

Lattice - Gas Model for Intercalation Compounds: Voltage-Discharge Behavior.

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Abstract

The problem of intercalation of ions of one type into the host matrix, initially occupied by ions of another type, is of interest because of its relation to the development of new types of rechargeable batteries. Intercalation occurs in materials that are used as cathodes. The important characteristic of the batteries is the voltage-discharge curve or open circuit voltage, describing the equilibrium voltage difference between electrodes as a function of the amount of intercalated ions.

From the structure of some materials that can be used as cathodes, the host matrix can be considered as two-dimensional. We use a hard-square lattice gas to model the interaction between the ions (1). This problem is closely related to the antiferromagnetic Ising model in an external magnetic field. We have carried out Monte Carlo simulations to calculate voltage-discharge and isothermal compressibility curves for the square, honeycomb and triangular lattices at different temperatures. In the limit of strong interactions for the square and honeycomb lattices, there exist two regions where the voltage almost

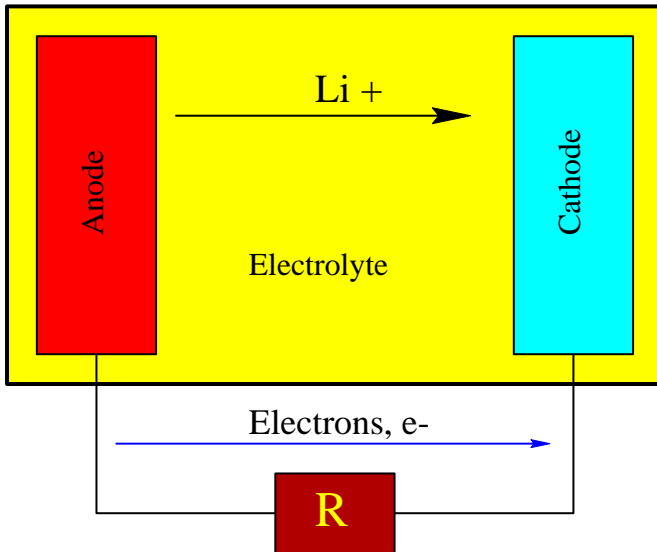
does not depend on the amount of intercalated charge. In the case of the triangular lattice there are three such regions. In the same limit a second order phase transitions has been found for all three lattices, which results in the divergence of the isothermal compressibility at certain critical concentrations. The positions of phase transitions are in agreement with phase diagrams known for the lattices under consideration.

There are many different ways to choose the form of the interaction between the intercalation ions on the plain. We consider here one that is relatively simple. In more realistic models one should take into account the fact that the real interaction between the ions is the long-range Coulomb interaction¹. The modeling of the intercalation process using more realistic Coulomb potential is the subject of future studies.

¹ Yuqing Xiao, M. F. Thorpe and J. B. Parkinson, Phys. Rev. B 59, 277-285 (1999).

How Rechargeable Batteries Work?

Discharge Cycle in Battery



Anode:

Li or Lithium intercalating graphite

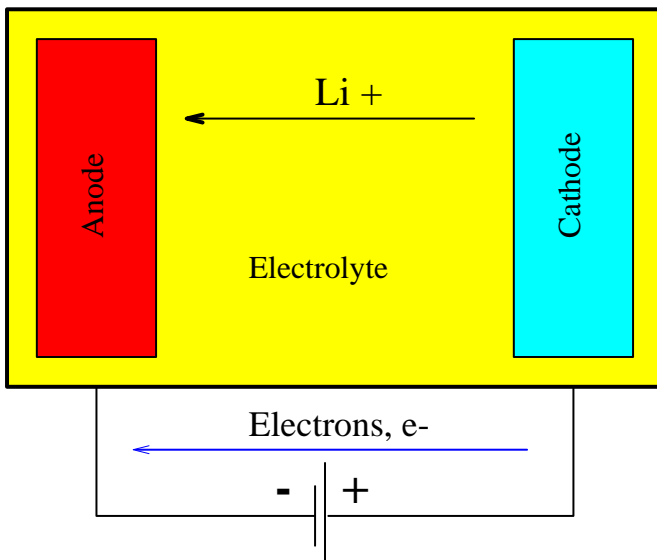
Cathode:

Li_xMO_2 *M*-metal
(i.e. $NaFeO_2$, $LiScO_2$)

Electrolyte:

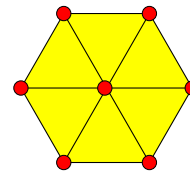
Li-salts (i.e. $LiPF_6$) in organic solvents

Charge Cycle in Battery



Structure of the Cathode

● - Oxygen or Metal or Lithium



Structure of $NaFeO_2$:

Plane of Li

Plane of Oxygen

Plane of Na and Fe

Plane of Li

Plane of Oxygen

Structure of $LiScO_2$

Plane of Oxygen

Plane of Li and Sc

Plane of Oxygen

- 1) Lithium in cathode is fully ionized.
- 2) There is no electron transfer through electrolyte.

Open Circuit Voltage (OCV)

$$V(x) = \frac{\mu_{Li}^{anode} - \mu_{Li}^{cathode}}{Z_{Li}}$$

μ_{Li}^{anode} -- Chemical potentials of Li ion on anode.

$\mu_{Li}^{cathode}$ -- Chemical potential of Li ion on cathode.

Z_{Li} -- Charge of the Lithium ion in electrons.

- 1) How OCV depends on the amount of Li intercalated into cathode?
- 2) Are there phase transitions?
- 3) What is the dependence of OCV on temperature?

Models of Intercalation Mechanism

- 1) Non Interacting Lattice Gas
- 2) Hard Sphere Lattice Gas
- 3) Lattice Gas with long range Coulomb interaction.

Geometry of the Intercalation Planes

- 1) 1D - Linear chain, as example where it is possible to find the exact solution.
- 2) 2D - Square, Honeycomb and Triangular Lattices.

Non - Interacting Lattice Gas (NILG). Exact Solution.

The results are the same for the all system since there is no interaction between the sites.

$$H = -\mu \sum_i n_i \quad x = \frac{1}{N} \sum_i n_i$$

n_i -Is the occupancy number of the site. Zero if the site is empty and unity if the site is occupied. μ - Chemical Potential. x - Concentration.

$$\beta\mu = \ln\left(\frac{x}{1-x}\right) \quad \frac{1}{\beta} \frac{\partial x}{\partial \mu} = \frac{\exp(\beta\mu)}{1 + \exp(\beta\mu)} \left(1 - \frac{\exp(\beta\mu)}{1 + \exp(\beta\mu)}\right) = x(1-x)$$

Hard Sphere Lattice Gas (HSLG)

$$H_L = J_L \sum_{\langle ij \rangle} n_i n_j - \mu \sum_i n_i \quad n_i = 0, 1$$

It is possible in this model to obtain exact solution for the linear chain using the Transfer Matrix Method. Final Formulas:

$$\mu(x) = 1 + 2T \sinh^{-1} \left[\frac{x - \frac{1}{2}}{\sqrt{x(1-x)}} \exp\left(\frac{1}{2T}\right) \right] \quad \frac{dx}{d\mu} = \left(\sqrt{1 + \frac{\left(x - \frac{1}{2}\right)^2}{x(1-x)} \exp\left(\frac{1}{T}\right)} \left(\frac{2T \exp\left(\frac{1}{2T}\right)}{\sqrt{x(1-x)}} \left(1 + \frac{\left(x - \frac{1}{2}\right)^2}{x(1-x)}\right) \right) \right)^{-1}$$

