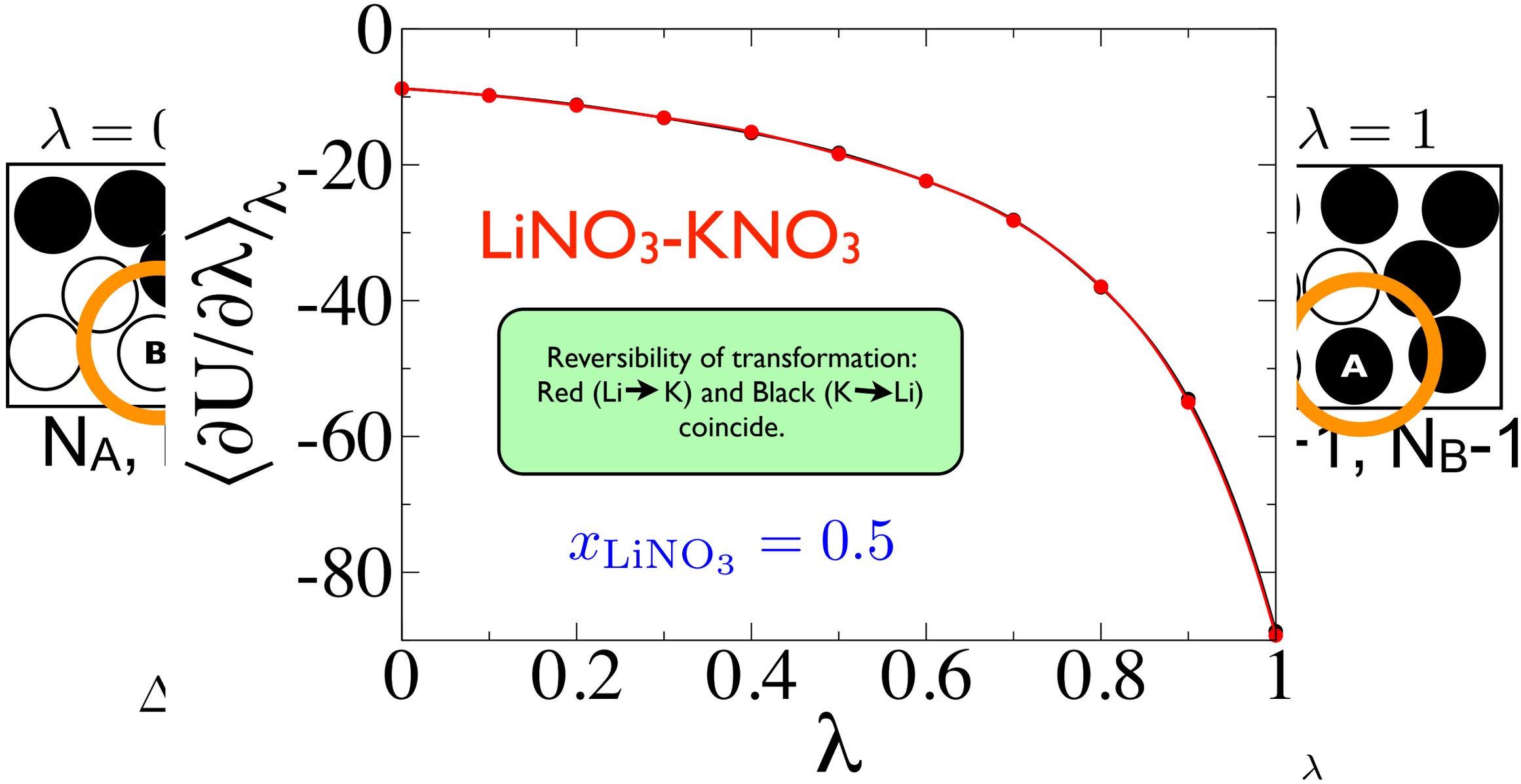
$$\frac{\partial G^{excess}}{\partial x} \approx \frac{\Delta G}{\Delta x}$$



