



**ICTS School on
Understanding Molecular Simulation**

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Free energy calculations

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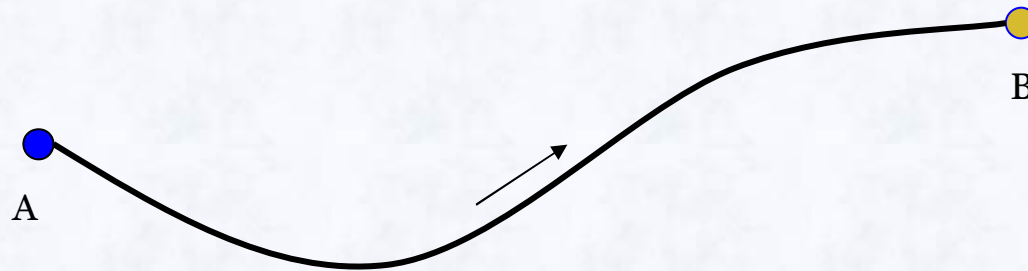


Free energy calculations

- Thermodynamic integration
- Free energy perturbation

Thermodynamic integration(TDI)

Change in free energy along a
reversible path



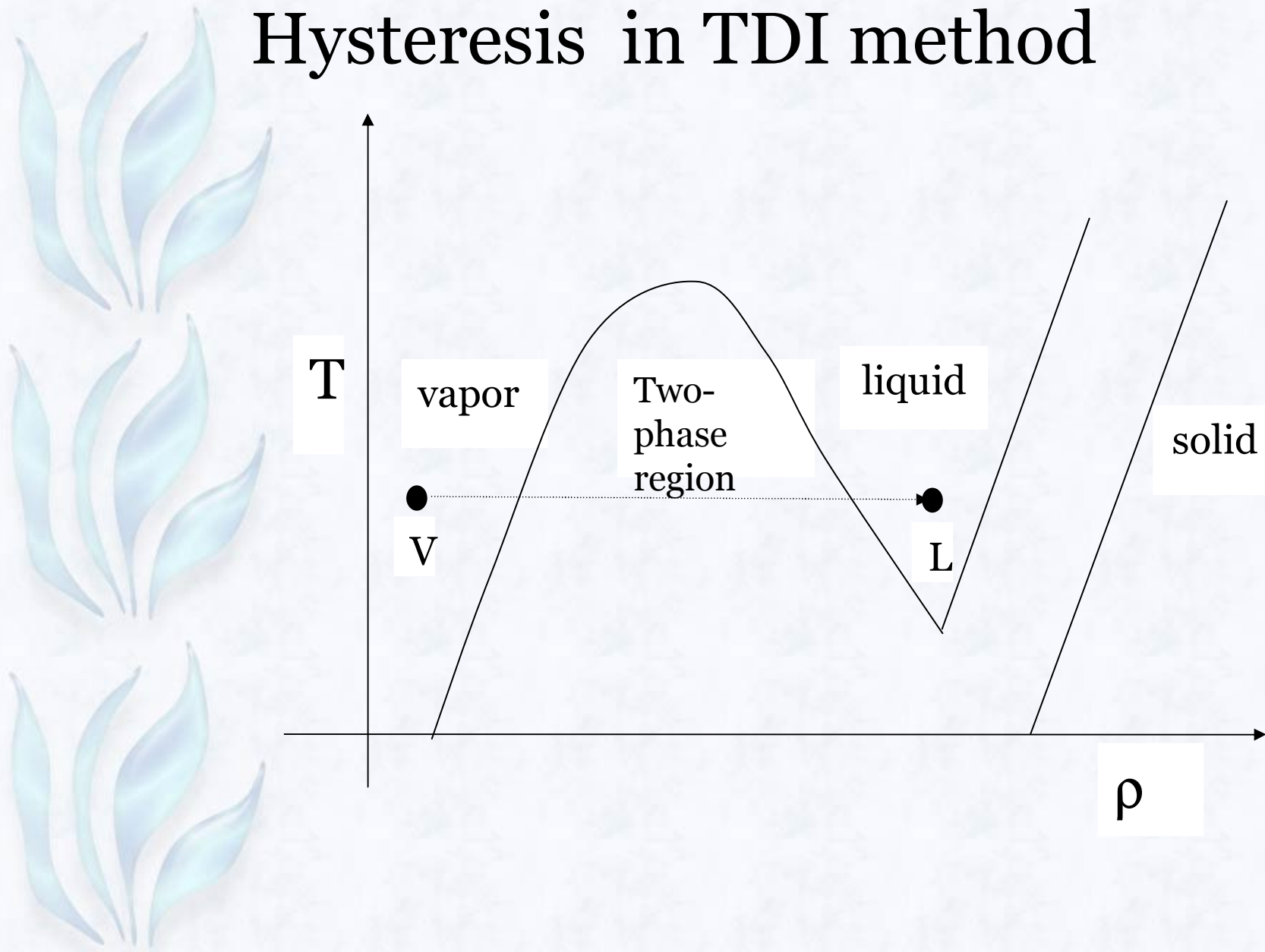
Reversible path:
succession of
equilibrium states



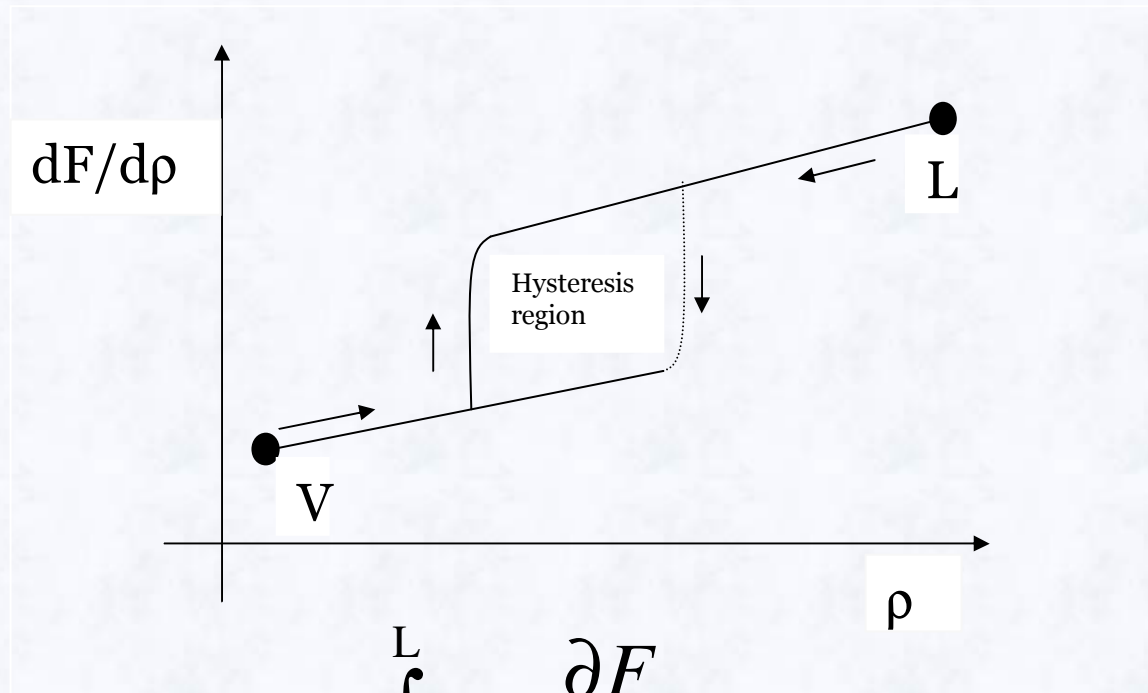
Hysteresis in TDI method

- arises from difference in forward and reverse paths
- is a sign of irreversibility
- usually associated with a first-order phase transition

