KMC Short Course

Peter Smereka

University of Michigan, Ann Arbor

Thanks to Kris Reyes for help with this presentation

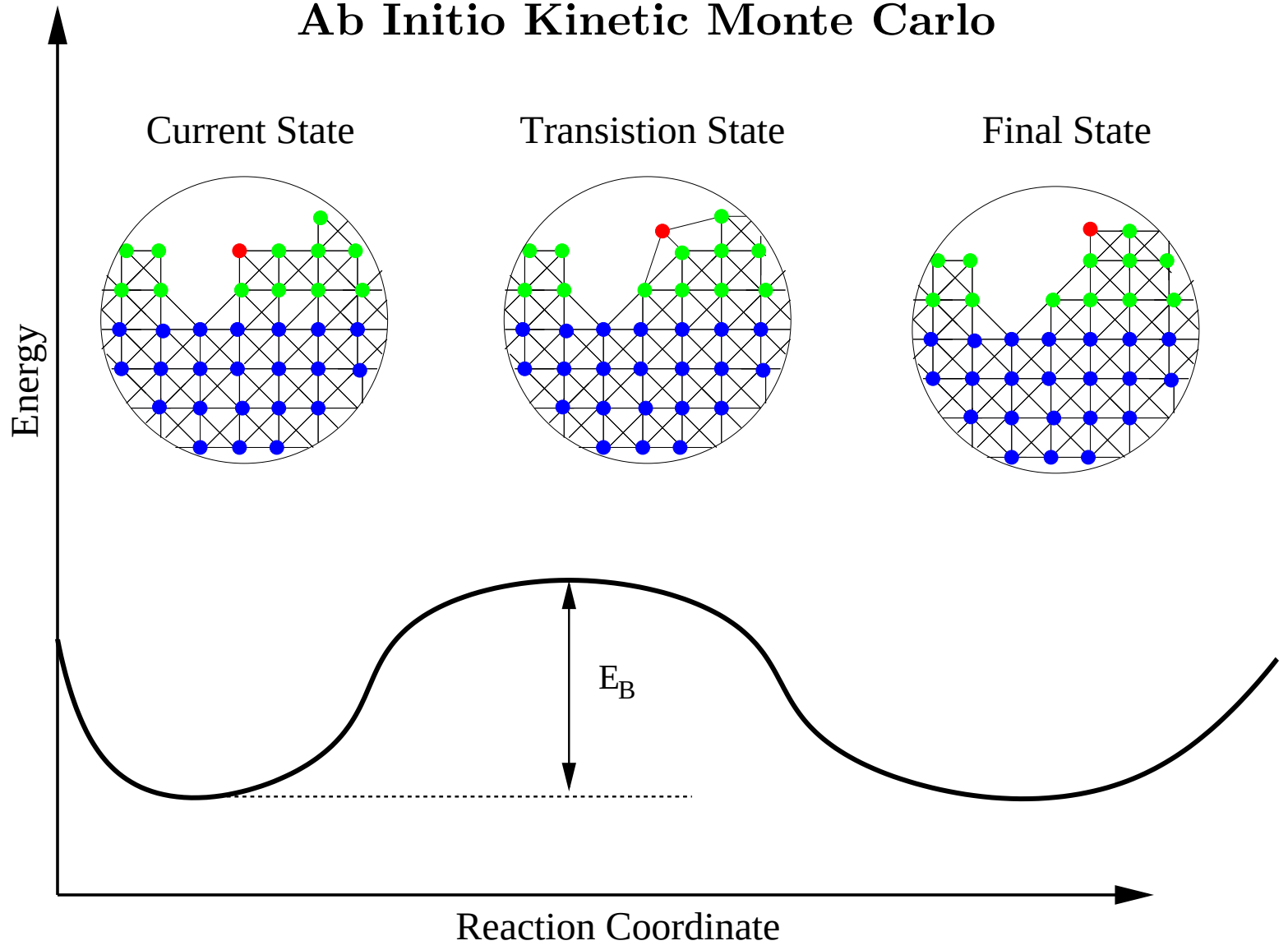
"The world (at the nanoscale) is cruel. And the only morality in a cruel world is chance. Unbiased. Unprejudiced. Fair."

Two-Face (from the Dark Knight)

Much of what is presented here relies on the following papers, however some new material has been presented which, in part, will be included in the PhD thesis of Kris Reyes.

- H.J. Leamy, G.H. Gilmer, and K.A. Jackson, Statistical Thermodynamics of Clean Surfaces, in Surface Physics of Material vol. 1, ed J.M. Blakely, Academic Press, New York 1975.
- J. Krug, H.T. Dobbs, and S. Majaniemi, Adatom mobility for the solid-on-solid model, *Zeitschrift Für Physik B* **97**, 281-291 (1995).
- A. Zangwill, C.N. Luse, D.D. Vvedensky, and M.R. Wilby, Equations of motion for epitaxial grow th, *Surface Science Letter* **274** L529-L534 (1992).

Ab Initio Kinetic Monte Carlo



KMC is based on transition state theory

Ab Initio Kinetic Monte Carlo

- $E_B = E(\text{transition state}) - E(\text{current state})$
- E is calculated with a Molecular Potential or using Density Functional Theory
- Rates are based on transition state theory which gives $TR_{\text{Initial State}\rightarrow\text{Final State}} = \omega \exp(-E_B/k_BT)$
- ω is the "attempt" frequency, k_BT is the thermal energy

Detailed Balance

A natural property of transition state theory is the following

- $e^{-E_A/k_BT}TR_{\mathrm{A}\to\mathrm{B}} = e^{-E_B/k_BT}TR_{\mathrm{B}\to\mathrm{A}} = \omega e^{-E_T/k_BT}$
- E_A and E_B are the energies of states A and B
- The above relationship between $TR_{\mathrm{A}\to\mathrm{B}}$ and $TR_{\mathrm{B}\to\mathrm{A}}$ is called detailed balance

Bond Counting Kinetic Monte Carlo

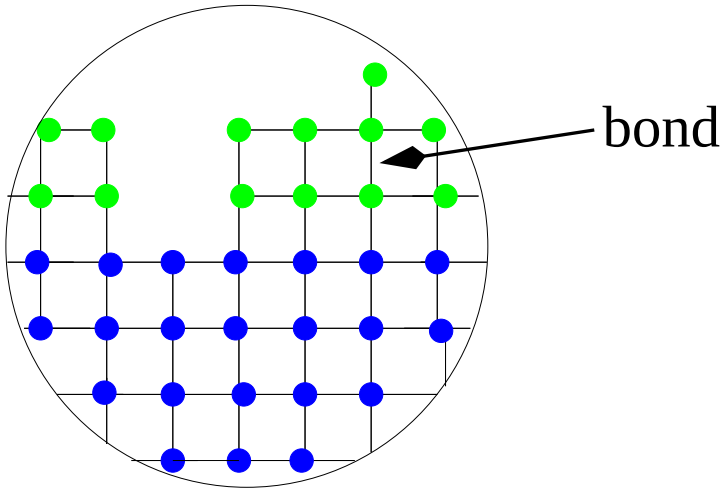
$$TR_{\text{Initial State}\rightarrow\text{Final State}} = \omega \exp(-\gamma n_b / k_B T)$$

where n_b is number of bonds of the atom in its initial state.