$$u_{ij}(\lambda) = \lambda u_{i\mathrm{A}} + (1-\lambda) u_{i\mathrm{B}}$$

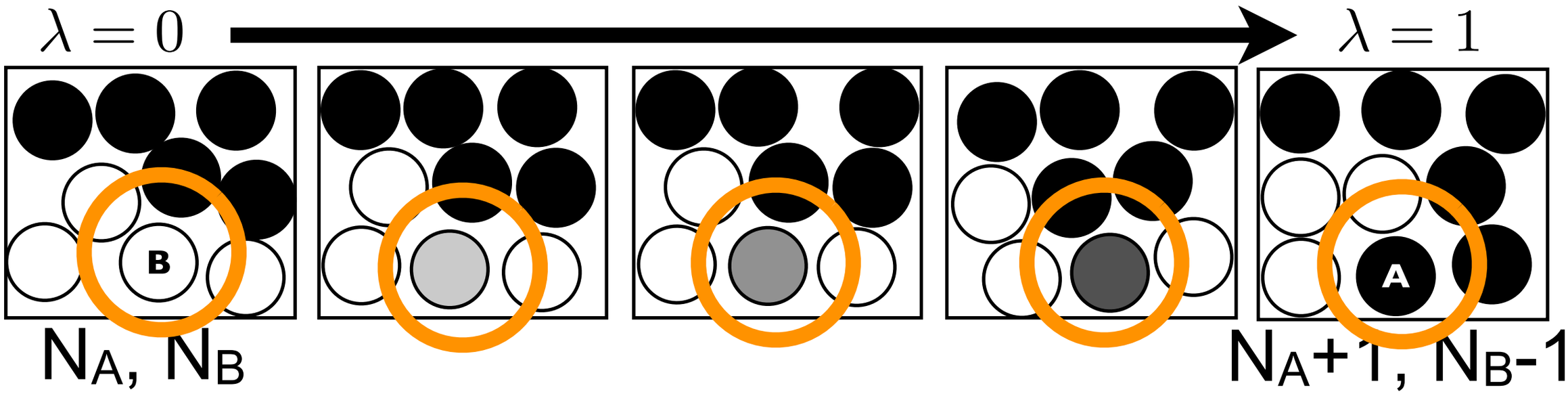
$$\Delta\mu_{\mathrm{AB}} = \int_0^1 d\lambda \left\langle \frac{\partial U}{\partial \lambda} \right\rangle_\lambda = \int_0^1 d\lambda \left\langle \sum_i (u_{i\mathrm{A}} - u_{i\mathrm{B}}) \right\rangle_\lambda$$

Alchemical Transformation



Alchemical Transformation

$$\frac{\partial G^{excess}}{\partial x} \approx \frac{\Delta G}{\Delta x}$$



$$u_{ij}(\lambda) = \lambda u_{i\mathrm{A}} + (1-\lambda) u_{i\mathrm{B}}$$

$$\Delta\mu_{\mathrm{AB}} = \int^{1} d\lambda \left\langle \frac{\partial U}{\partial \lambda} \right\rangle_{\lambda} = \int^{1} d\lambda \left\langle \sum (u_{i\mathrm{A}} - u_{i\mathrm{B}}) \right\rangle$$

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fix 1 all adapt 1 pair lj/cut epsilon 5 * v_lj scale yes
compute 1 all ti lj/cut 5 v_lj v_dlj tail v_lj v_dlj
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Excess free energies from $\Delta\mu_{AB}$

Binary:

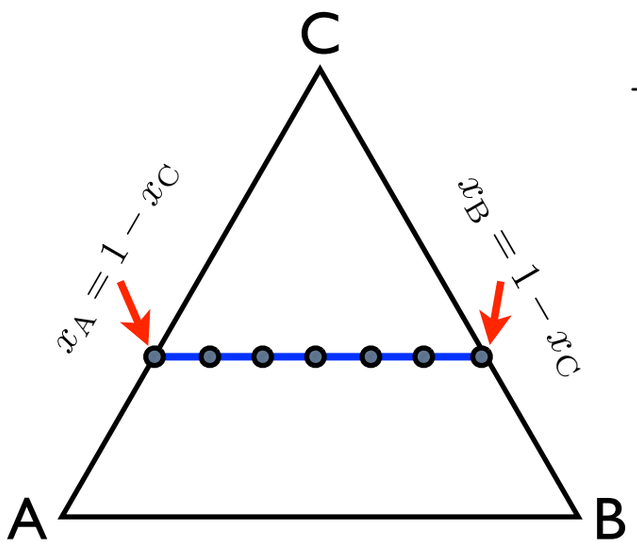
$$g_\ell^{ex}(x_\mathrm{A}, x_\mathrm{B}) = \int_0^{x_\mathrm{A}} dx'_\mathrm{A}\ \Delta\mu_{\mathrm{AB}}(x'_\mathrm{A}) - x_\mathrm{A} \int_0^1 dx'_\mathrm{A} \Delta\mu_{\mathrm{AB}}(x'_\mathrm{A})$$

Ternary:

Area under $\Delta\mu_{AB}$

$$g_\ell^{ex}(x_\mathrm{A}, x_\mathrm{B}, x_\mathrm{C}) = \int_0^{x_\mathrm{A}} dx'_\mathrm{A} \Delta\mu_{\mathrm{AB}}(x'_\mathrm{A}, x_\mathrm{C}) - \frac{x_\mathrm{A}}{x_\mathrm{A}+x_\mathrm{B}} \int_0^{x_\mathrm{A}+x_\mathrm{B}} dx'_\mathrm{A} \Delta\mu_{\mathrm{AB}}(x'_\mathrm{A}, x_\mathrm{C})$$

$$+ \frac{x_\mathrm{A}}{x_\mathrm{A}+x_\mathrm{B}} g^{ex}_{\mathrm{AC}\ell}(x_\mathrm{C}) + \frac{x_\mathrm{B}}{x_\mathrm{A}+x_\mathrm{B}} g^{ex}_{\mathrm{BC}\ell}(x_\mathrm{C})$$