Hysteresis in TDI method




Hysteresis in TDI method



$$\Delta F = \int_V^L d\rho \frac{\partial F}{\partial \rho}$$

➔ First order transition must be avoided



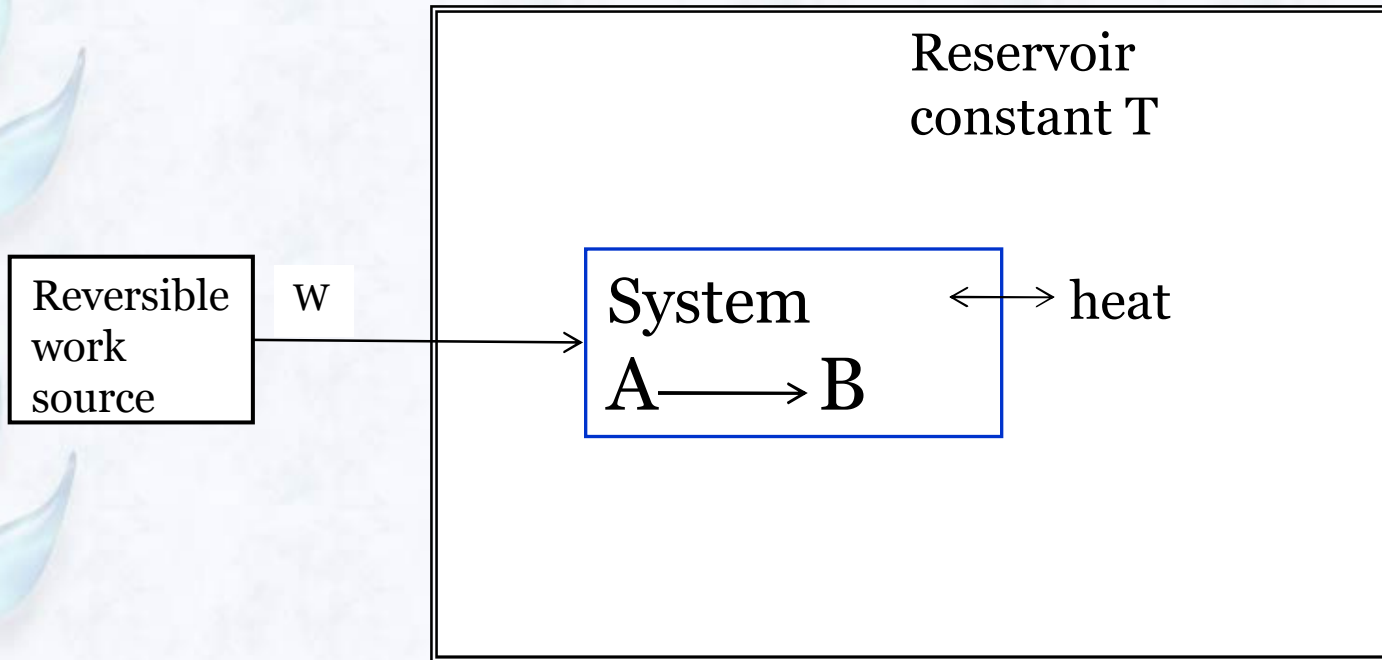
TDI method using molecular simulations:

- Advantage is that non-physical paths possible

→ Versatility : reversible paths & reference states

- Important applications include:
 - (1) phase diagram calculation
 - (2) interfacial properties

Maximum work theorem



$$\begin{aligned}W &= \Delta U + \Delta U_R \\ \Delta U_R &= T \Delta S_R \\ \Delta S_{\text{tot}} &= \Delta S + \Delta S_R \\ \Delta U_R &= T(\Delta S_{\text{tot}} - \Delta S)\end{aligned}$$

$$\begin{aligned}W &= \Delta U + T(\Delta S_{\text{tot}} - \Delta S) \\ &= \Delta F + T\Delta S_{\text{tot}}\end{aligned}$$

Maximum work theorem

$$W = \Delta F + T\Delta S_{\text{tot}}$$

Second law of Thermodynamics: $\Delta S_{\text{tot}} \geq 0$

$$W \geq \Delta F$$

System
 $A \longrightarrow B$

Forward path :

$$W^{\text{F}} \geq \Delta F$$

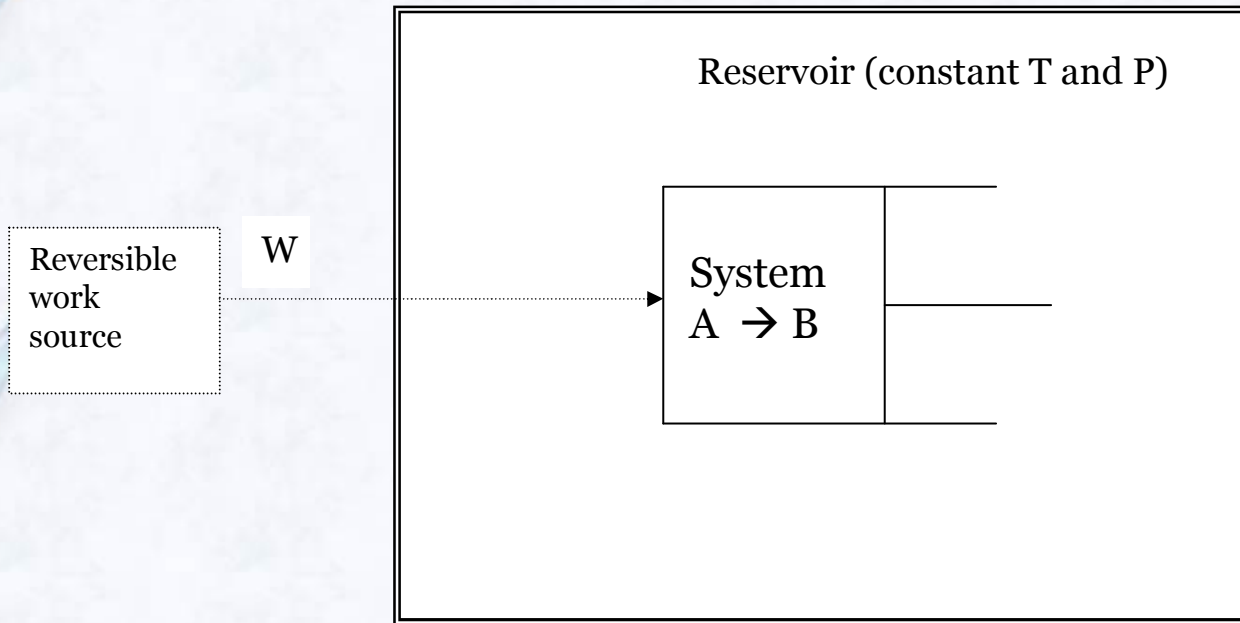
System
 $B \longrightarrow A$

Reverse path :

$$W^{\text{R}} \geq -\Delta F$$

$$W^{\text{R}} \leq \Delta F \leq W^{\text{F}}$$

Maximum work theorem



$$W^R \leq \Delta G \leq W^F$$

Phase diagram calculations:

Conditions of coexistence are:

$$T^I = T^{II}$$

$$P^I = P^{II}$$

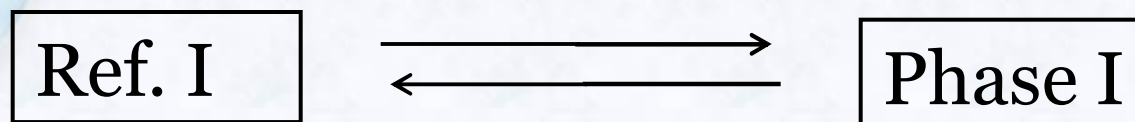
$$\mu^I = \mu^{II}$$

At a given T and P, calculate $\Delta\mu$

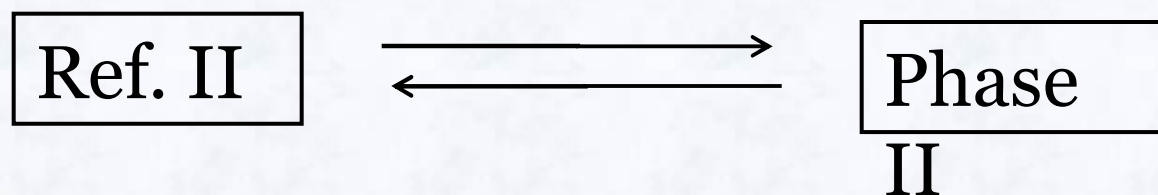
$$\Delta\mu = \frac{\Delta G}{N} = \frac{\Delta F + \Delta(PV)}{N}$$

Phase diagram calculations:

At a given T and P, compute ΔF or ΔG

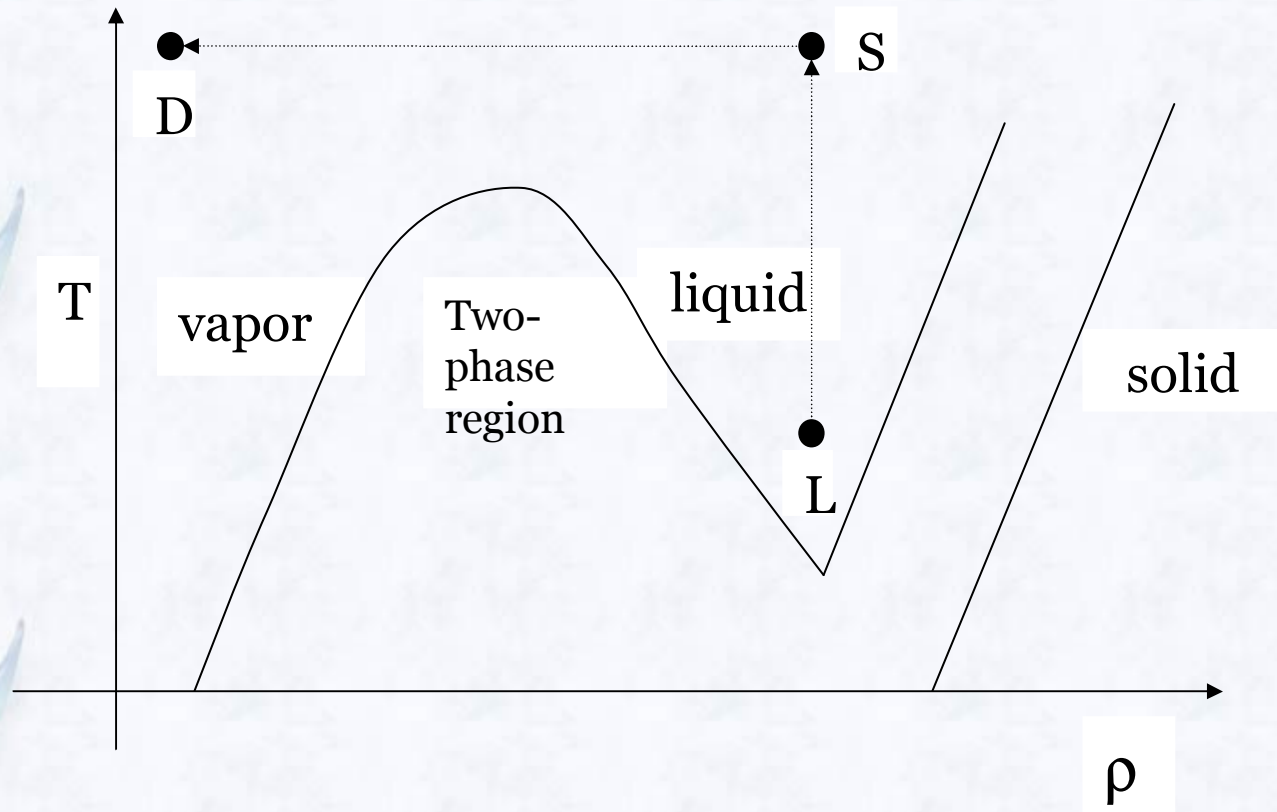


NVT or NPT simulations along the path



Phase diagram calculations:

Liquid phase free energy: Ideal gas as a reference state.



Phase diagram calculations:

Liquid phase free energy:

$$\Delta(\beta F) = \int_L^S d\beta U(\beta, V, N)$$

$$(\Delta F)_s = N \int_D^S d\rho \left(\frac{P - \rho kT}{\rho^2} \right)$$

Phase diagram calculations:

Solid phase free energy: (non-physical path)

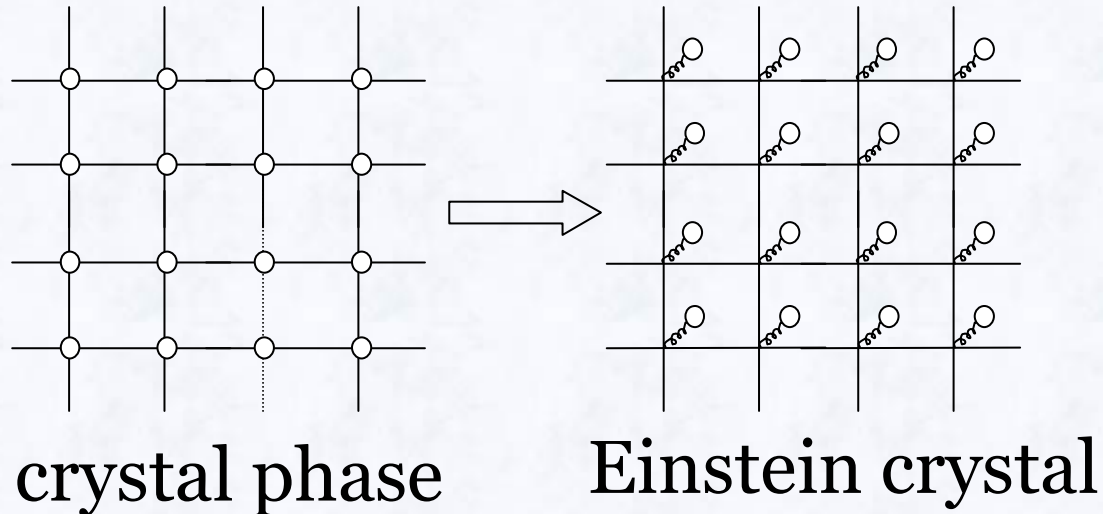
$$\varphi(\lambda) = \lambda \varphi_S + (1 - \lambda) \varphi_E$$

$$\beta(F - F_E) = \int_0^1 d\lambda \left(\frac{\partial F}{\partial \lambda} \right) = \int_0^1 d\lambda \left\langle \frac{\partial \varphi}{\partial \lambda} \right\rangle$$

NVT-simulation

Phase diagram calculations:

Solid phase free energy: (non-physical path)



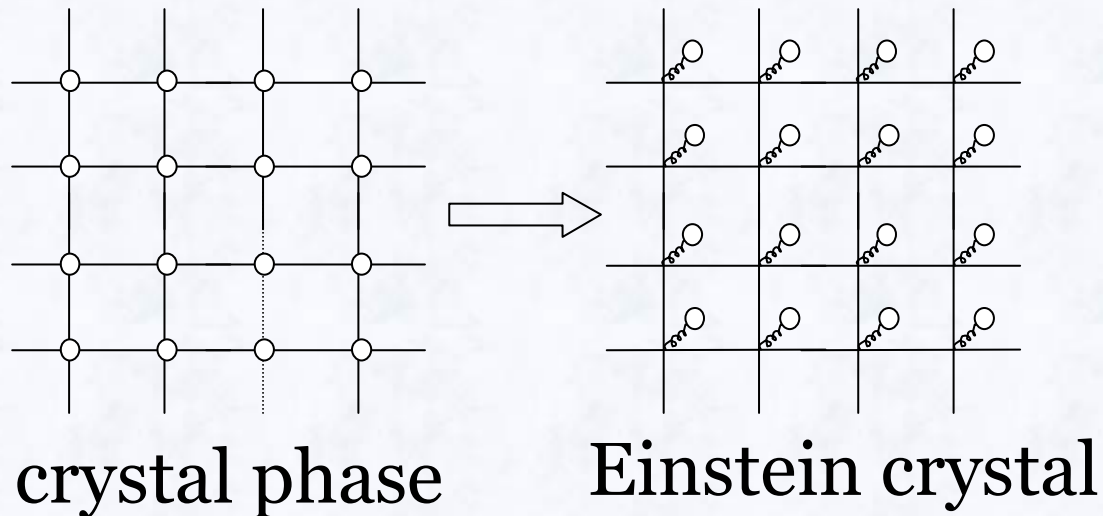
$$\varphi_E(\vec{r}_1, \dots, \vec{r}_N) = N\varphi_0 + \frac{K}{2} \sum_{i=1}^N (\vec{r}_i - \vec{R}_i)^2$$

K = harmonic spring constant,
 φ_0 = static lattice energy, $\varphi_E > \varphi_0$

Ref: *J. Chem. Phys.*, **79**, 5095-5104, 1983

Phase diagram calculations:

Solid phase free energy: (non-physical path)



$$\beta F_E = 3N \ln \left(\frac{\beta h \sqrt{K}}{2\pi} \right) + \beta N \varphi_0$$