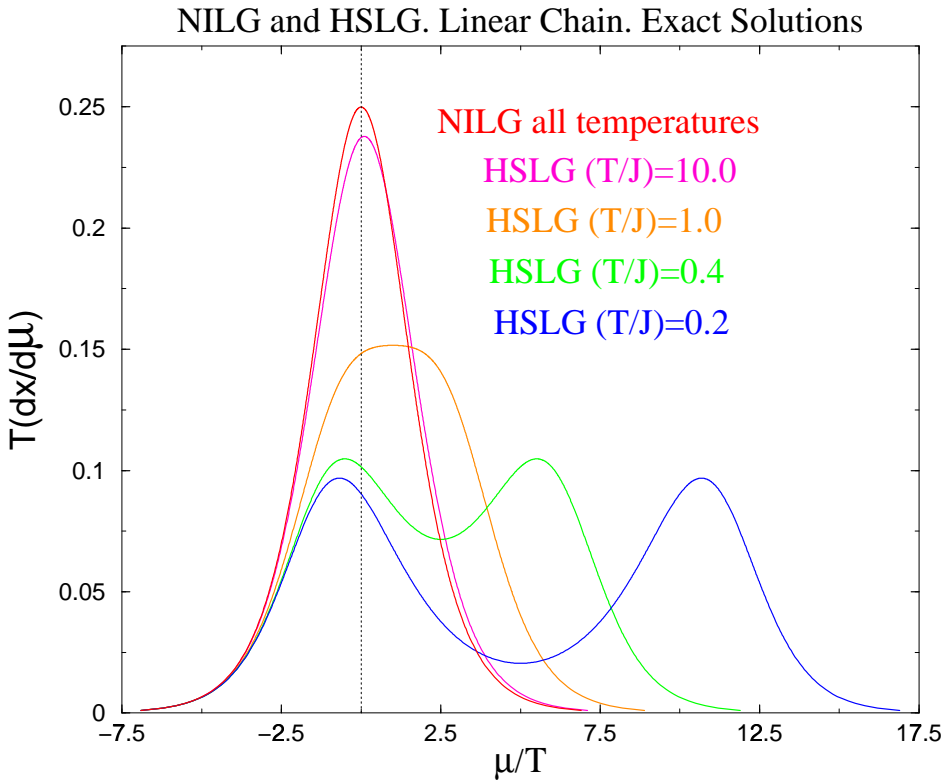
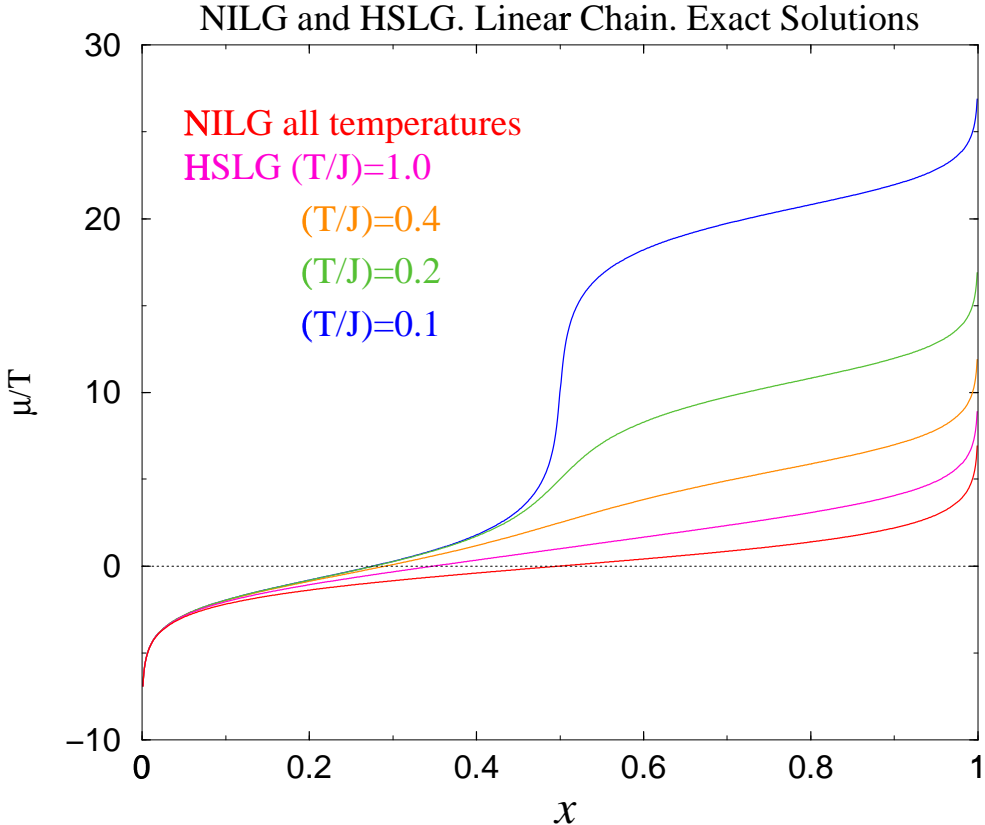
It is known that there is correspondence between HSLG model and Antiferromagnetic Ising Model (AFIM). There are the following relationship between the parameters of those two models.

$$s_i^z = 2n_i - 1 \quad J_I = \frac{J_L}{4} \quad \frac{T_I}{J_I} = 4 \frac{T_L}{J_L} \quad \frac{1}{2} \left(\frac{h}{J_I} \right) = \left(\frac{\mu}{J_L} \right) - \frac{q}{2}$$

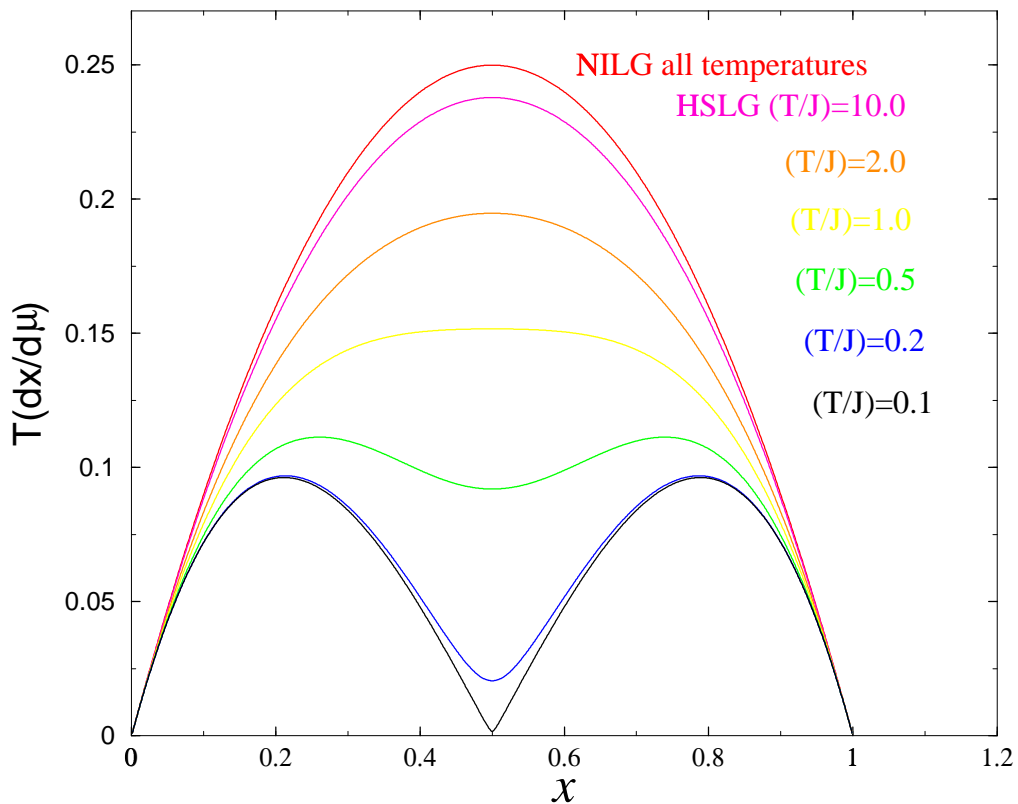
Where q -is the coordination number of the lattice.

Because of these relations the results known for the Ising model, can be easily transformed into results for Lattice Gas Model. There were made a lot of efforts to determine phase diagrams and the dependence of magnetization in Ising model on magnetic field for different structures. In lattice gas terminology it means that the behavior of the function $x(\mu)$ were studied. But in our case we are interested also in the dependence of $dx/d\mu$ on concentration x .

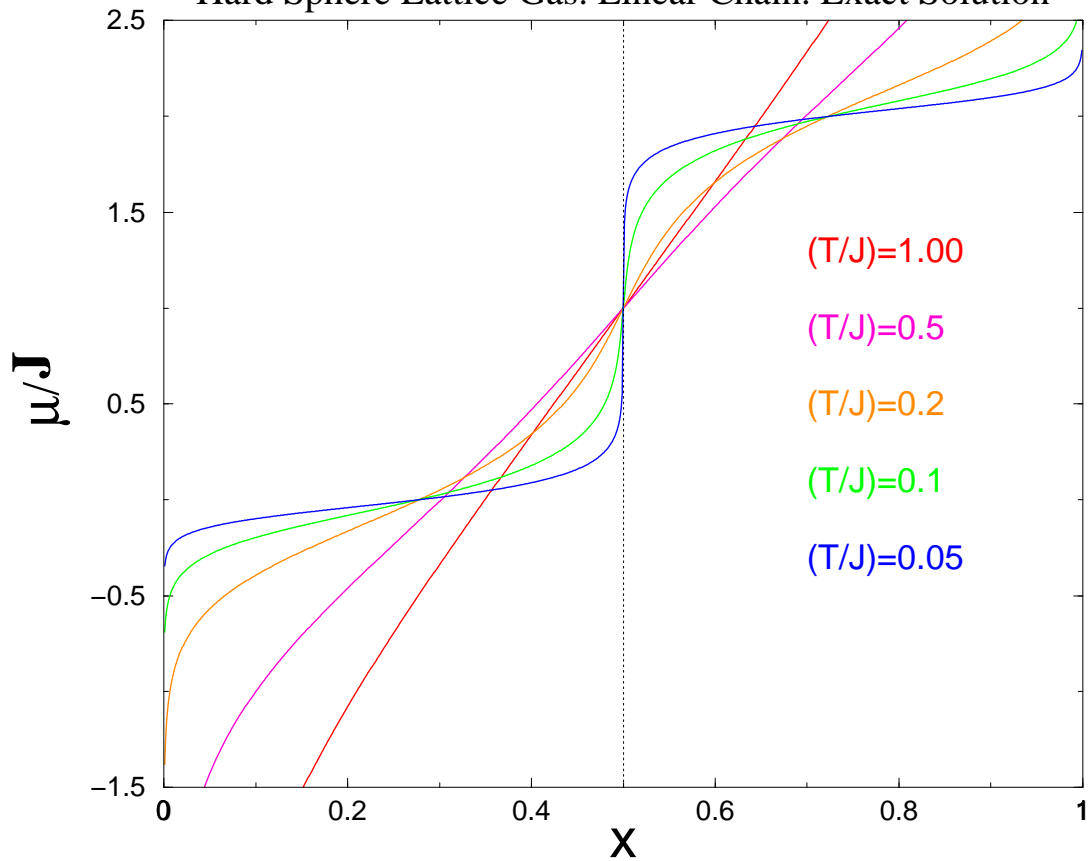
Exact Solutions for the Linear Chain in NILG and HSLG Models.