Bond Counting Kinetic Monte Carlo

- One considers a system where all the atoms are on a fixed lattice.
- We shall use a simple cubic lattice
- $E = -\gamma \cdot$ number of bonds

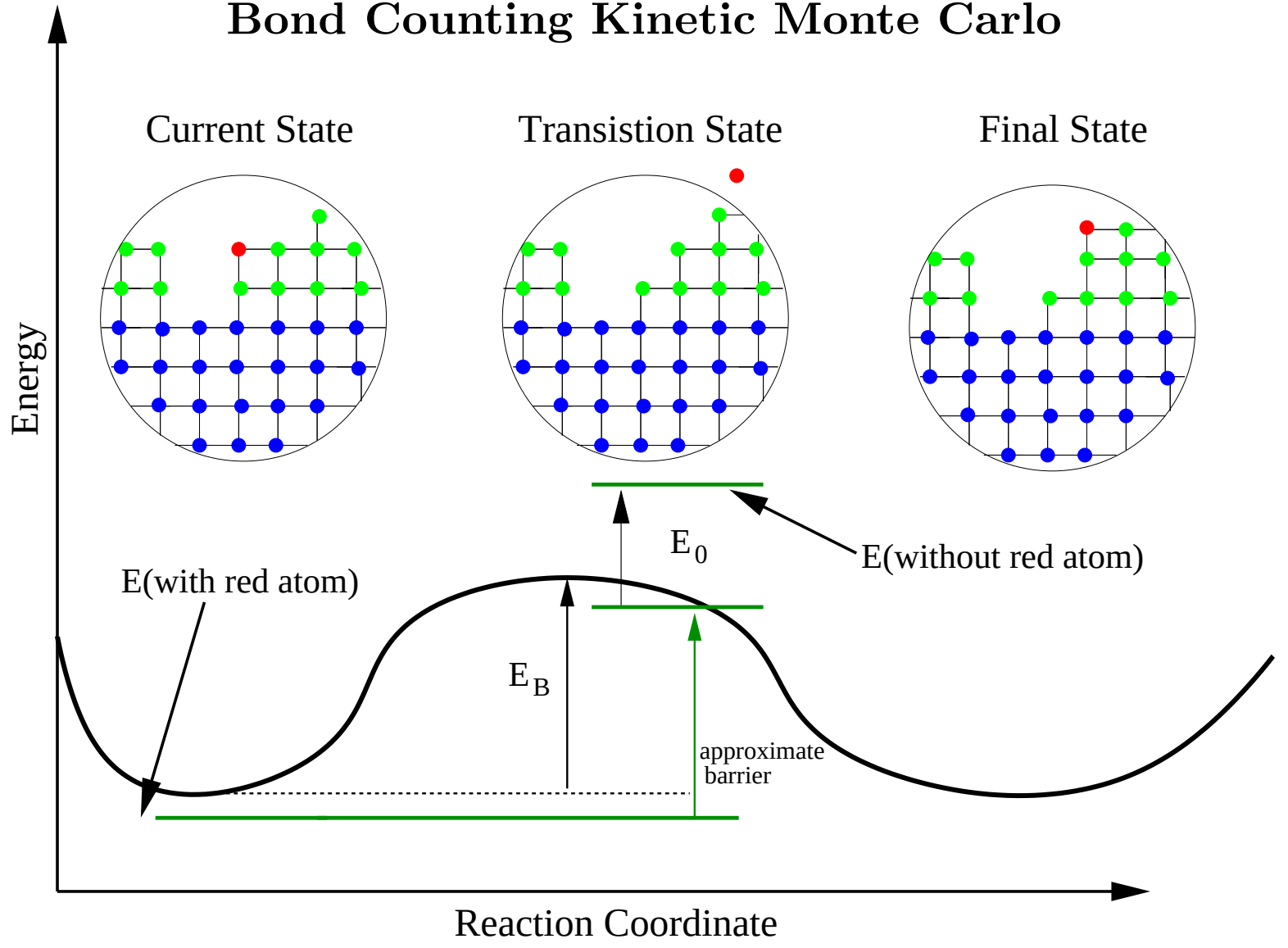
Bond Counting Kinetic Monte Carlo



Simple Cubic Lattice

Nearest Neighbor Interactions

Bond Counting Kinetic Monte Carlo



Bond Counting Kinetic Monte Carlo

- $E_B = E(\text{transition state}) - E(\text{current state})$
- $E(\text{transition state}) \approx E(\text{without red atom}) - E_0$
- $E(\text{current state}) = E(\text{with red atom})$
- $E_B \approx -\Delta E - E_0$
- $\Delta E = E(\text{with red atom}) - E(\text{without red atom})$
- $TR_{\text{Initial State}\rightarrow\text{Final State}} = \omega \exp((E_0 + \Delta E)/k_B T))$

Bond Counting Kinetic Monte Carlo

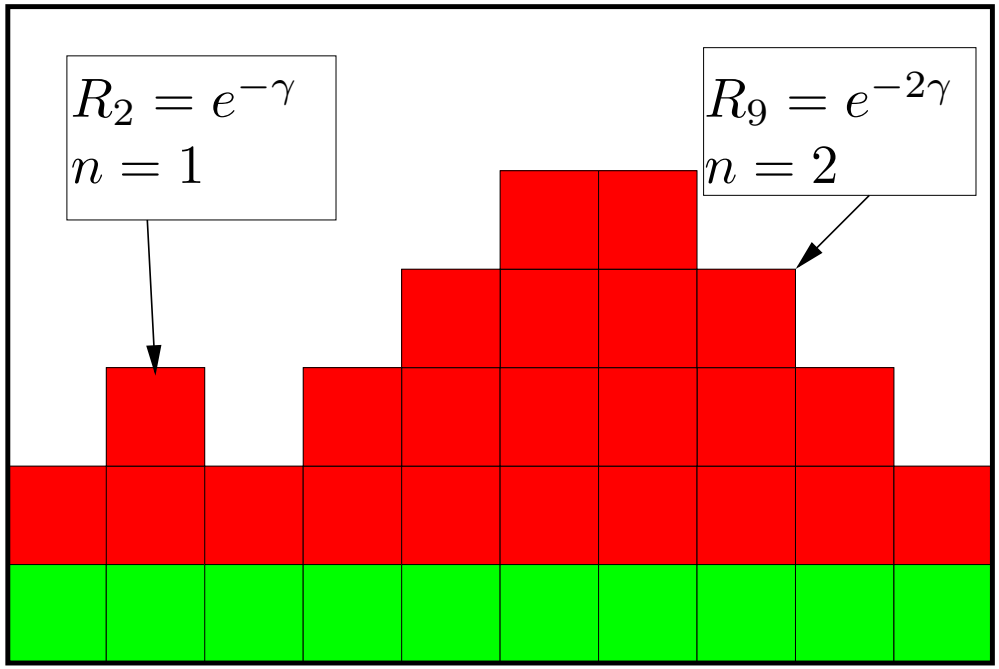
- $\Delta E = E(\text{with red atom}) - E(\text{without red atom})$
- $\Delta E = -\gamma n_b$
- $n_b =$ number of bonds of the red atom
- $TR_{\text{red}} = \omega e^{E_0/k_BT} e^{-n_b\gamma/k_BT}$
- Hopping Rate $\Rightarrow \quad R_{\text{red}} = 2\omega e^{E_0/k_BT} e^{-n_b\gamma/k_BT}$

Solid-on-Solid Bond Counting Kinetic Monte Carlo

Consider 1+1 dimensions with M sites in the x-direction

- Film profile is given by a function h_i, $i = 1, ..., M$.
- We use periodic boundary conditions
- When an atom hops it moves to left or right with equal probability.
- Hopping rate of an atom is at site i is $R_i = \Omega \exp(-\gamma n_b / k_B T)$
- $\Omega = 2\omega e^{E_0/k_B T}$
- Deposition is easily included.