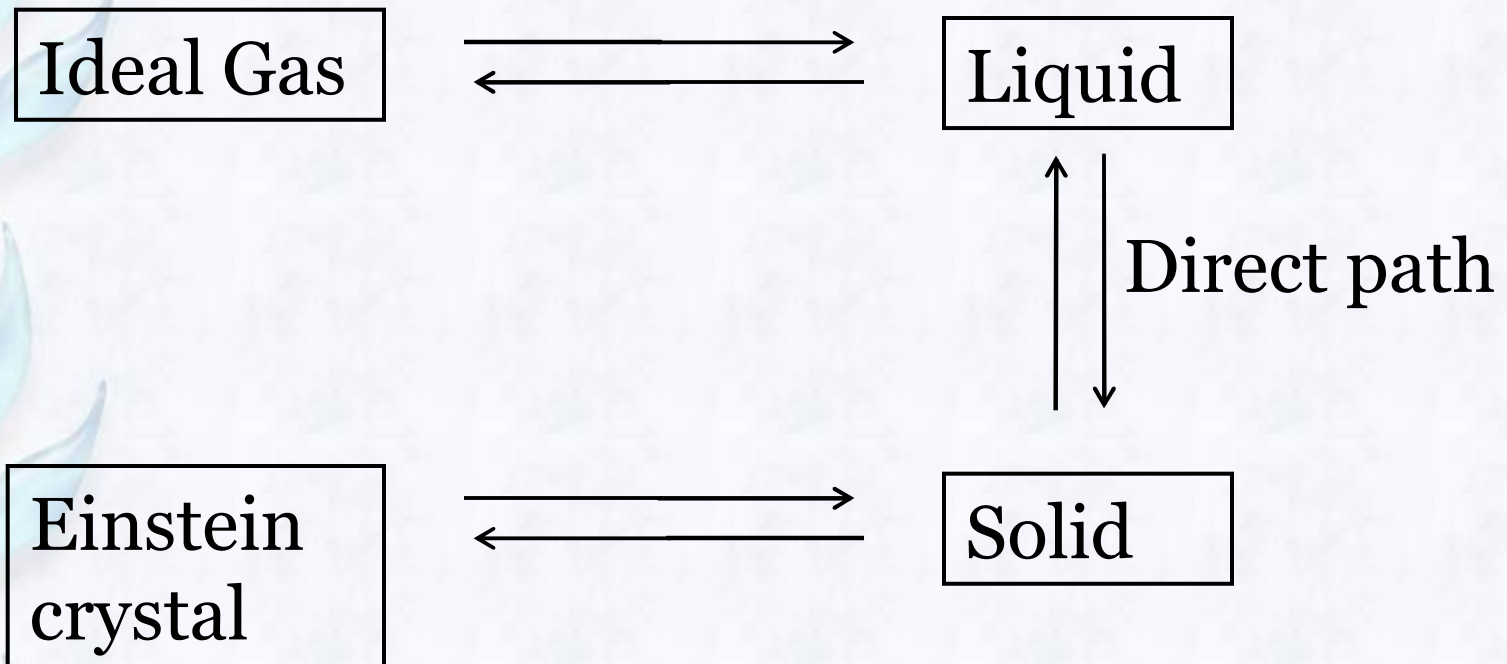
K = harmonic spring constant,
 φ_0 = static lattice energy, $\varphi_E > \varphi_0$

Ref: *J. Chem. Phys.*, **79**, 5095-5104, 1983

Other methods for solid free energy

- single occupancy cell method
- Harmonic solid method

Direct calculation of free energy difference



Refs : J. Chem. Phys., **120**, 2122 ,2004 $\rightarrow \Delta F$ (NVT)
Phys. Rev. E, **73**, 016704, 2006 $\rightarrow \Delta G$ (NPT)

Constrained fluid λ -integration Method

- Direct computation of crystal-melt free energy
- 3-stage reversible path
- Can be applied to both NVT and NPT ensembles

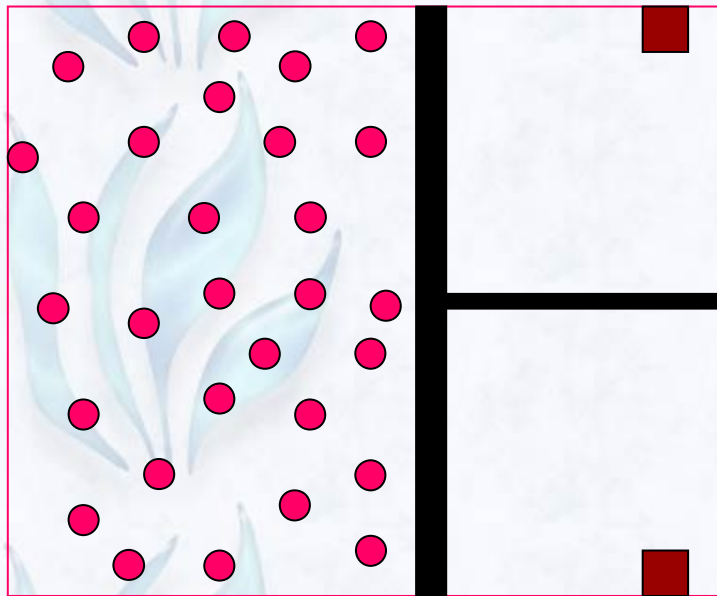
Refs : J. Chem. Phys., **120**, 2122 ,2004 $\rightarrow \Delta F$ (NVT)

Phys. Rev. E, **73**, 016704, 2006 $\rightarrow \Delta G$ (NPT)

Constrained fluid λ -integration Method (NPT version)

STAGE 1

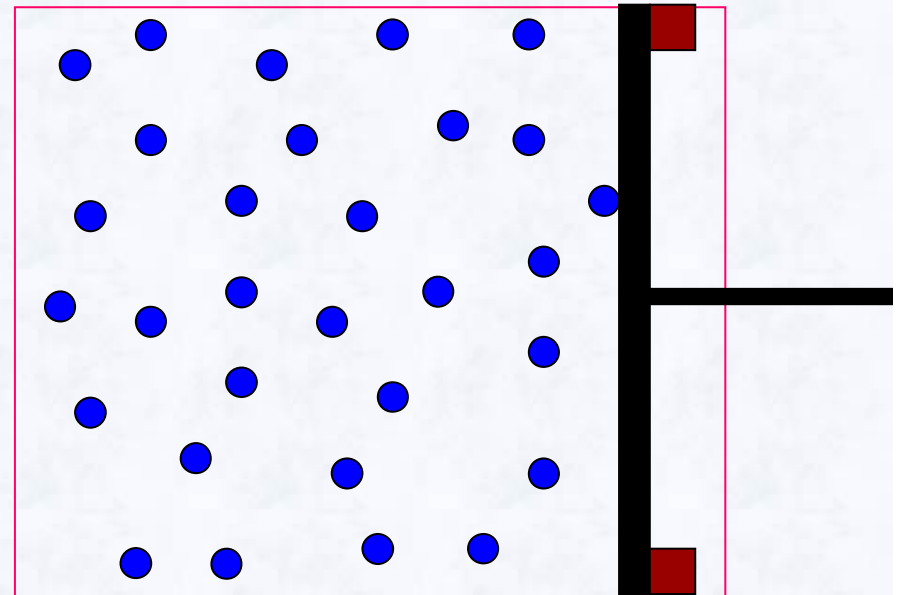
Liquid state



$$\lambda_1 = 0.0$$



Gas like state



$$\lambda_1 = 1.0 \text{ or } \lambda_2 = 0.0$$

STAGE 1

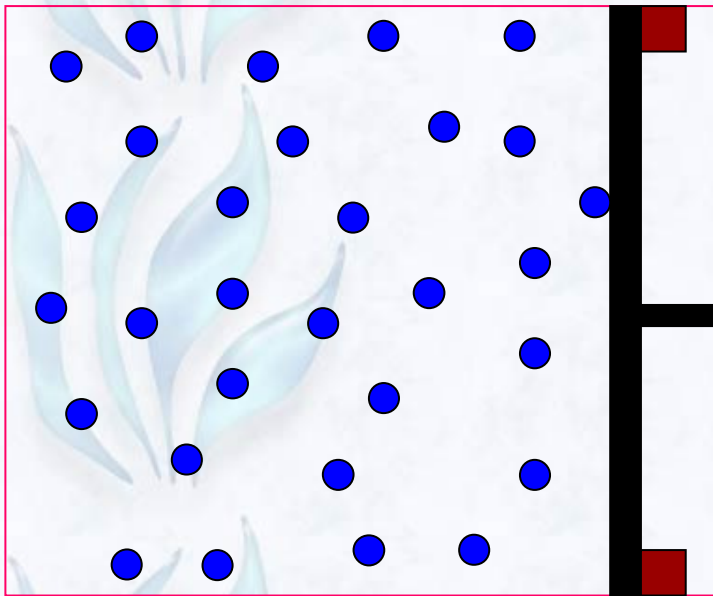
The potential energy states along the path is given by

$$\phi_1(\lambda_1) = (1 - \eta\lambda_1)U \quad (1.7)$$

$$\Delta G_1 = \int_0^1 d\lambda_1 \langle -\eta U \rangle_{\lambda_1} \quad (1.8)$$