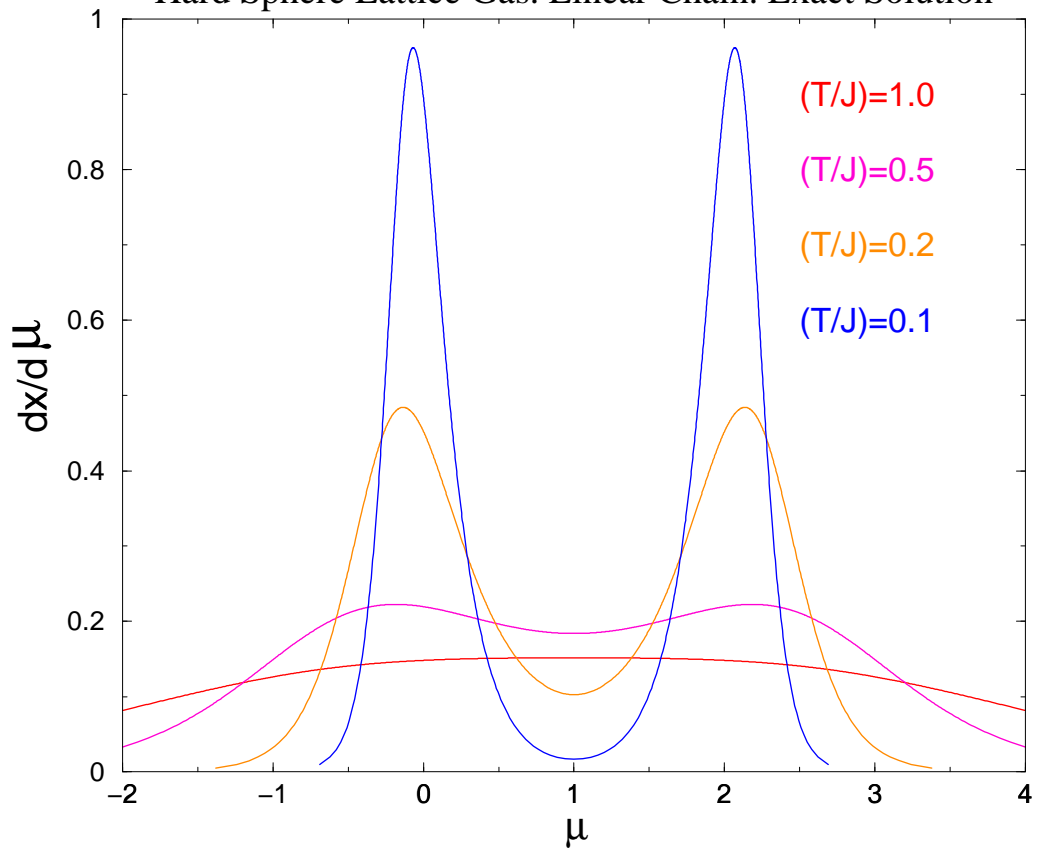
NILG and HSLG. Linear Chain. Exact Solutions



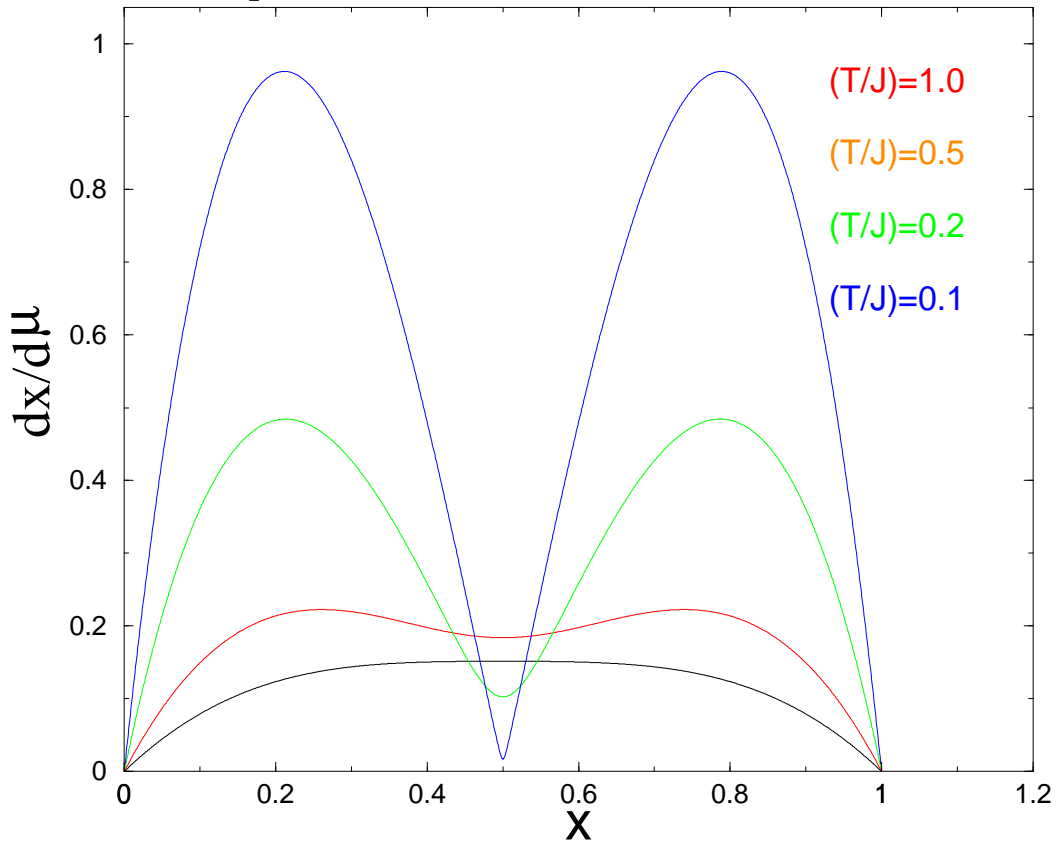
Hard Sphere Lattice Gas. Linear Chain. Exact Solution



Hard Sphere Lattice Gas. Linear Chain. Exact Solution



Hard Sphere Lattice Gas. Linear Chain. Exact Results



Hard Sphere Lattice Gas. Square Lattice.

Phase Diagram:

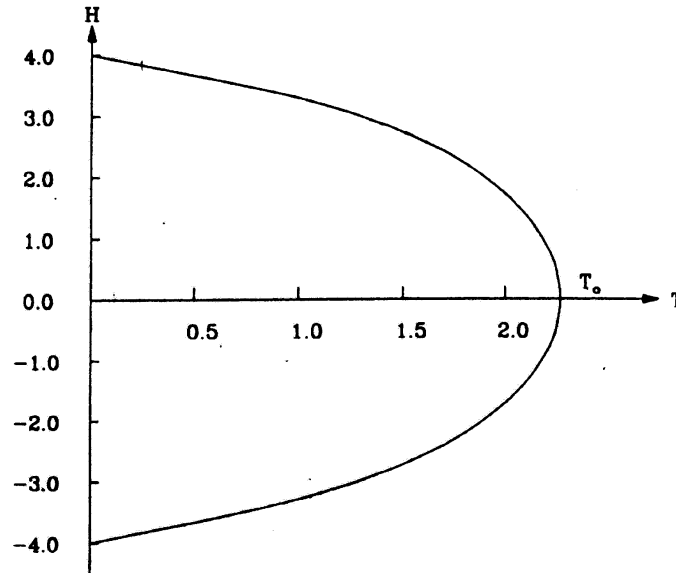


Fig. 1. The critical line (10) for the square lattice, where H is in units of $|J|$, T in units of $|J|/k$, and $T_0 = 2/\ln(\sqrt{2}+1) = 2.26918\dots$ is the zero-field critical point.

1

Fig. 1.