Schematic for SOS BC KMC

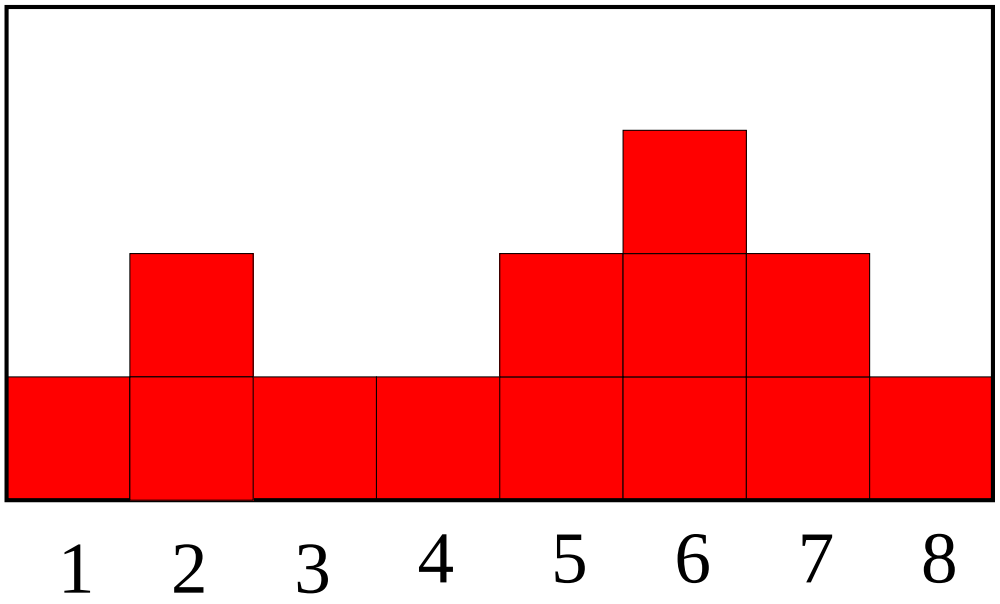


- For convenience $k_B T = 1$ and $\Omega = 1 \quad \Rightarrow \quad R_i = e^{-n_b \gamma}$
- n_b = number of nearest neighbors

Implementation

- Make a list of rates, R_i, for all atoms
- $Z = \sum_{i=1}^{N} R_i$ is the total transition rate
- $P_i = R_i/Z$ is the hopping probability
- Choose an site with a probability given by P_i
- Hop the surface atom at site i to either site $i-1$ or $i+1$ with equal probability
- Update the values of R_i and P_i that have changed
- Repeat the above steps

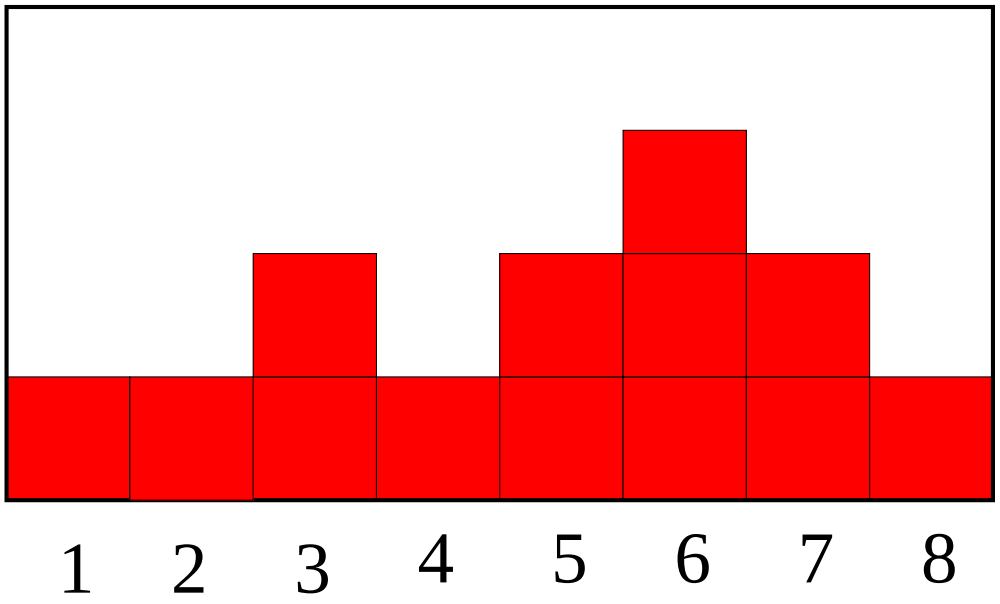
Example - $\gamma = \log(100) \approx 4.6052$



$$
\begin{aligned}
R_1 &= 10^{-6} \quad (n_b = 3) \\
R_2 &= 10^{-2} \quad (n_b = 1) \\
R_3 &= 10^{-6} \quad (n_b = 3) \\
R_4 &= 10^{-6} \quad (n_b = 3) \\
R_5 &= 10^{-4} \quad (n_b = 2) \\
R_6 &= 10^{-2} \quad (n_b = 1) \\
R_7 &= 10^{-4} \quad (n_b = 2) \\
R_8 &= 10^{-6} \quad (n_b = 3)
\end{aligned}
$$

Site 2 was picked $\Rightarrow$

Example - $\gamma = \log(100) \approx 4.6052$



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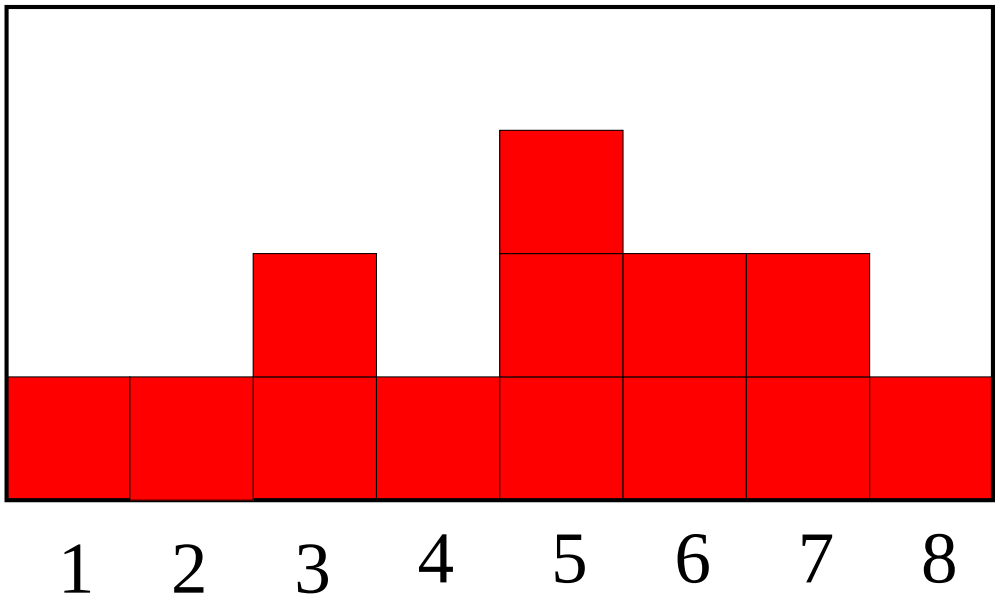
R_5 &= 10^{-4} \quad (n_b = 2) \\
R_6 &= 10^{-2} \quad (n_b = 1) \\
R_7 &= 10^{-4} \quad (n_b = 2) \\
R_8 &= 10^{-6} \quad (n_b = 3)
\end{aligned}
$$