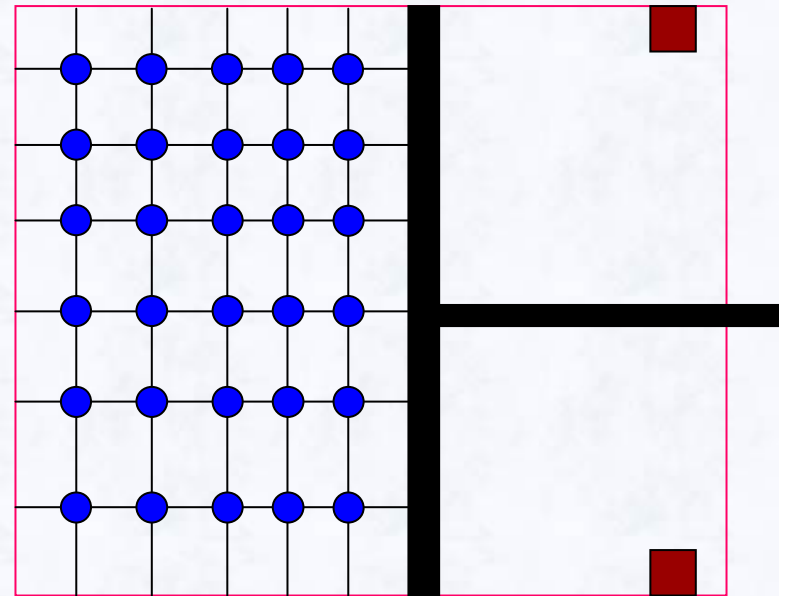
STAGE 2

Gas like state



$$\lambda_1 = 1.0 \text{ or } \lambda_2 = 0.0$$

solid like state



$$\lambda_2 = 1.0 \text{ or } \lambda_3 = 0.0$$

STAGE 2

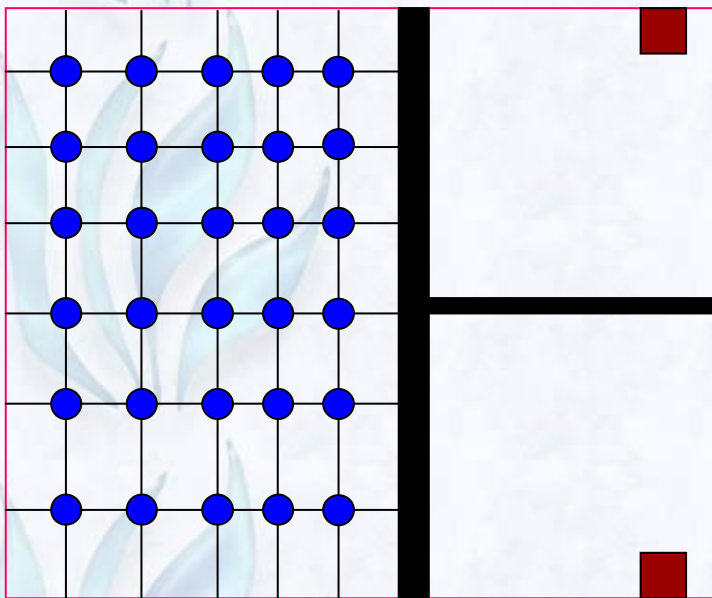
The total potential energy state for the second stage is given by

$$\phi_2(\lambda_2) = (1 - \eta)U + \lambda_2 U_{ext} \quad (1.9)$$

$$\Delta G_2 = \int_0^1 d\lambda_2 \langle U_{ext} \rangle_{\lambda_2} \quad (1.10)$$

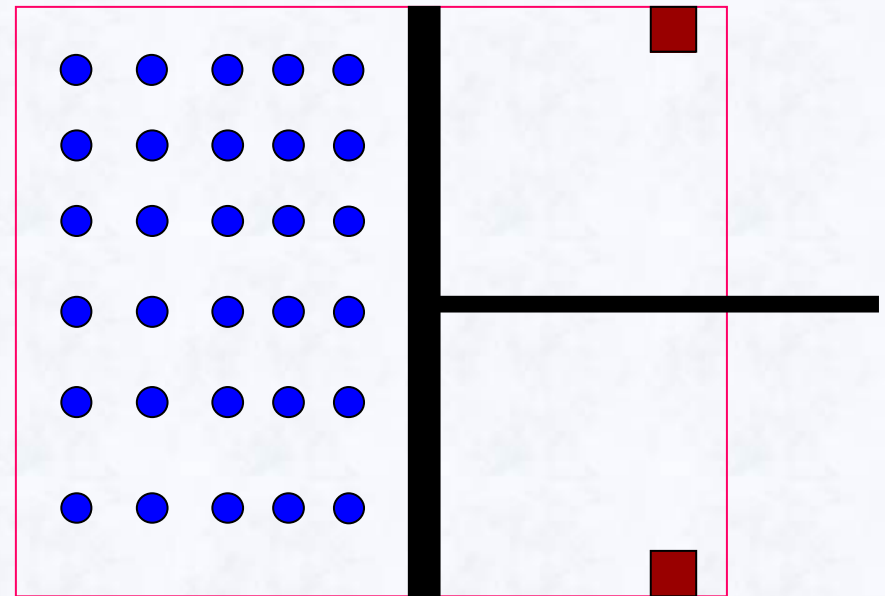
STAGE 3

solid like state



$$\lambda_2 = 1.0 \text{ or } \lambda_3 = 0.0$$

Solid phase



$$\lambda_3 = 1.0 \text{ or } \lambda_1 = 0.0$$

STAGE 3

The total potential energy in the third stage is given by

$$\phi_3(\lambda) = [(1 - \eta) + \lambda_3 \eta]U + (1 - \lambda_3)U_{ext} \quad (1.11)$$

$$\Delta G_3 = \int_0^1 d\lambda_3 \langle \eta U - U_{ext} \rangle_{\lambda_3} \quad (1.12)$$



Applications:

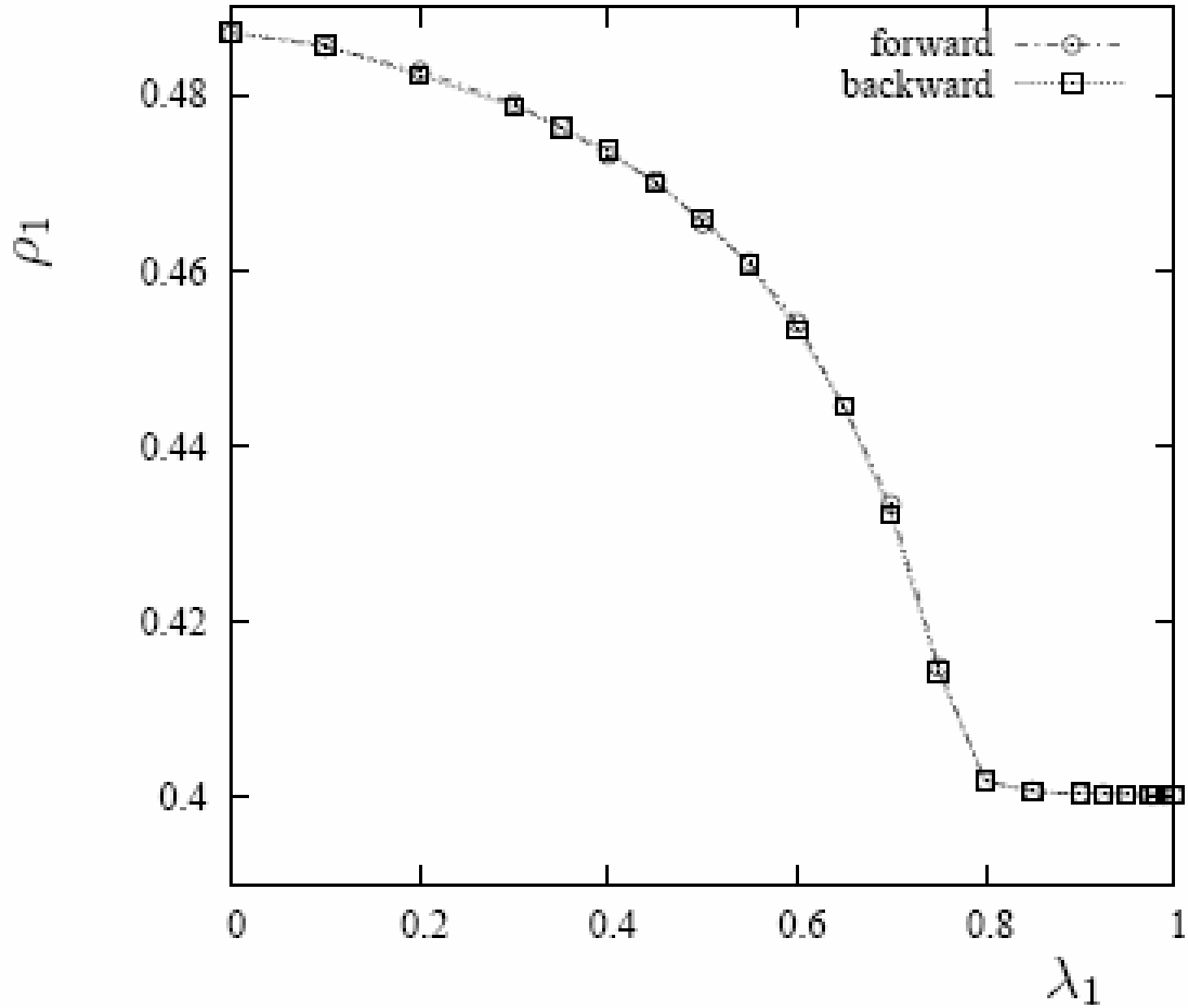
1. Melting temperature of Benzene, NaCl
(J. Chem.Phys., 122, 014115, 2005)
2. Surface energy calculation of Au [110] crystal
(J. Chem. Phys., vol. 122, p. 064711, 2005)
3. Melting temperature of binary mixture
(J.Chem.Phys, 123 , 194503, 2005)
4. Sublimation temperature
(J. Chem Phys, 124, 184106, 2006)