Three temperatures are below the critical temperature and one is above. For the square lattice the critical temperature above which there is no order-disorder phase transition is $(T_c / J) = 0.56$. (Onsager The dependence of chemical potential, V on concentration x for 4 different temperatures). The dot lines denote the critical the values of the chemical potential at which phase transitions occur. The values of the critical chemical potential here were taken from the approximate solution for the boundary order-disorder curve².

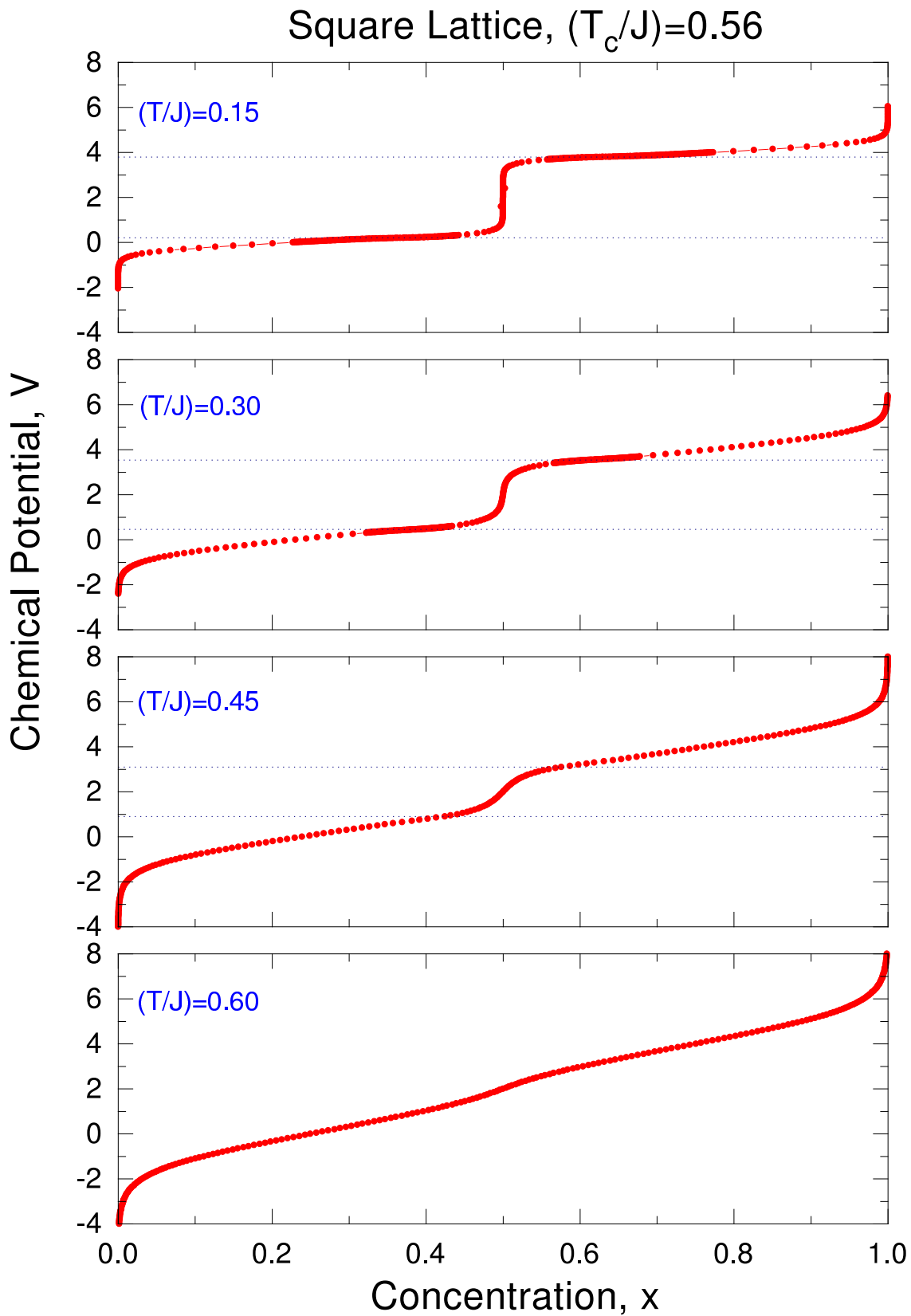
Fig.2.

The dependence of dx/dV on concentration x for 4 different temperatures. Three temperatures are below the critical temperature and one is above. The dot lines denote the critical values of the concentration at which phase transitions occur. The peaks correspond to the phase transitions.

² Muller-Hartmann and J.Zittartz, Z.Phys. B 27 (1977) 261

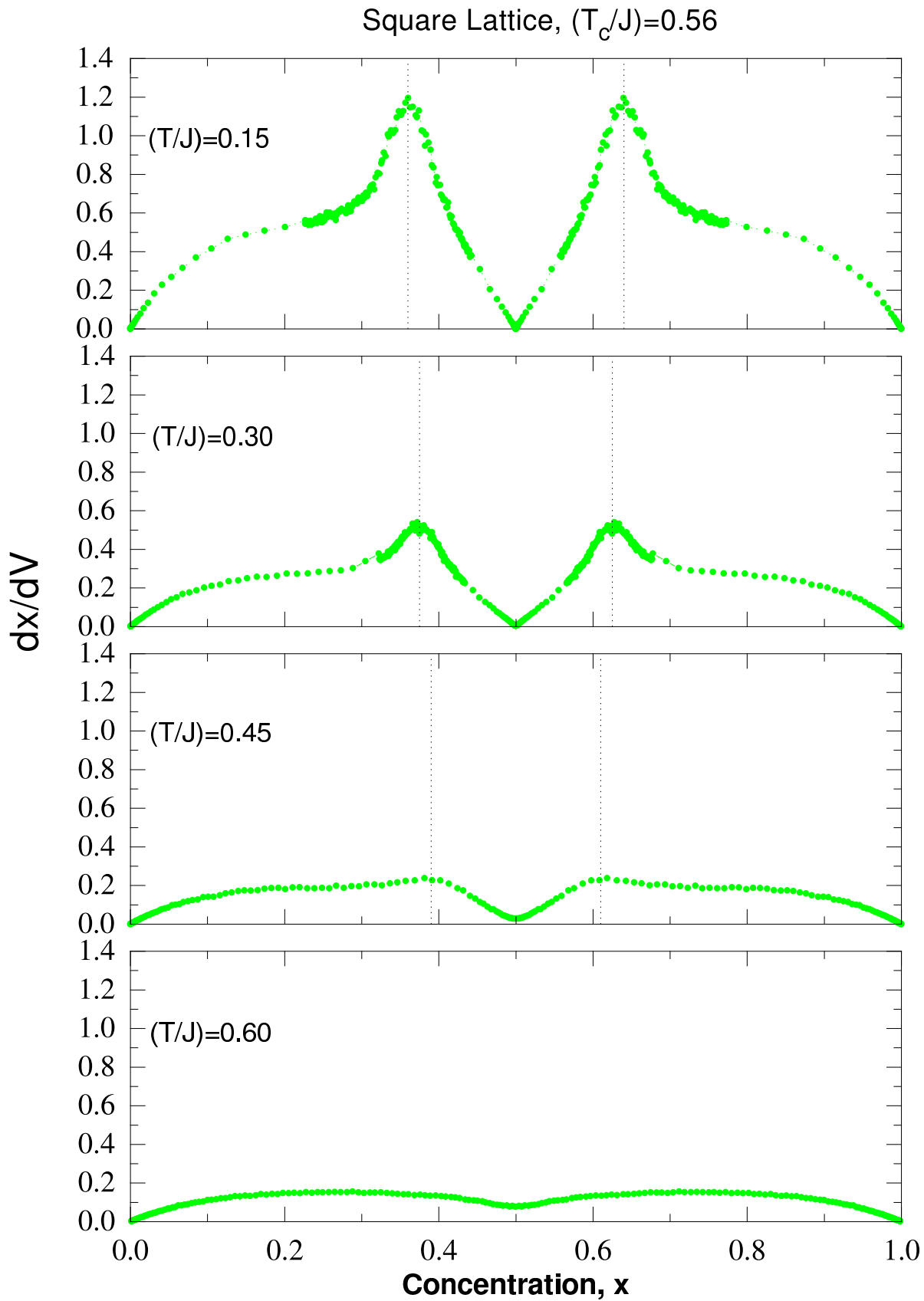
Hard Sphere Lattice Gas. Square Lattice. Fig.1.

Method of Solution: Monte-Carlo Simulations



Hard Sphere Lattice Gas. Square Lattice. Fig.2.

Method of Solution: Monte-Carlo Simulations



Hard Sphere Lattice Gas. Honeycomb Lattice.