Site 6 was picked $\Rightarrow$

Example - $\gamma = \log(100) \approx 4.6052$



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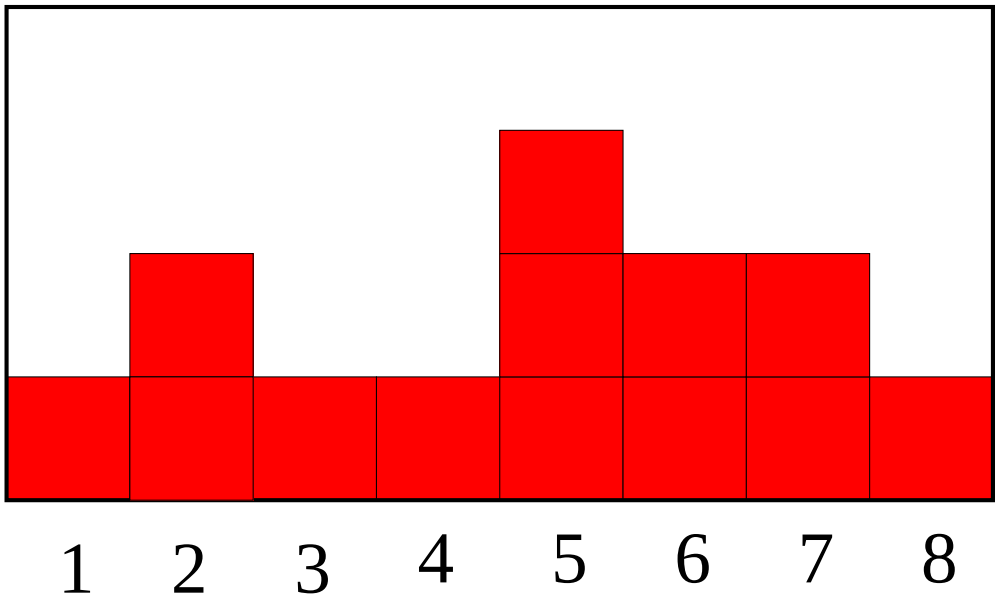
R_5 &= 10^{-2} \quad (n_b = 1) \\
R_6 &= 10^{-6} \quad (n_b = 3) \\
R_7 &= 10^{-4} \quad (n_b = 3) \\
R_8 &= 10^{-6} \quad (n_b = 2)
\end{aligned}
$$

Site 3 was picked $\Rightarrow$

Example - $\gamma = \log(100) \approx 4.6052$



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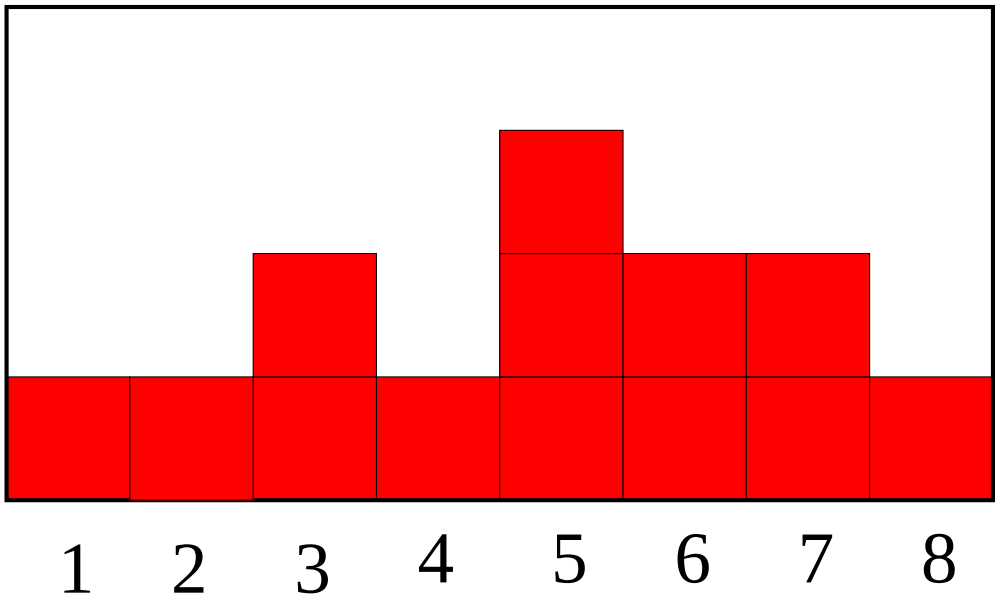
R_7 &= 10^{-4} \quad (n_b = 2) \\
R_8 &= 10^{-6} \quad (n_b = 3)
\end{aligned}
$$

Site 2 was picked $\Rightarrow$

Example - $\gamma = \log(100) \approx 4.6052$



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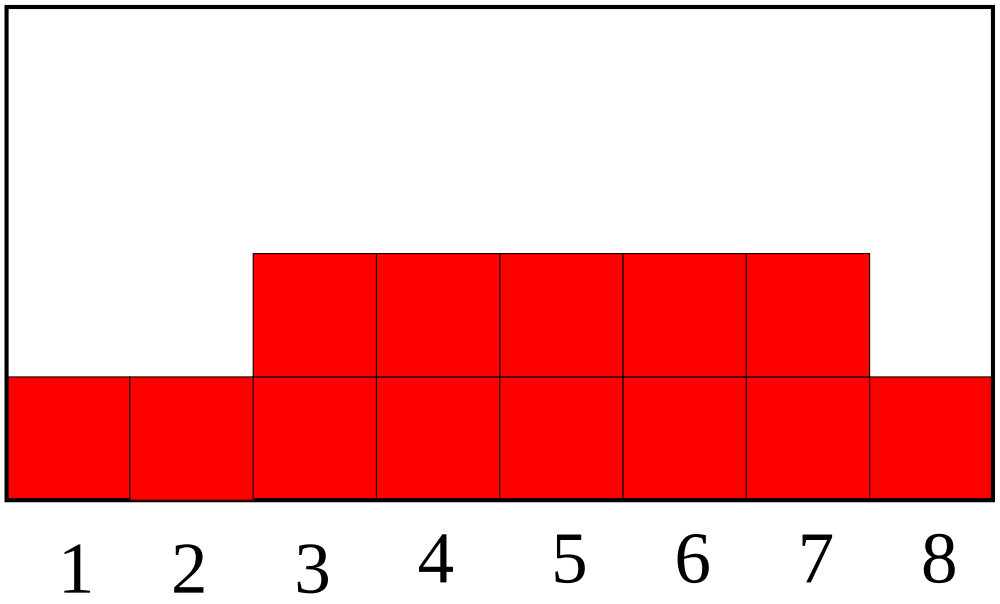
R_7 &= 10^{-4} \quad (n_b = 2) \\
R_8 &= 10^{-6} \quad (n_b = 3)
\end{aligned}
$$