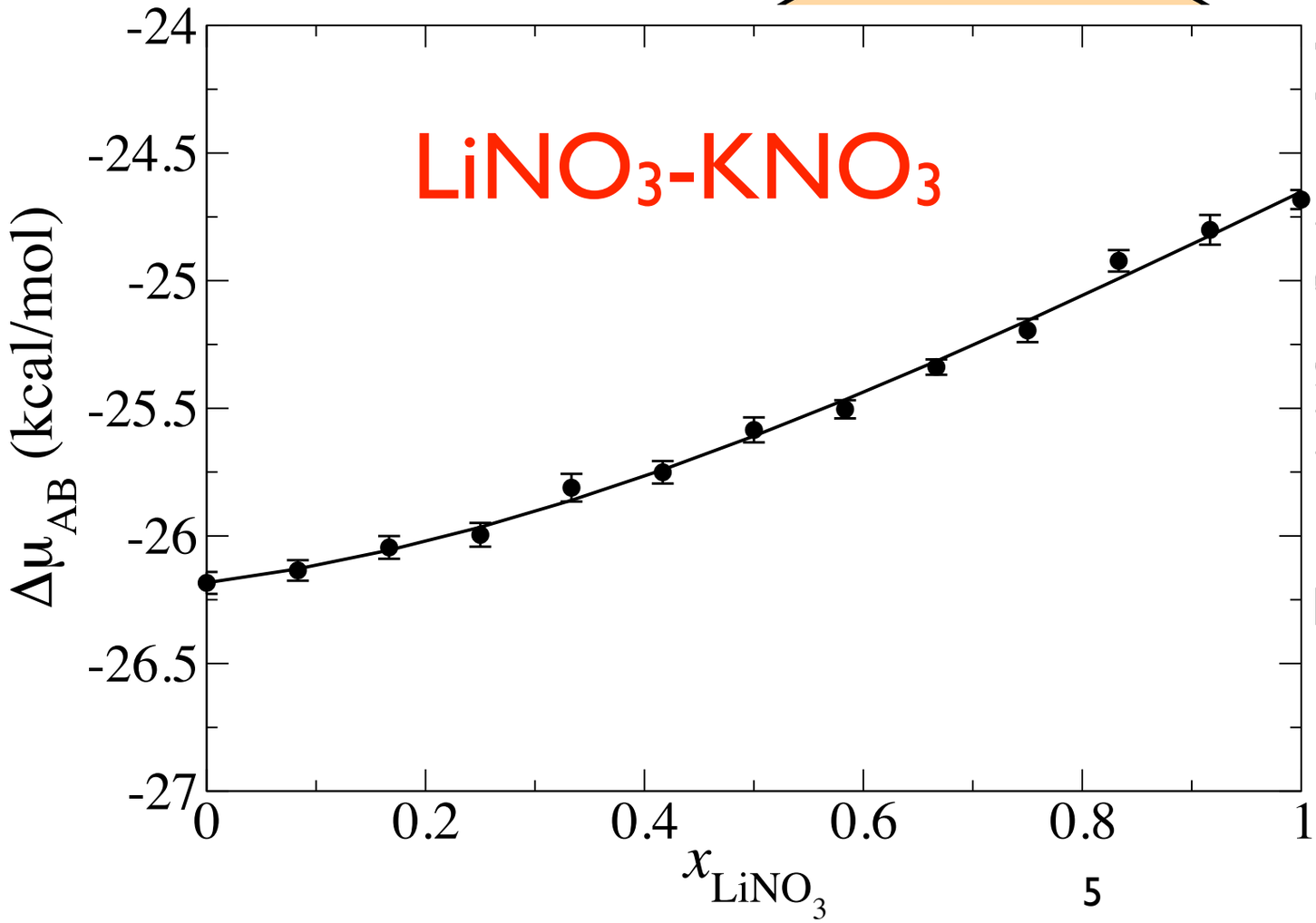


At each x_C, alchemical changes conducted at x_A mesh points

Excess free energies from $\Delta\mu_{AB}$

Binary:

$$g_\ell^{ex}(x_\mathrm{A}, x_\mathrm{B}) = \int_0^{x_\mathrm{A}} dx'_\mathrm{A}\ \Delta\mu_{\mathrm{AB}}(x'_\mathrm{A}) - x_\mathrm{A} \int_0^1 dx'_\mathrm{A} \Delta\mu_{\mathrm{AB}}(x'_\mathrm{A})$$