Phase Diagram:

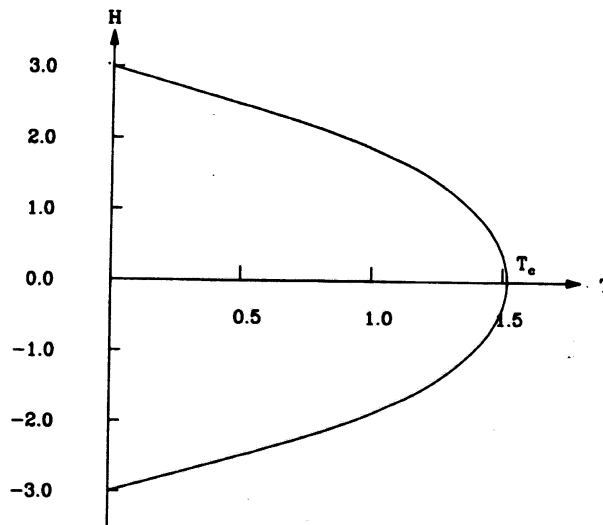


FIG. 2. The critical frontier (14) for the antiferromagnetic honeycomb Ising lattice, where H is in units of $|J|$ and T in units of $|J|/k$.

Fig. 3.

The dependence of chemical potential, V on concentration x for 4 different temperatures. Three temperatures are below the critical temperature and one is above. For the honeycomb lattice the critical temperature above which there is no order-disorder phase transition is $(T_c / J) = 0.375$ (for example³). The dot lines denote the critical values of the chemical potential at which phase transitions occur. The critical values of the chemical potentials correspond to the peaks on the fig.5 that represents the dependence of dx/dV on x (follows).

Fig. 4.

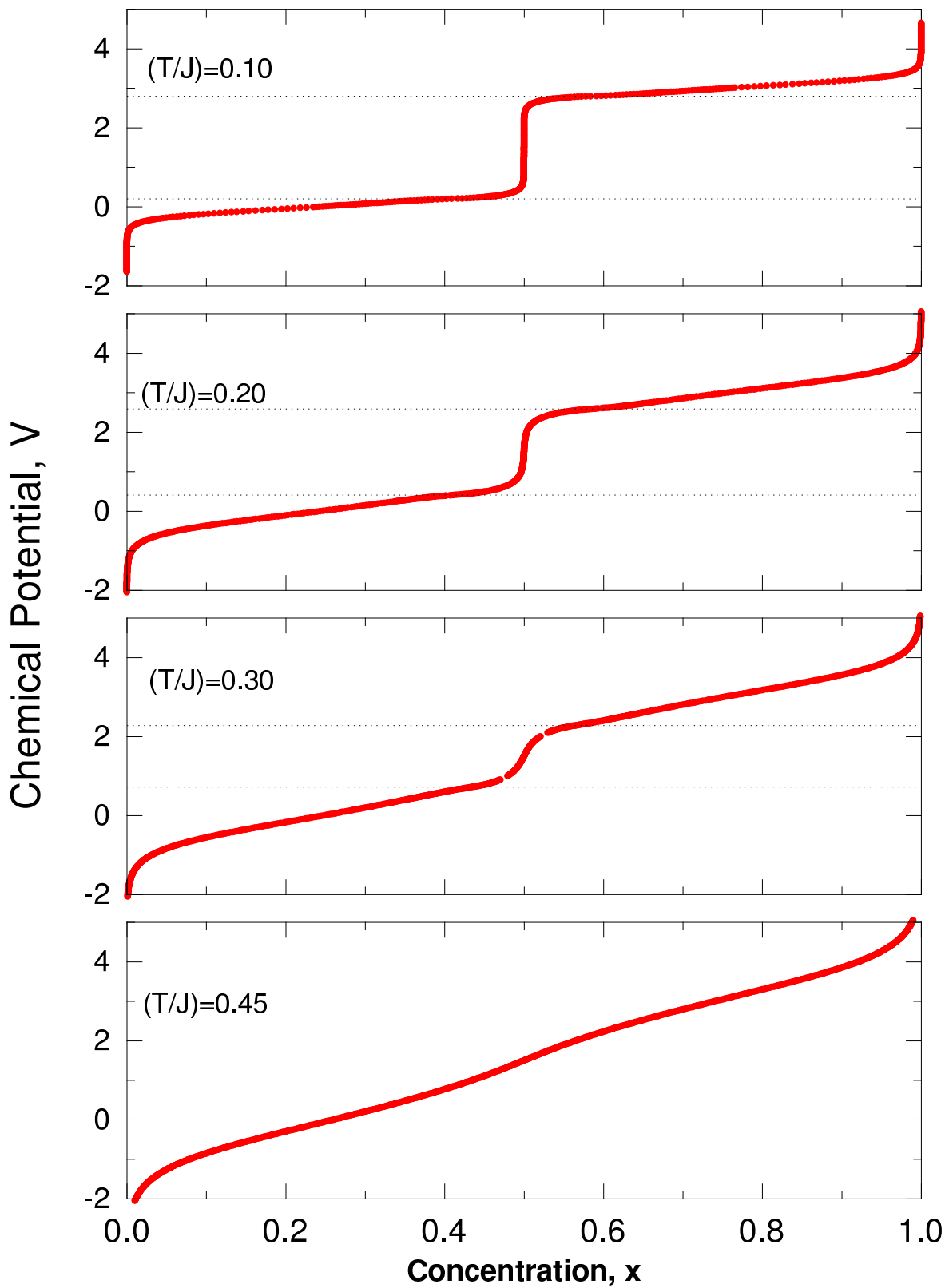
The dependence of dx/dV on concentration x for 4 different temperatures. Three temperatures are below critical temperature and one is above. The dot lines denote the critical values of the concentration at which phase transitions occur. The peaks correspond to the phase transitions.

³ Phys. Rev. B 62, 24 (1989) 2773

Hard Sphere Lattice Gas. Honeycomb Lattice. Fig.3

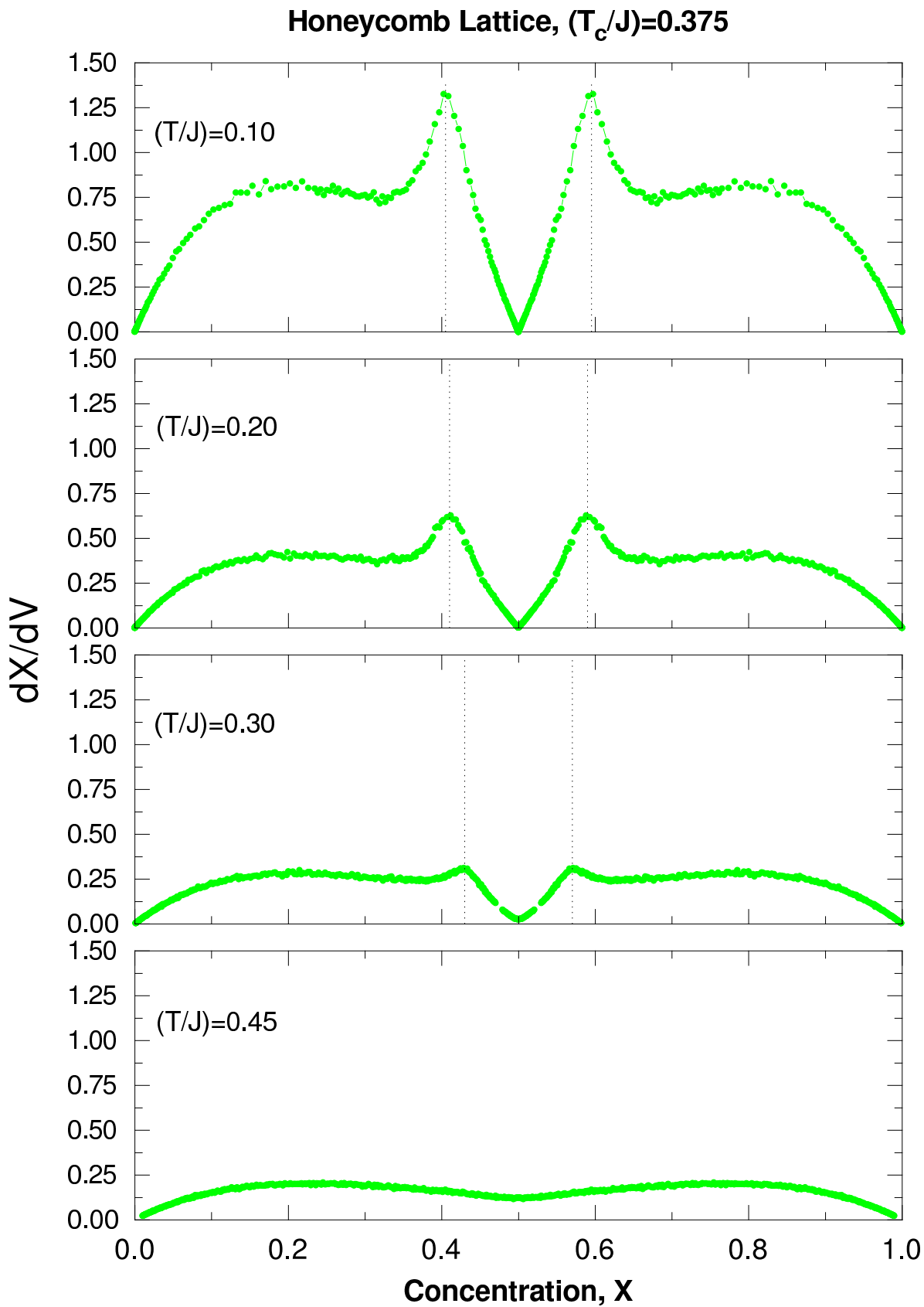
Method of Solution: Monte-Carlo Simulations

Honeycomb Lattice, $(T_c/J)=0.375$



Hard Sphere Lattice Gas. Honeycomb Lattice. Fig.4

Method of Solution: Monte-Carlo Simulations



Hard Sphere Lattice Gas. Triangular Lattice.