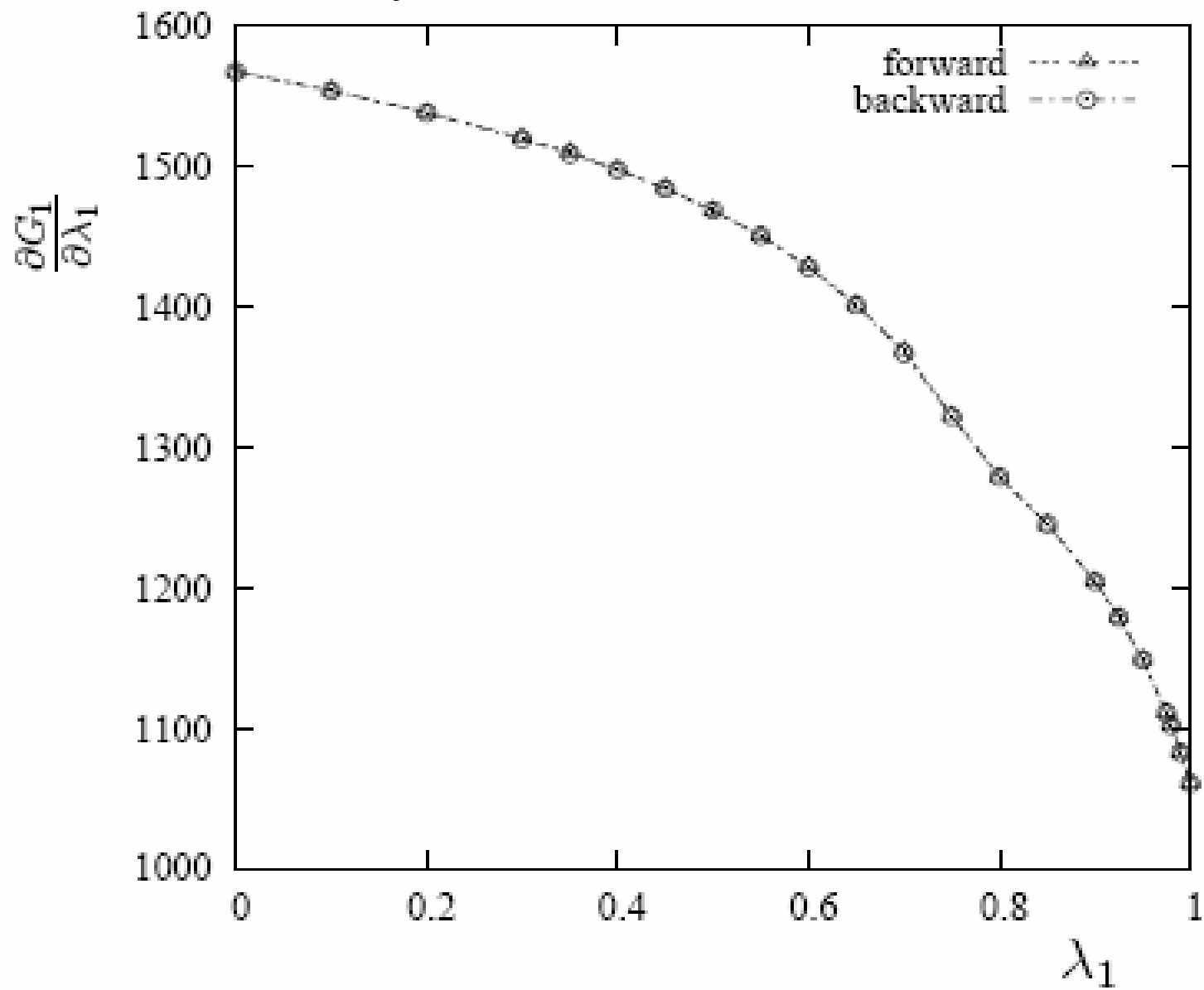
Example

- Melting temperature of silicon
- Stillinger weber potential
(Phys. Rev. B, vol. 31, 5262, 1985)
- Pressure $P^* = 0$
- Temperature $T^* = 0.0667$ (1678 K)
- $N=1000$ particles

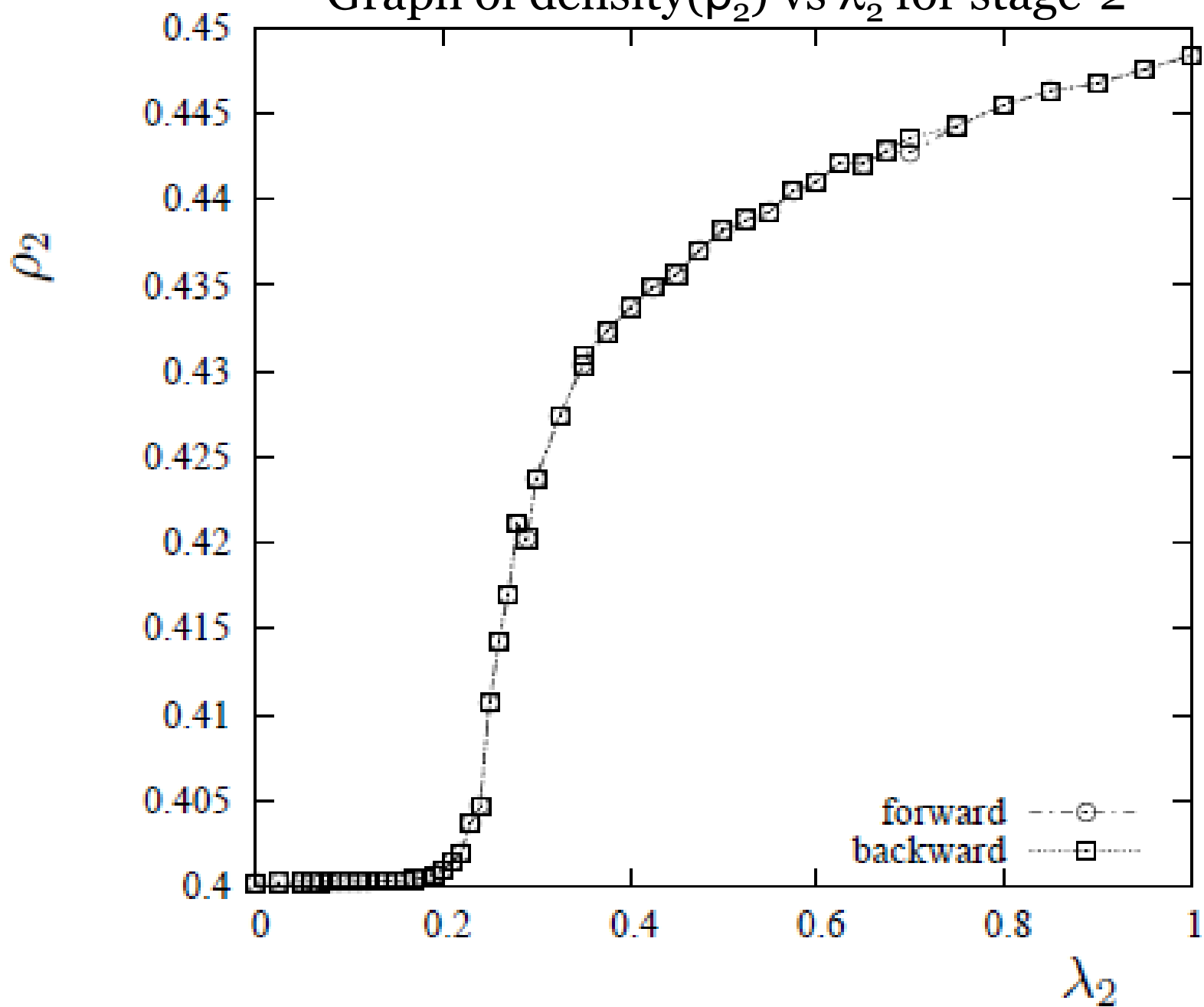
Graph of density(ρ_1) vs λ_1 for stage-1