Site 5 was picked $\Rightarrow$

Example - $\gamma = \log(100) \approx 4.6052$



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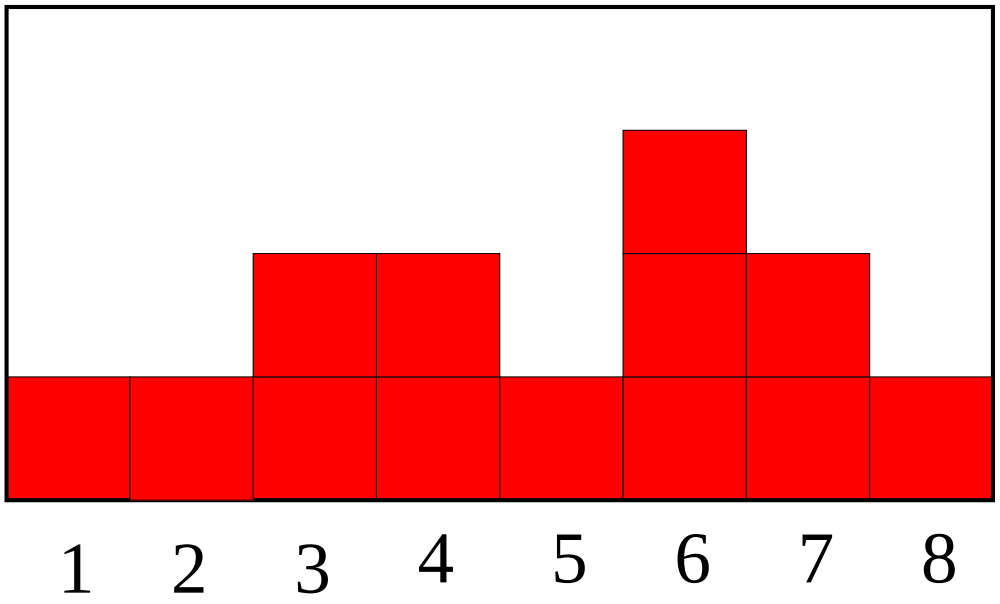
R_7 &= 10^{-4} \quad (n_b = 2) \\
R_8 &= 10^{-6} \quad (n_b = 3)
\end{aligned}
$$

Site 5 was picked (an unlikely choice) $\Rightarrow$

Example - $\gamma = \log(100) \approx 4.6052$



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R_5 &= 10^{-4} \quad (n_b = 3) \\
R_6 &= 10^{-2} \quad (n_b = 1) \\
R_7 &= 10^{-4} \quad (n_b = 2) \\
R_8 &= 10^{-6} \quad (n_b = 3)
\end{aligned}
$$

$\Rightarrow$

How do we choose the site ?

- Choose an site with a probability given by P_i
- where $P_i = R_i/Z$ is the hopping probability
- and $Z = \sum_{i=1}^{N} R_i$
- In other words we need to sample a distribution

Rejection Method

1. Suppose we wish to generate a random variable whose pdf is $f(x)$ with $f(x) > 0$ for $a < x < b$.
2. Let f_m be the maximum value of $f(x)$
3. Let $U = \text{uniform}(0, 1)$ and $Y = \text{uniform}(a, b)$
4. Sample Y and let the value be y.
5. Sample U and let the value be u.
6. If $u \leq f(y)/f_m$ then $X = y$ (success)
7. If $u > f(y)/f_m$ then go back to step 4 (rejection)
8. The pdf for the random variable X is $f(x)$
9. If f takes on wide range of values then this is quite inefficient as much time will be spent rejecting choices

Proof

- $P(X \leq x) = P(Y \leq x \,|\, U \leq f(Y)/f_m)$
- $P(X \leq x) = \dfrac{P(Y \leq x,\, U \leq f(Y)/f_m)}{P(U \leq f(Y)/f_m)}$
- Since Y and U are independent random variables, their joint pdf is $\begin{cases} \frac{1}{b-a} & a < y < b \quad \text{and} \quad 0 < u < 1 \\ 0 & \text{otherwise} \end{cases}$
- $P(U \leq f(Y)/f_m) = \int_a^b \int_0^{f(y)/f_m} \frac{1}{b-a} du dy$
- $= \frac{1}{(b-a)f_m} \int_a^b f(y) dy = \frac{1}{(b-a)f_m}$

Proof Continued

- $P(Y \leq x,\, U \leq f(Y)/f_m) = \int_a^x \int_0^{f(y)/f_m} \frac{1}{(b-a)} du dy$
- $= \frac{1}{(a-b)f_m} \int_a^x f(y) dy$
- Therefore, $P(X \leq x) = \int_a^x f(y) dy$
- Therefore pdf of X is $f(x)$

Rejection Method for KMC

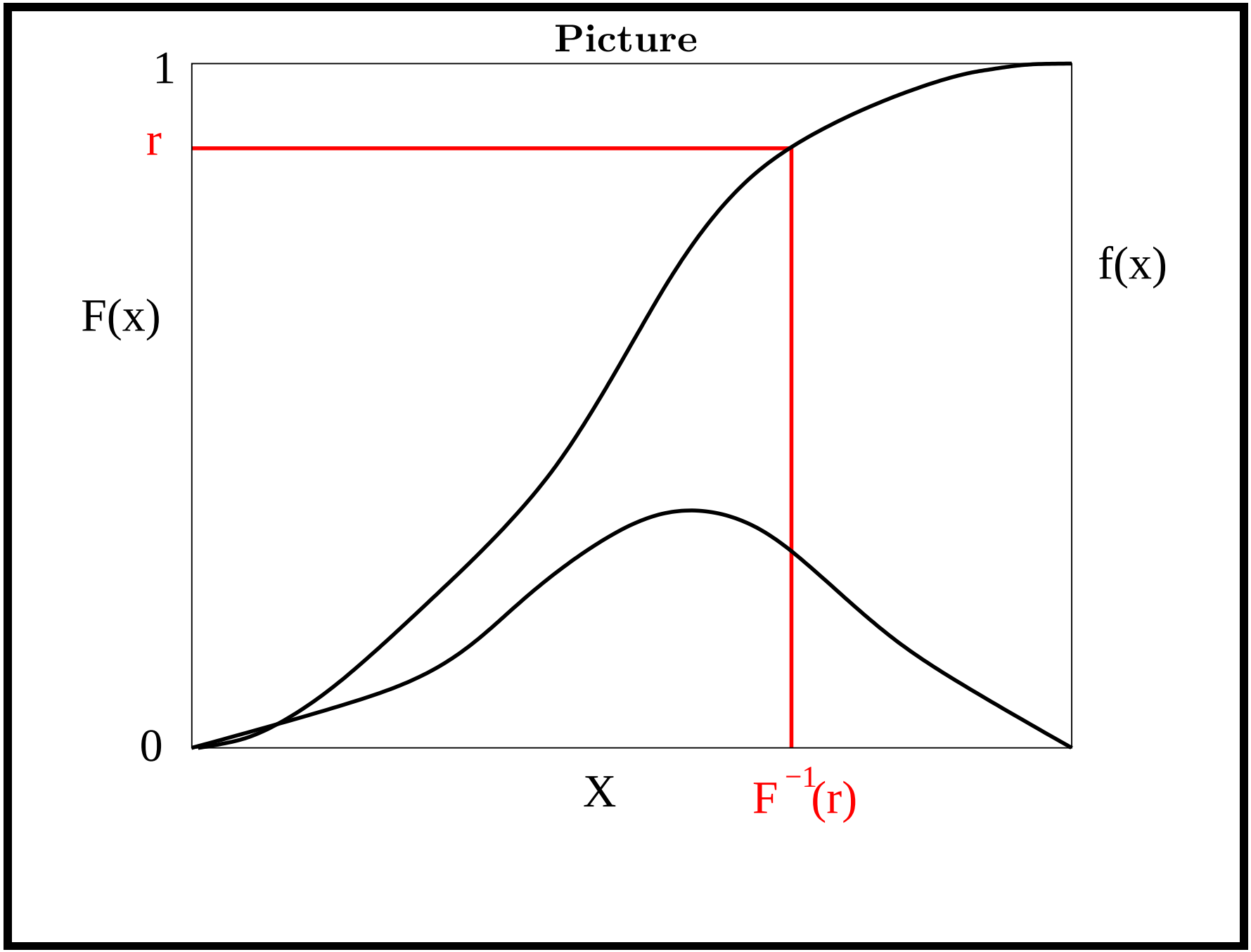
- Let P_M be chosen such that $P_i \leq P_M$ for all i
- Pick a site random with equal probability.
- Let $r = U(0, 1)$.
- If $r \leq P_i/P_M$ then pick that site.
- If $r \geq P_i/P_M$ got back to step one
- If $P_1, P_2, ...$ take on wide range of values then this is quite inefficient as much time will be spent rejecting choices