Phase Diagram

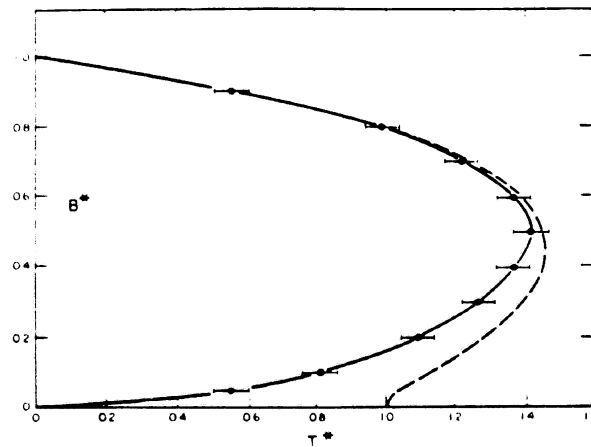


Fig. 2. Phase diagram for triangular antiferromagnet. Data points are Monte Carlo results. A solid curve is freely drawn through these points. Broken line is from Burley's Kikuchi approximation.

Fig.5.

The dependence of chemical potential, V on concentration x for 4 different temperatures. Three temperatures are below the critical temperature and one is above. For the triangular lattice the critical temperature above which there is no order-disorder phase transition is $(T_c / J) = 0.35^4$. The dot lines denote the critical values of the chemical potential at which phase transitions occur. The critical values of the chemical potential were taken from the approximate curve for the boundary order-disorder¹.

Fig.6.

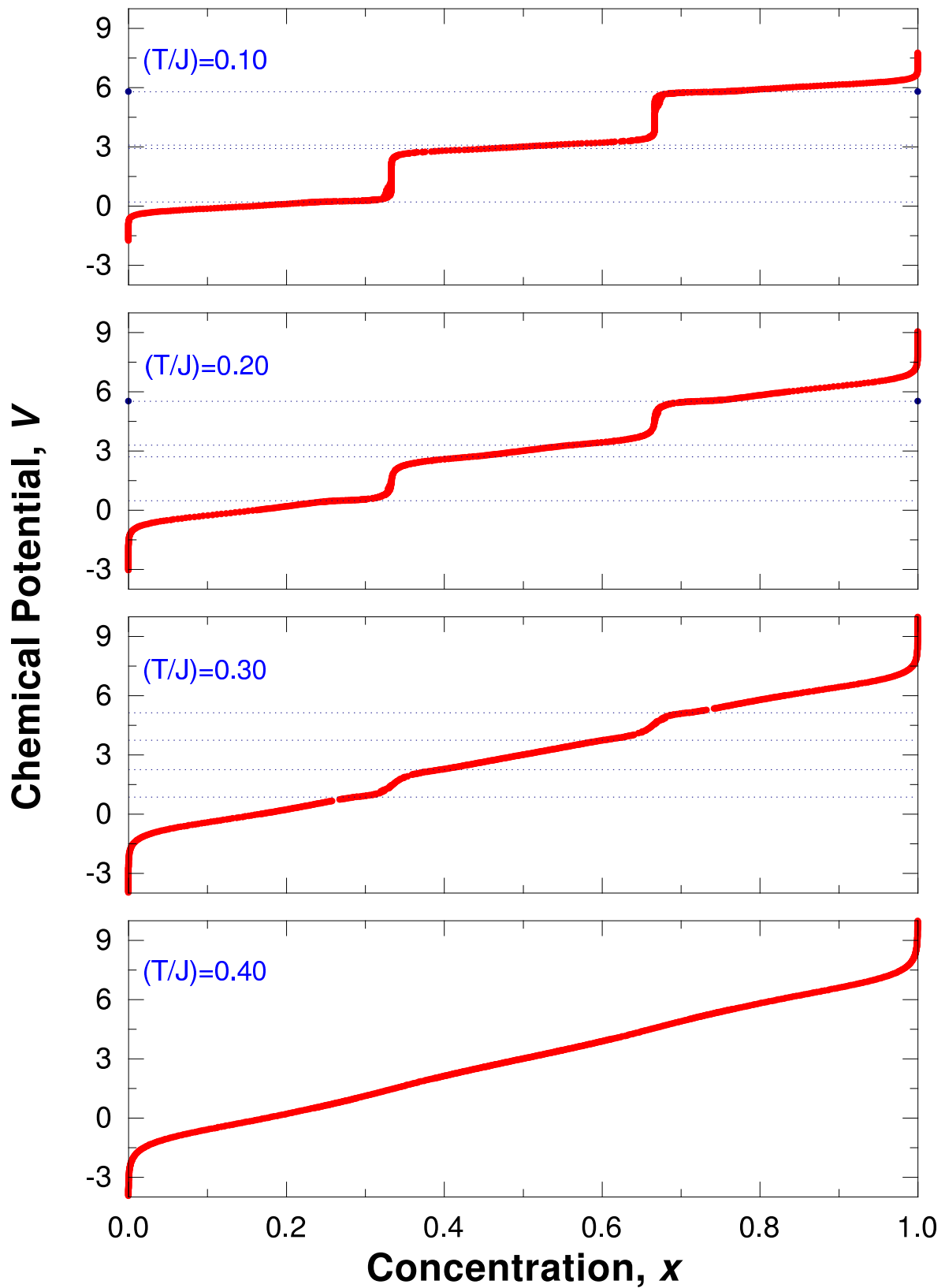
The dependence of dx/dV on concentration x for 4 different temperatures. Three temperatures are below critical temperature and one is above. The dot lines denote the critical values of the concentration at which phase transitions occur. The peaks correspond to the phase transitions.