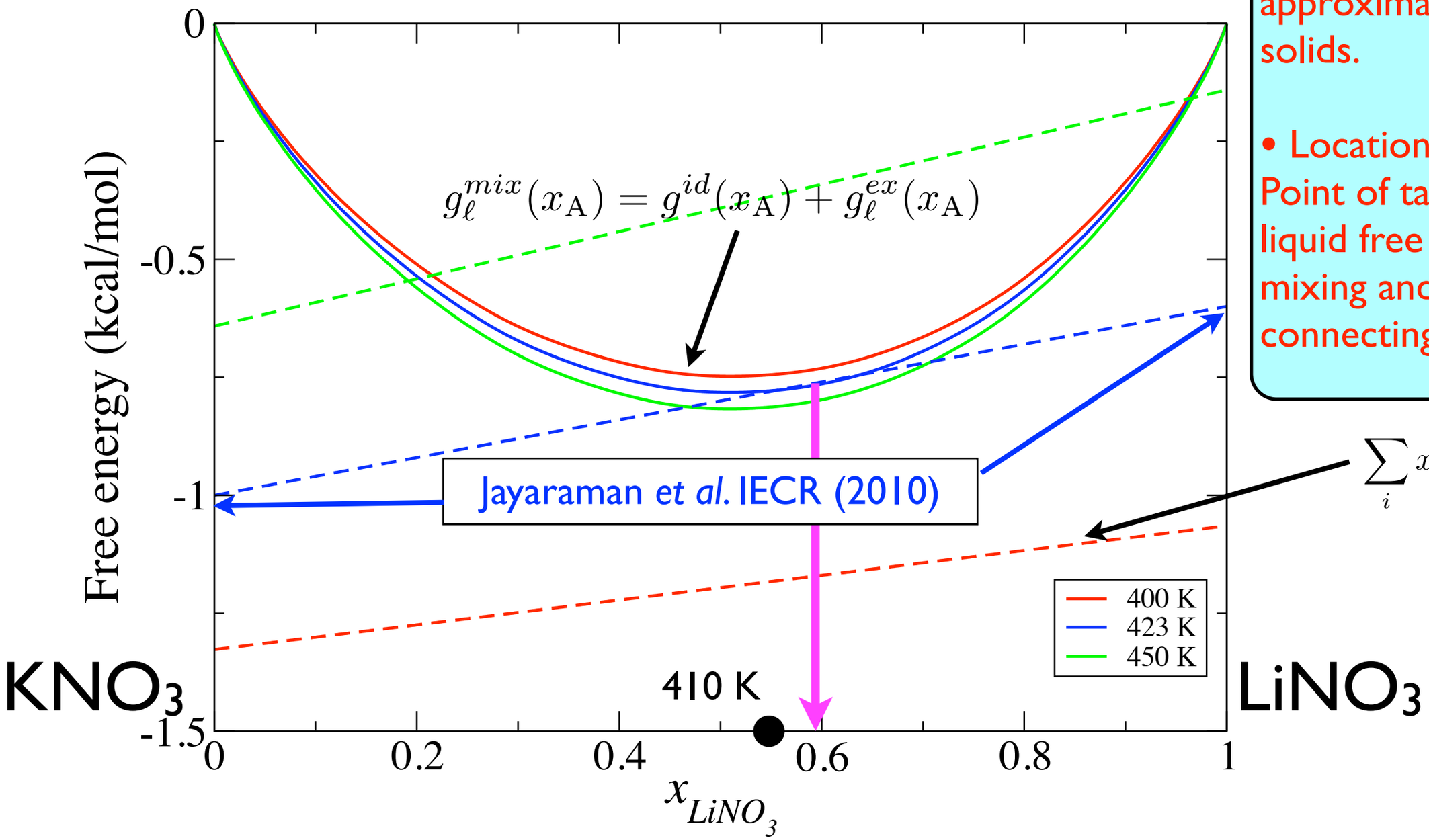


$$\frac{x_\mathrm{A}}{+ x_\mathrm{B}} \int_0^{x_\mathrm{A}+x_\mathrm{B}} dx'_\mathrm{A} \Delta\mu_{\mathrm{AB}}(x'_\mathrm{A}, x_\mathrm{C})$$

$$\frac{{}^{c}\mathrm{B}}{+ x_\mathrm{B}} g^{ex}_{\mathrm{BC}\ell}(x_\mathrm{C})$$

hanges conducted at x_A mesh points

$LiNO_3$-KNO_3 mixture - Free energy vs composition



- Approximation: "Simple Eutectic" - Solid phases approximated by pure solids.
- Location of eutectic : Point of tangency between liquid free energy of mixing and solid-liquid connecting line

M.J. Maeso and J. Largo, Thermochimica Acta, **223**, 145-156 (1993)