Rejection Free Sampling

- Let X be a random variable whose pdf is $f(x)$
- Let $F(x) = \int_{-\infty}^{x} f(y)dy$ (i.e. The cdf of X)
- Let $R = U[0, 1]$
- Claim: The random variable $Y = F^{-1}(R)$ has a pdf given by $f(x)$

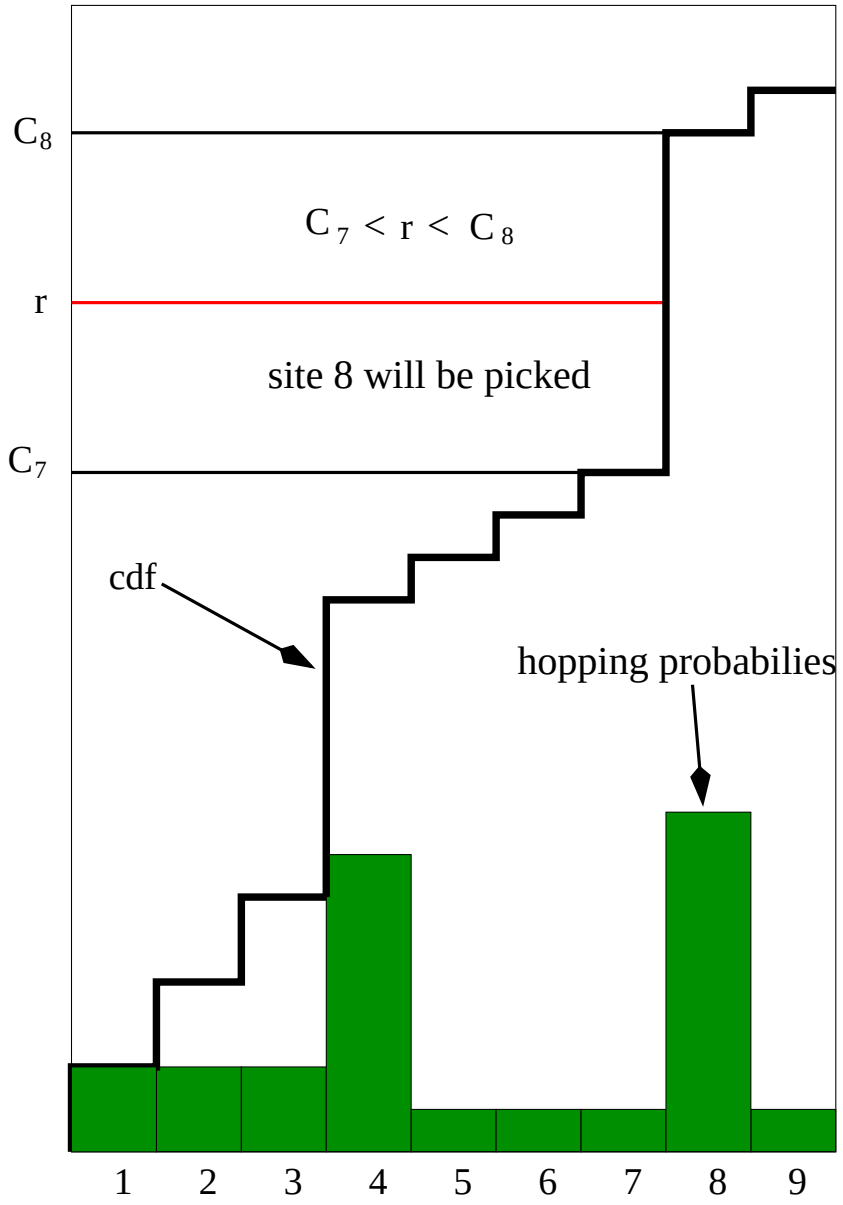
Proof

- Let $g(y)$ be the pdf for Y
- $P(Y \leq a) = \int_{-\infty}^{a} g(y)dy$
- $P(F^{-1}(R) \leq a) = \int_{-\infty}^{a} g(y)dy$
- $P(R \leq F(a)) = \int_{-\infty}^{a} g(y)dy$
- $F(a) = \int_{-\infty}^{a} g(y)dy$
- $f(a) = g(a)$
- $\Rightarrow Y = F^{-1}(R)$ has a pdf given by $f(x)$


Picture
1
r
F(x)
f(x)
0
X
F −1(r)