⁴ B.D. METCALF, Phy.Lett. (45A) 1, 1973

Hard Sphere Lattice Gas. Triangular Lattice. Fig.5

Method of Solution: Monte-Carlo Simulation

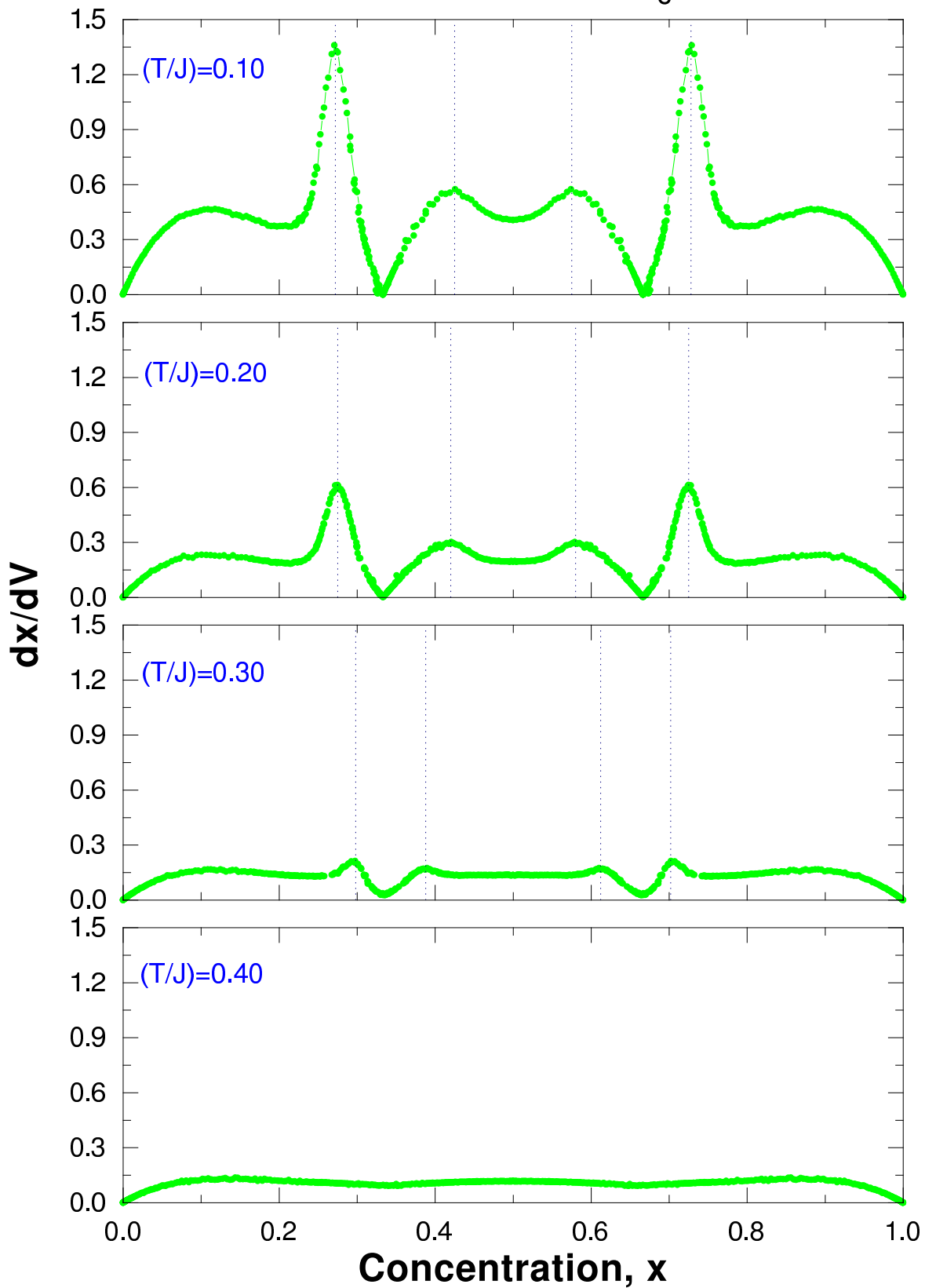
Triangular Lattice, $(T_c/J)=0.35$



Hard Sphere Lattice Gas. Triangular Lattice. Fig.6

Method of Solution: Monte-Carlo Simulation

Triangular Lattice, $(T_c/J)=0.35$



Non - Interacting Lattice Gas. Exact Solution.

The results are the same for the all system since there is no interaction between the sites.

$$H = -\mu \sum_i n_i \quad x = \frac{1}{N} \sum_i n_i$$

n_i -Is the occupancy number of the site. Zero if the site is empty and unity if the site is occupied.

μ - Chemical Potential. x - Concentration.

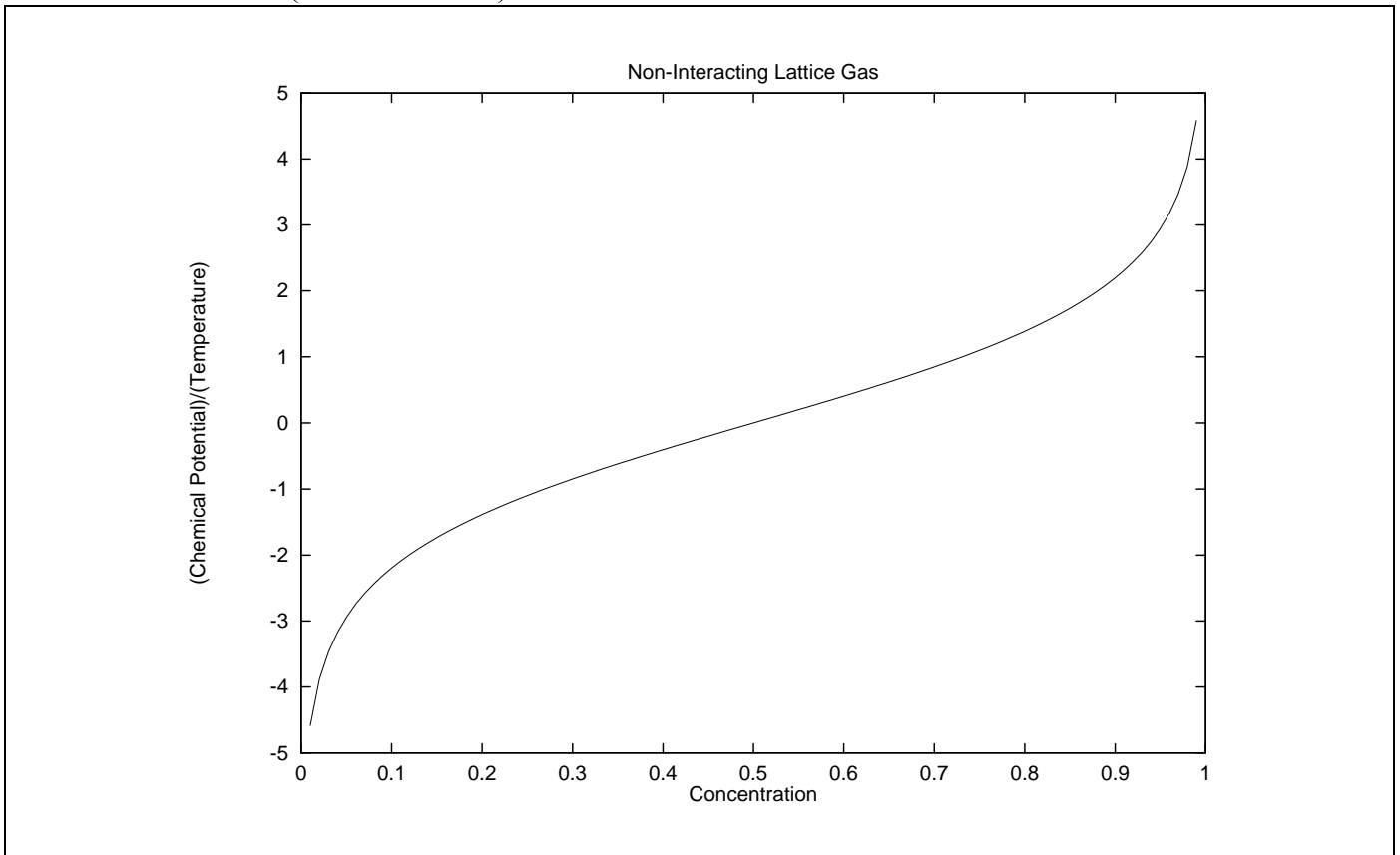
$$Z = \sum_{\text{configurations}} \exp(-\beta H) = \sum_{\text{configuration}} \exp\left(-\beta\mu \sum_i n_i\right) = \sum_{\text{configurations}} \prod_i \exp(\beta\mu n_i) = \prod_i \sum_{\text{configurations}} \exp(\beta\mu n_i)$$

$$Z = \sum_{\text{configurations}} \exp(-\beta H) = \prod_i \sum_{\text{configurations}} \exp(\beta\mu n_i) = \prod_i (1 + \exp(\beta\mu)) = (1 + \exp(\beta\mu))^N$$

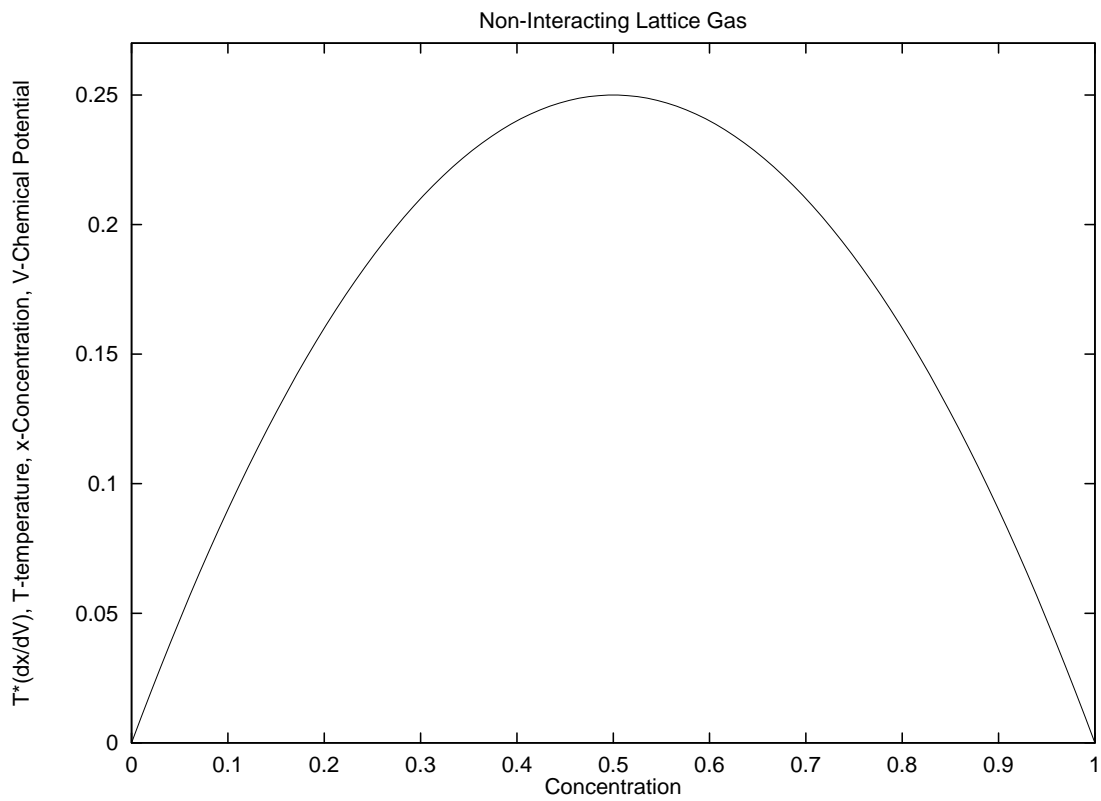
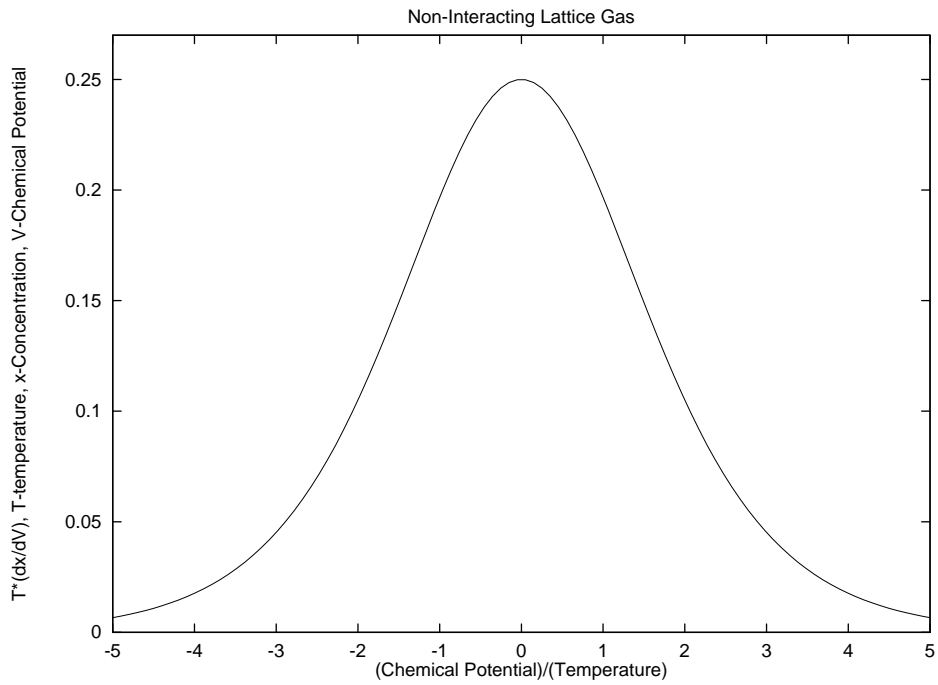
$$F = -T \ln(Z) = -NT \ln(1 + \exp(\beta\mu))$$