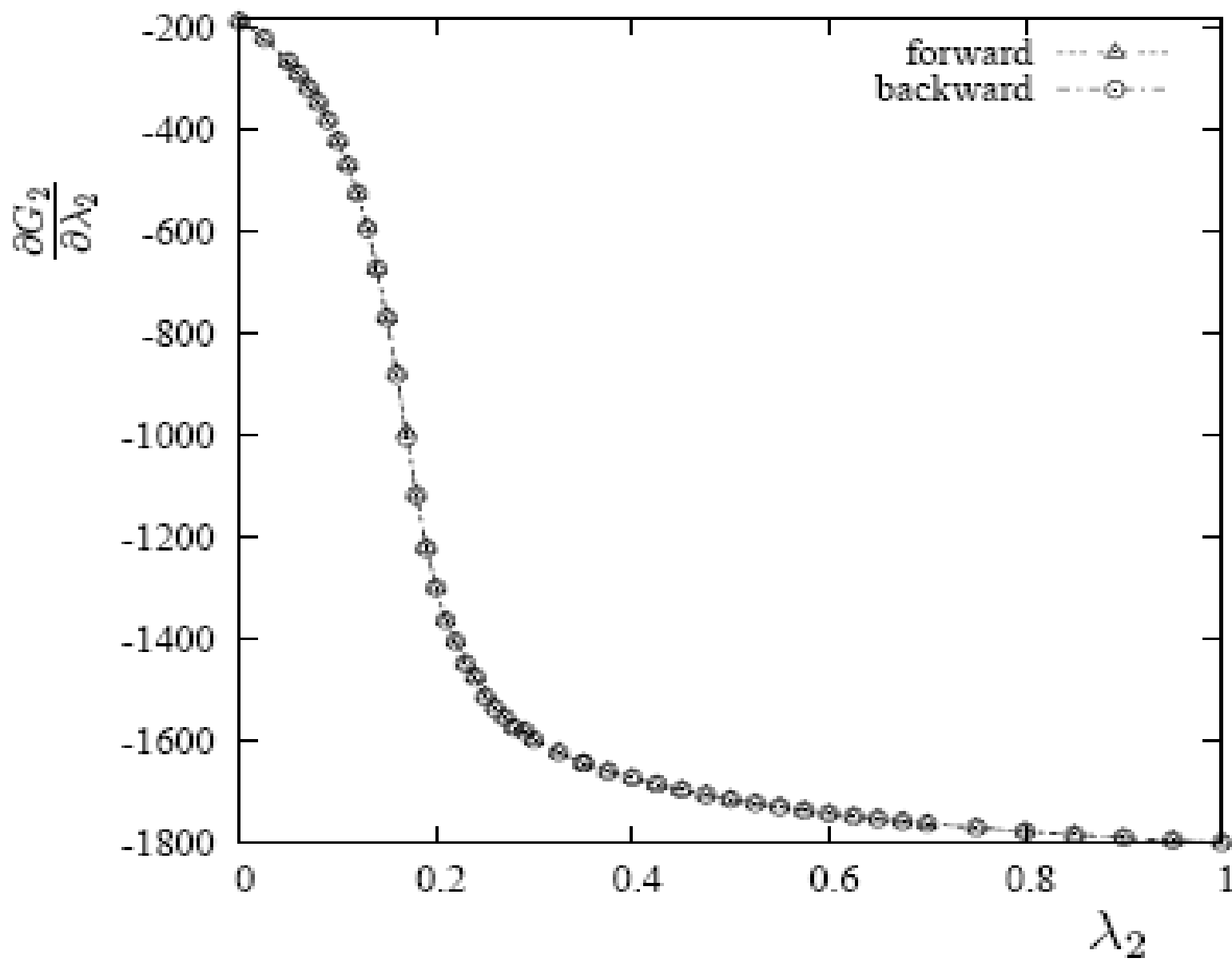
$\frac{\partial G_1}{\partial \lambda_1}$ Vs λ_1 for stage 1



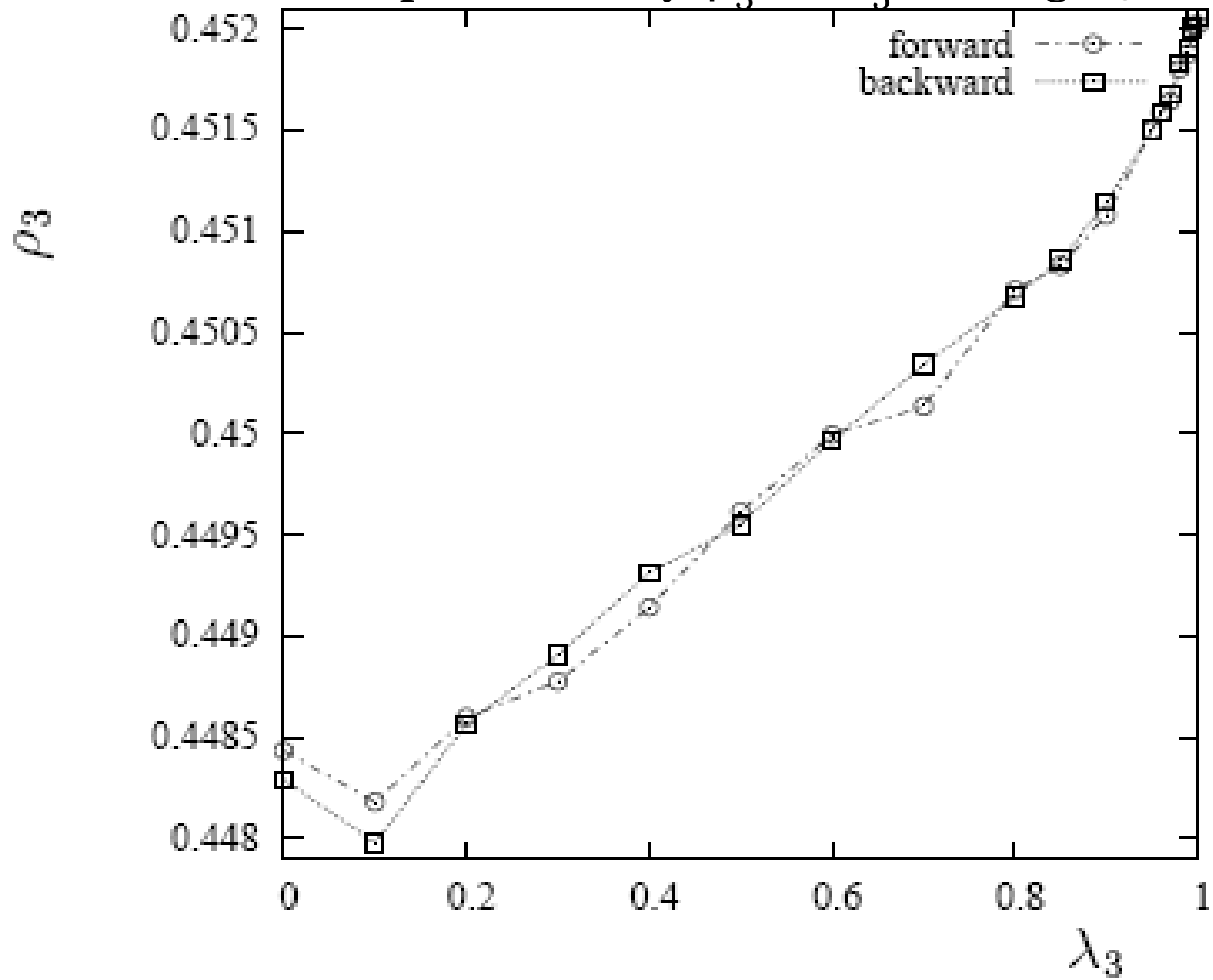
Graph of density(ρ_2) vs λ_2 for stage-2