Rejection Free Sampling for KMC

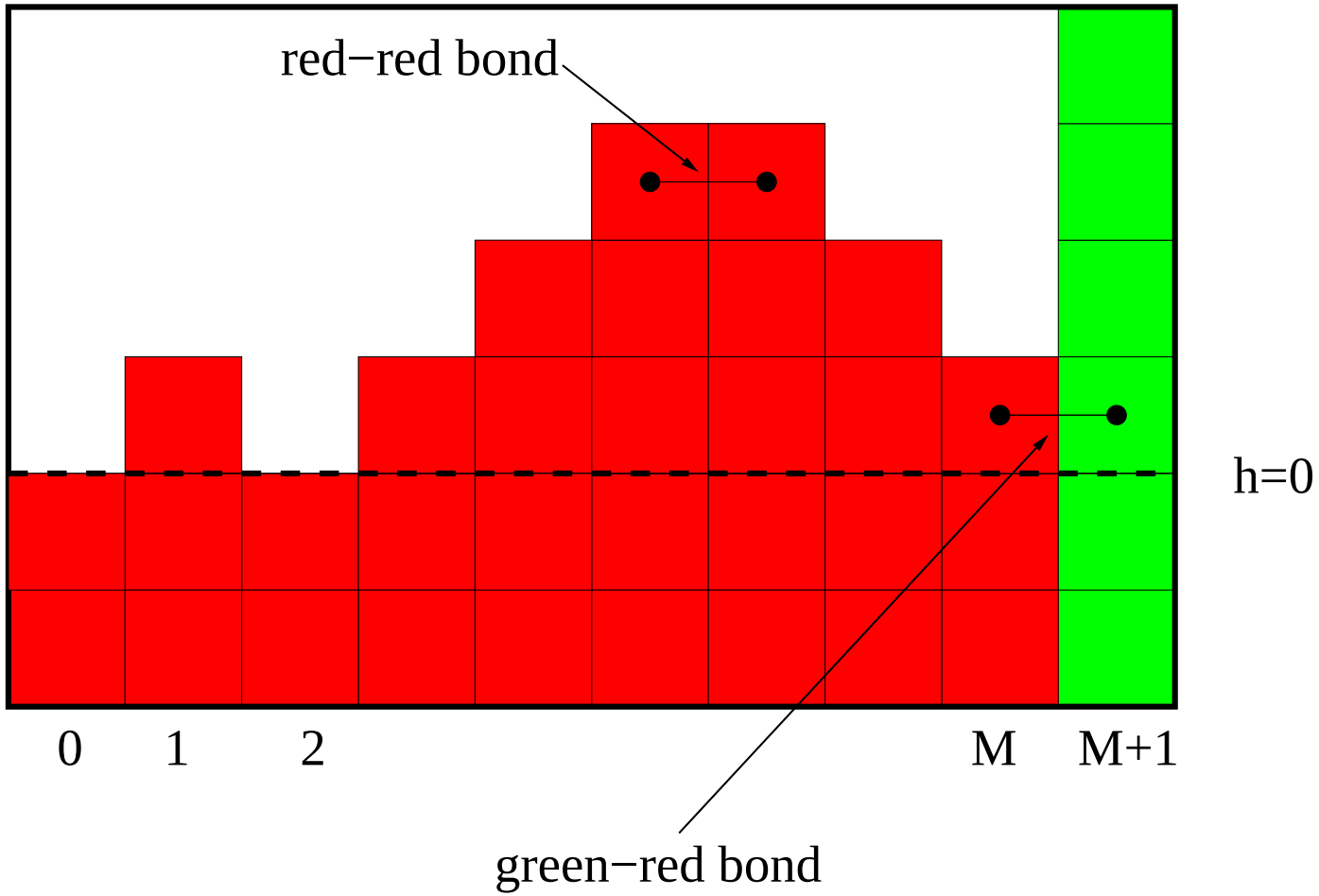
- Let $C_i = \sum_{j=1}^{i} P_j$ ($C_M = 1$ – Discrete cdf)
- Define $C_0 = 0$
- Let $R = U[0, 1]$
- Pick site j such that $C_{j-1} < R < C_j$


C8
C7 < r < C8
r
site 8 will be picked
C7
cdf
hopping probabilies
1
2
3
4
5
6
7
8
9

Detailed Analysis of KMC Model

Our Solid-on-Solid KMC Model

- Film is pinned at one end
- Film is "free" at the other



Our Solid-on-Solid KMC Model

- There are M active sites of a semi-infinite 1+1 dimensional crystal
- $i = 1$ and $i = M$ are boundary sites
- $i = 0$ and $i = M + 1$ are ghost sites
- $h_0 = 0$ and $h_{M+1} = h_M$
- $h = (h_0, h_1, h_2, ..., h_M)$

Rates

- Ignore the boundary terms for now
- Recall Hopping Rate $R_i = 2\omega e^{E_0/k_BT} e^{-\gamma n_b/k_BT}$
- Let $E_0 = -E_D + \gamma$ and $n_i =$ number of lateral bonds
- $\Rightarrow R_i = 2\omega e^{-\beta E_D} e^{-\gamma\beta n_i}$
- Adatom hopping rate $2\omega e^{-\beta E_D}$
- E_D is the energy barrier for diffusion

Rates

- Choose the time scale so that adatom hopping rate = 1
- $\Rightarrow 2\omega e^{-\beta E_D} = 1$
- $\Rightarrow R_i = e^{-\gamma \beta n_i}$
- Rates satisfy detailed balance

KMC dynamics

1. A site is chosen with a probability $p_i = r_i / \sum_{i=1}^{M} r_i$. Let i_C denote the chosen site.
2. If $2 \leq i_C \leq M-1$ then that atom hops sites $i_C + 1$ or $i_C - 1$ each with probability $\frac{1}{2}$.
3. If $i_C = 1$ then the atom hops to the right with probability $\frac{1}{2}$ or does not hop with probability $\frac{1}{2}$
4. If $i_C = M$ then the atom hops to the left with probability $\frac{1}{2}$ or does not hop with probability $\frac{1}{2}$

KMC dynamics

These dynamics ensure that the system conserves mass and our consistent with $h_0 = 0$.

Our KMC simulations will have the following restriction on the dynamics

$$\sum_{i=1}^{M} h_i = 0 \tag{1}$$

Since the dynamics conserves mass, then the above condition is enforced by the choice of initial conditions.

Energy

- Total Energy
  $\mathcal{E} = -\gamma \cdot (\ \#$ red-red bonds$) - \frac{1}{2}\gamma \cdot (\#$ red-green bonds$)$
- $E(h_0, h_1, h_2, ..., h_M) = \mathcal{E} - \mathcal{E}_{h=0}$
- $E(h) = \gamma \sum_{i=1}^{M} \min(h_i, h_{i-1}) - (\gamma/2) h_M - \gamma \sum_{i=1}^{M} h_i$
- First two terms are due to horizontal bonds and the last one is from vertical bonds

Energy

- Let $\sum_{i=1}^{M} h_i = N$
- Then $E(h) = -2\gamma N + H(h)$
- where $H(h) = \frac{1}{2}\gamma \sum_{i=1}^{M} |h_i - h_{i-1}|$
- $H(h)$ is the "perturbed" energy. Notice that for a flat interface $H(h) = 0$.
- $\Delta E_i = E(h) - E(h(i)) = \Delta H_i - 2\gamma = H(h) - H(h(i)) - 2\gamma$
- where $h(i)$ is the configuration where the surface atom at site i is removed

Rates

- $R_i = e^{-\gamma\beta n_i}$
- $\Rightarrow R_i = e^{\beta\gamma} e^{\beta\Delta E_i}$
- $\Delta E_i = E(h) - E(h(i))$
- $h(i)$ is the configuration where the surface atom at site i is removed
- $\Delta E_i = E(\text{with}) - E(\text{without})$
- Rates satisfy detailed balance
- The expression above for R_i is valid at the boundary sites.