$$x = -\frac{1}{N} \frac{\partial F}{\partial \mu} = \frac{\exp(\beta\mu)}{1 + \exp(\beta\mu)}, \quad \beta\mu = \ln\left(\frac{x}{1-x}\right)$$

$$\frac{1}{\beta} \frac{\partial x}{\partial \mu} = \frac{\exp(\beta\mu)}{1 + \exp(\beta\mu)} \left(1 - \frac{\exp(\beta\mu)}{1 + \exp(\beta\mu)}\right) = x(1-x)$$



Non - Interacting Lattice Gas



Hard Sphere Lattice Gas (HSLG)

It is known that there is correspondence between HSLG model and Antiferromagnetic Ising Model (AFIM):

HSLG:

$$H_L = J_L \sum_{\langle ij \rangle} n_i n_j - \mu \sum_i n_i \quad n_i = 0, 1$$

AFIM:

$$H_I = J_I \sum_{\langle ij \rangle} s_i^z s_j^z - h \sum_i s_i^z \quad s_i^z = \pm 1$$

There are the following relationship between the parameters of those two models.

$$s_i^z = 2n_i - 1 \quad J_I = \frac{J_L}{4} \quad \frac{T_I}{J_I} = 4 \frac{T_L}{J_L} \quad \frac{1}{2} \left(\frac{h}{J_I} \right) = \left(\frac{\mu}{J_L} \right) - \frac{q}{2}$$

Where q -is the coordination number of the lattice.

Because of these relations the results known for the Ising model, can be easily transformed into results for Lattice Gas Model. There were made a lot of efforts to determine phase diagrams and the dependence of magnetization in Ising model on magnetic field for different structures. In lattice gas terminology it means that the behavior of the function $x(\mu)$ were studied.

But in our case we are interested also in the dependence of $\frac{dx}{d\mu}$ on concentration x . Divergence of this function can signal about the existence of second order phase transition.

Hard Sphere Lattice Gas. Linear Chain. Exact Solution.

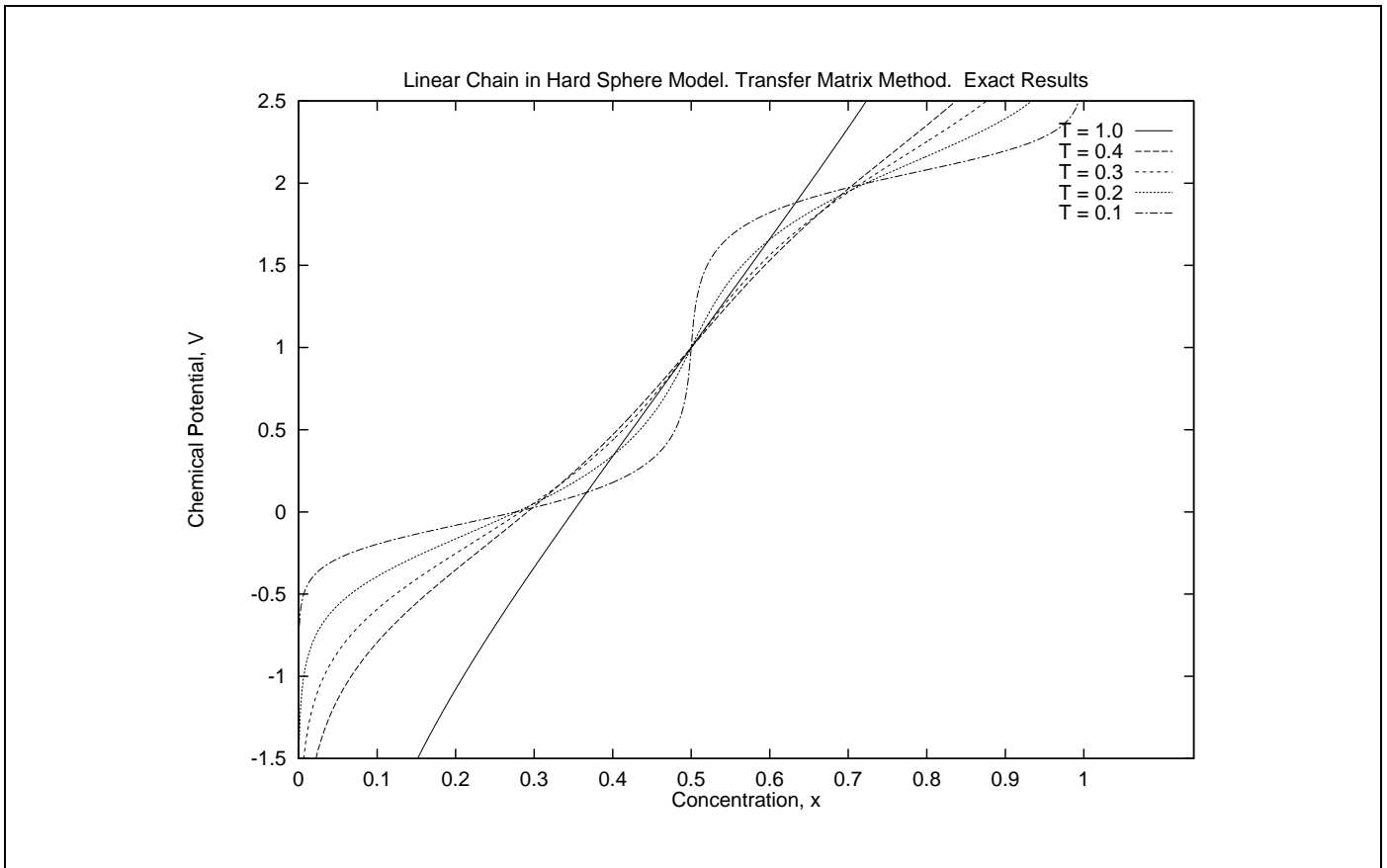
Method of Solution: Transfer Matrix Method.

Final Formulas:

$$\mu(x) = 1 + 2T \sinh^{-1} \left[\frac{x - \frac{1}{2}}{\sqrt{x(1-x)}} \exp\left(\frac{1}{2T}\right) \right]$$

$$\frac{dx}{d\mu} = \frac{\sqrt{1 + \frac{\left(x - \frac{1}{2}\right)^2}{x(1-x)} \exp\left(\frac{1}{T}\right)}}{2T \exp\left(\frac{1}{2T}\right) \left(1 + \frac{\left(x - \frac{1}{2}\right)^2}{x(1-x)}\right)}$$

$$T = T/J \quad \mu = \mu/J$$



Hard Sphere Lattice Gas. Linear Chain.

Exact Solution.