$\frac{\partial G_2}{\partial \lambda_2}$ Vs λ_2 for stage 2

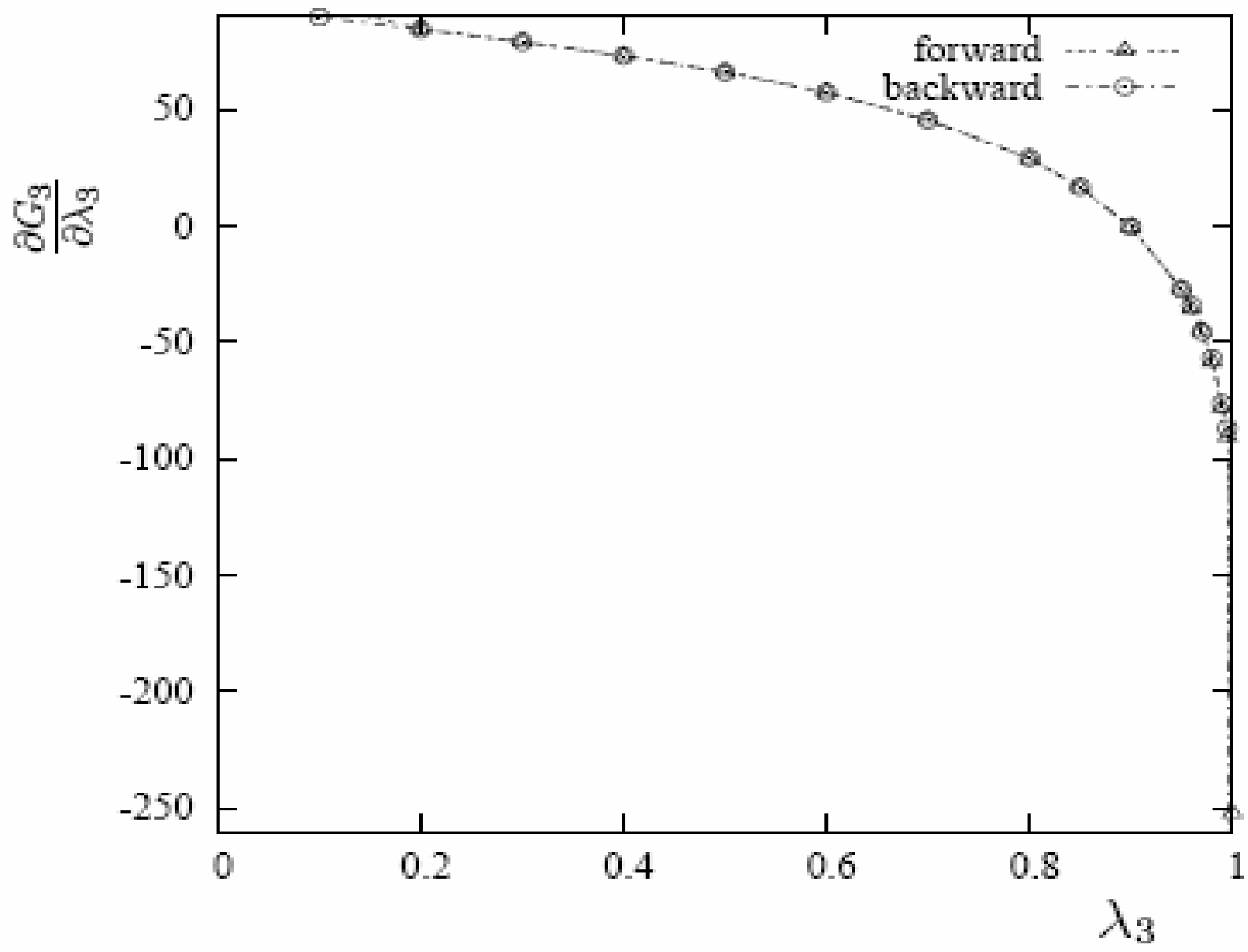


Graph of density(ρ_3) vs λ_3 for stage-3



$\frac{\partial G_3}{\partial \lambda_3}$ Vs λ_3 for stage 3

T=1677 K
P=0 atm



Extension to binary systems

$$T^I = T^{II}$$

$$P^I = P^{II}$$

$$\mu_1^I = \mu_1^{II}$$

$$\mu_2^I = \mu_2^{II}$$



$$T^I = T^{II}$$

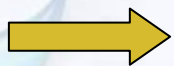
$$P^I = P^{II}$$

$$\mu_2^I - \mu_1^I = \mu_2^{II} - \mu_1^{II}$$

$$\mu_1^I = \mu_1^{II}$$

At a given value of T , P , $(\mu_2 - \mu_1)$: find

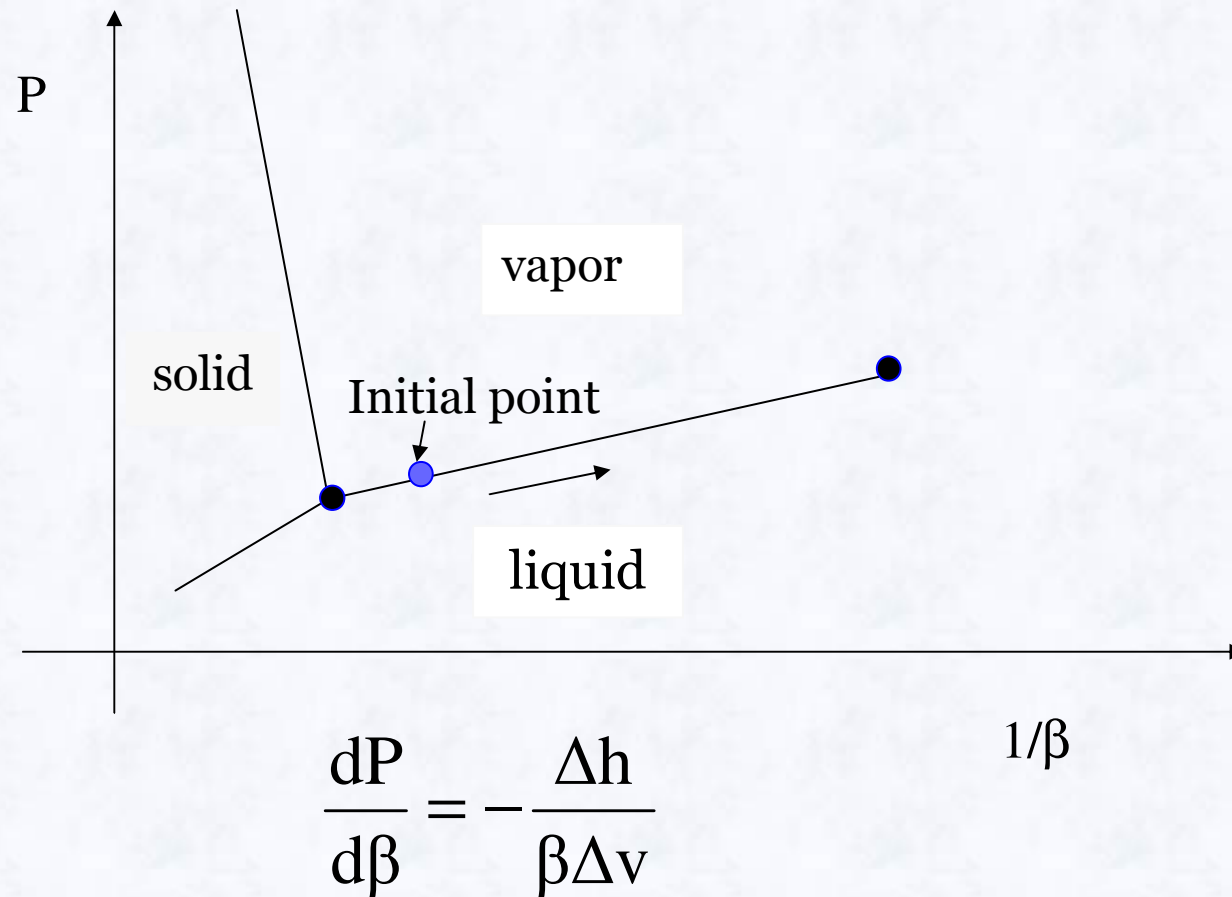
$$\Delta\mu_1 = \mu_1^{II} - \mu_1^I$$



Use semi-grand canonical ensemble

Ref: *J. Chem. Phys.*, 123 , 194503, (2005)

Gibbs-Duhem Integration



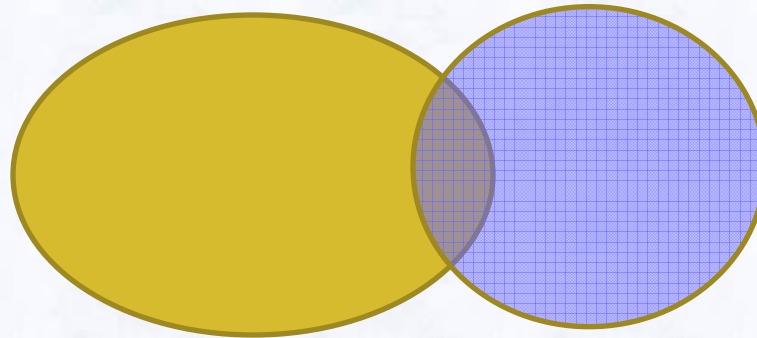
Ref: D. A. Kofke, *J. Chem. Phys.*, **98**, 4149-4150 (1993)

Free energy perturbation (FEP) method

$$\begin{aligned}\Delta F &= \log \frac{Z_0}{Z_1} \\ &= -\log \langle \exp[\Phi_0 - \Phi_1] \rangle_0 \\ &= \log \langle \exp[\Phi_1 - \Phi_0] \rangle_1\end{aligned}$$

Single stage FEP

Accuracy depends on Degree of overlap
of the two ensembles



Free energy perturbation (FEP) method

$$\Delta F = \log \frac{\sum_1 f(\phi_0 - \phi_1 + C)}{\sum_0 f(\phi_1 - \phi_0 - C)} + C - \log \frac{n_1}{n_0}$$

Bennett Acceptance Ratio method

$$\sigma^2 \approx \frac{\langle f^2 \rangle_0 - \langle f \rangle_0^2}{n_0 \langle f \rangle_0^2} + \frac{\langle f^2 \rangle_1 - \langle f \rangle_1^2}{n_1 \langle f \rangle_1^2}$$

$$\Delta F = C_B - \log \frac{n_1}{n_0}$$

Ref: C. H. Bennett, *J. Comput. Phys.*, **22**, 245-268 (1976)