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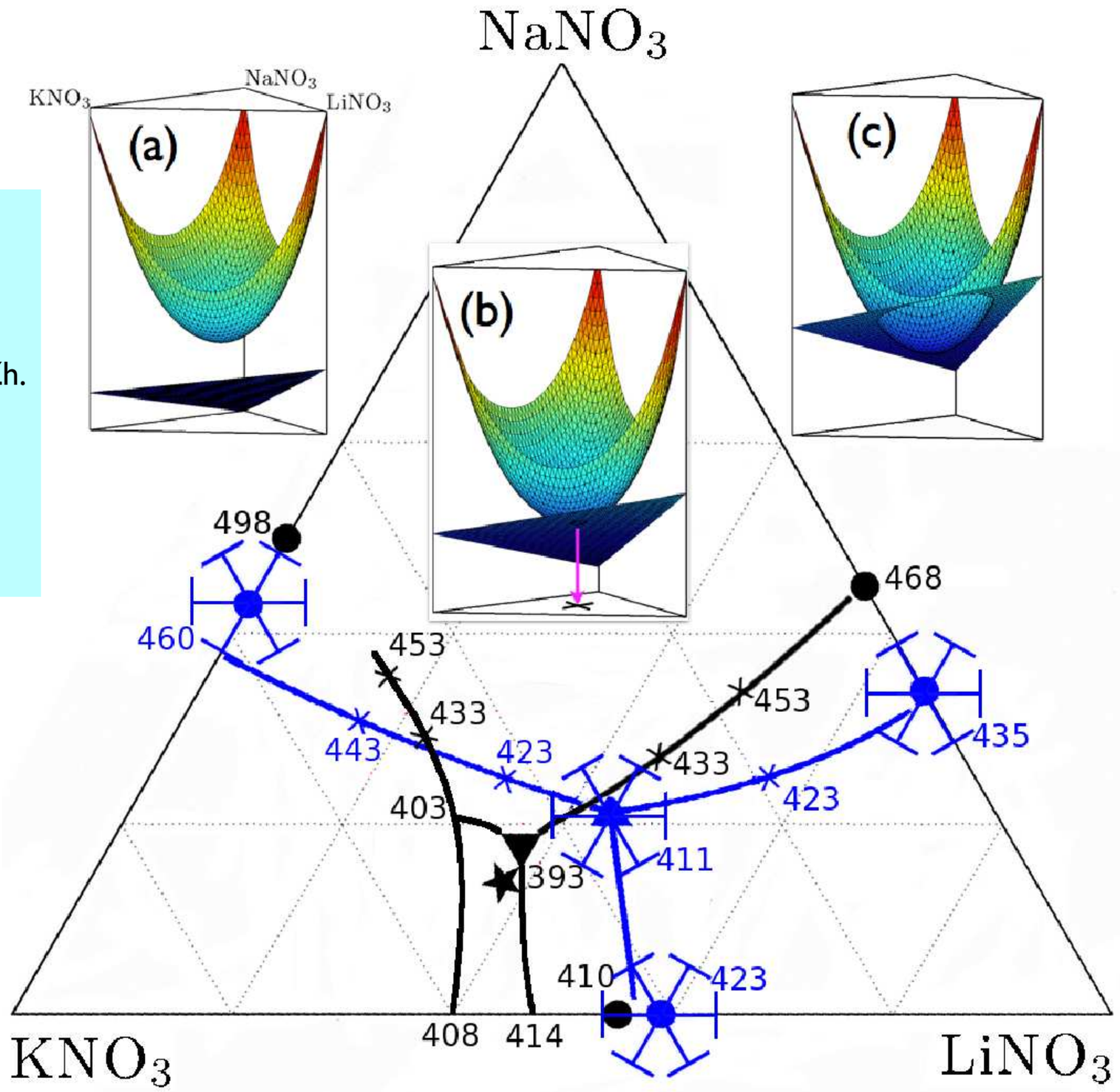
$LiNO_3$-$NaNO_3$-KNO_3 ternary



[1]M.J. Maeso and J. Largo, Thermochimica Acta, **223**, 145-156 (1993) - Binaries

[2]A.G. Bergman and K. Nogoev, Zh. Neorg. Khim., **9** 1423 (1964) - Ternary

[3]H. R. Carveth, J. Phys. Chem., **2**, 209 (1898) - ★

S. Jayaraman, A. P. Thompson and O. A. von Lilienfeld, PRE rapid communication, accepted (2011)

Conclusions

- Thermodynamic integration based method developed to compute free energies of mixing from MD simulations
- Tangent method extended to compute approximations of eutectic compositions assuming a “simple eutectic”
- Need per-atom contributions from pppm!

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fix 1 all adapt 1 pair lj/cut epsilon * 5 v_lj scale yes
compute 1 all ti lj/cut 5 v_lj v_dlj tail v_lj v_dlj
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