The Film in Thermodynamic Equilibrium

Statistical Mechanics

- Consider a system in equilibrium with a heat bath at temperature T
- Suppose the system has discrete energy levels E_j, $j = 1, 2, 3....$
- Define $Z = \sum_j e^{-E_j/k_B T}$ (The partition function)
- $P(\text{state j}) = e^{-E_j/k_B T}/Z$

Statistical Mechanics

- Free Energy $F = -k_B T \log Z$
- Ensemble Average $\langle g \rangle \equiv \frac{1}{Z} \sum_{\text{states}} g e^{-U(\text{state})/\text{k}_\text{B}\text{T}}$
- Chemical potential: $\mu = F - F'$, F' Free Energy with one atom removed
- The larger the chemical potential the easier it is for atoms to evaporate
- If $\mu > 0$ atoms have no energetic barrier from leaving the surface

The Partition Function

$$Z = \sum_{\text{all states}} e^{-E(\text{state})/k_B T}$$

in our case this becomes

$$Z = \sum_{h_1=-\infty}^{\infty} \sum_{\substack{h_2=-\infty \\ \sum_{i=1}^{M} h_i = 0}}^{\infty} \cdots \sum_{h_M=-\infty}^{\infty} e^{-E(h_0,h_1,\ldots,h_M)/k_B T} = \sum_{h,\overline{h}=0} e^{-E(h)/k_B T}$$

It is basic fact from statistical mechanics that finding the system in a given state h is given by

$$P(h) = \frac{e^{-E(h)/k_B T}}{Z}$$

In our system we have $\sum_{i=1}^{M} h_i = 0$ therefore

$$P(h) = Z^{-1} e^{-H(h)/k_B T} = Z^{-1} \exp\left[-\frac{\gamma}{2k_B T} \sum_{i=1}^{M} |h_i - h_{i-1}| \right]$$

It follows then, in equilibrium that,

$$P(h) = P(-h)$$

Unfortunately, the mass constraint makes a direct evaluation of Z quite difficult and instead most people compute the grand partition function, Ξ. When computing the grand partition function one removes the mass constraint but adds a term to the energy namely μN where μ is the chemical potential and N is the excess mass. The strategy is to compute the grand partition function and find μ so that the expectation of $\sum_{i=1}^{M} h_i$ is zero.

In what follows we shall use the notation

$$\sum_{h} = \sum_{h_1=-\infty}^{\infty} \sum_{h_2=-\infty}^{\infty} \cdots \sum_{h_M=-\infty}^{\infty}$$

The Grand Partition Function

The grand partition function is

$$\Xi(\mu) = \sum_h \exp\left(-\beta E(h) + \beta\mu \sum_{i=1}^{M} h_i\right)$$

in view of our formula for the energy we have

$$\Xi(\mu) = \sum_h \exp\left(-\beta H(h) + \beta(\mu + 2\gamma) \sum_{i=1}^{M} h_i\right)$$

However, in equilibrium, we have $P(h) = P(-h)$, therefore we need $\mu = -2\gamma \equiv \mu_e$

$$\Xi(\mu_e) = \sum_h \exp\left[\frac{-\beta\gamma}{2}\left(\sum_{i=1}^{M} |h_i - h_{i-1}|\right)\right] = \sum_h e^{-\beta H(h)}$$

Explicit Calculation of the Grand Partition Function

This sum can now be summed explicitly but it is crucial that we use $h_0 = 0$.

$$\Xi(\mu_e) = \sum_{h_1=-\infty}^{\infty} \sum_{h_2=-\infty}^{\infty} \cdots \sum_{h_M=-\infty}^{\infty} e^{-\theta|h_1|} e^{-\theta|h_2-h_1|} \ldots e^{-\theta|h_M-h_{M-1}|}$$

where $\theta = \frac{\beta\gamma}{2}$. we use the change of variables

$$g_1 = h_1 - h_0 = h_1 \quad \text{and} \quad g_i = h_i - h_{i-1} \quad \text{for} \quad i = 2, 3, ..., M$$

$$\begin{aligned} \Xi(\mu_e) &= \sum_{g_1=-\infty}^{\infty} \sum_{g_2=-\infty}^{\infty} \cdots \sum_{g_M=-\infty}^{\infty} e^{-\theta|g_1|} e^{-\theta|g_2|} e^{-\theta|g_3|} \ldots e^{-\theta|g_M|} \\ &= \left(\sum_{k=-\infty}^{\infty} e^{-\theta|k|} \right)^M \end{aligned}$$

Now

$$\sum_{k=-\infty}^{\infty} e^{-\theta|k|} = \frac{1+e^{\theta}}{-1+e^{\theta}} = \frac{\cosh(\theta/2)}{\sinh(\theta/2)} = \frac{\cosh(\beta\gamma/4)}{\sinh(\beta\gamma/4)}$$

So

$$\Xi(\mu_e) = \left[\frac{\cosh(\beta\gamma/4)}{\sinh(\beta\gamma/4)}\right]^M$$

Calculation of the Free Energy

$$Z \approx \Xi(\mu_e)$$

$$F \approx -k_B T M \log(\coth(\beta\gamma/4))$$

Free Energy per surface atom

$$-\frac{1}{\beta}\log(\coth(\beta\gamma/4)$$

Calculation of the Entropy

The Entropy is

$$S = -k \sum_{h,N=0} P(h) \log P(h) = k \log Z + \frac{1}{TZ} \sum_{h,N=0} E(h) e^{-E(h)/k_B T}$$

Recalling

$$F = -k_B T \log \left(\sum_{h,N=0} e^{-E(h)/k_B T} \right)$$

It then follows,

$$S = -\frac{\partial F}{\partial T}$$

Now we use $\Xi(\mu_e)$ for Z to find

$$\frac{1}{M} S \approx \frac{\gamma}{2T} \mathrm{csch}(\gamma\beta/2) + k \log(\coth(\gamma\beta/4))$$

Surface Atom Mobility

We wish to calculate the hopping rate of a surface atom when the film is in equilibrium. That is to say we wish to compute

$$\langle R_j \rangle$$

Using the Partition Function

$$Z = \sum_h e^{-\beta E(h)} \quad \text{with the constraint} \quad \sum_{i=1}^{M} h_i = 0$$

which we will write as

$$Z = \sum_{h, N=0} e^{-\beta E(h)}$$

The probability of the system being in state h is

$$\frac{1}{Z} e^{-\beta E(h)}$$

and the ensemble average of a quantity is given by

$$\langle g \rangle = \frac{1}{Z} \sum_{h,N=0} g e^{-\beta E(h)}$$

The hopping rate of of the jth atom is

$$R_j = e^{\beta\gamma} e^{\beta(E(h)-E(h_j))}$$

so

$$\begin{aligned}
\langle R_j \rangle &= e^{\beta\gamma} \langle e^{\beta(E(h)-E(h(j)))} \rangle \\
&= \frac{e^{\beta\gamma}}{Z} \sum_h e^{-\beta E(h)} e^{\beta(E(h)-E(h(j)))} \\
&= \frac{e^{\beta\gamma}}{Z} \sum_h e^{-\beta E(h(j))} \\
&= \frac{Z'}{Z} e^{\beta\gamma}
\end{aligned}$$

where

$$Z' = \sum_{h,N=0} e^{-\beta E(h(j))} = \sum_{h,N=-1} e^{-\beta E(h)}$$

Recalling that

$$F = -\beta^{-1} \log Z \quad \text{and} \quad \mu = F - F'$$

where F and F' are the free energy with and without an surface atom.

It follows

$$\frac{Z'}{Z} = e^{\beta\mu}$$

and

$$\langle R_j \rangle = e^{\beta\gamma} e^{\beta\mu} \qquad (\text{recall} \quad R_j = e^{\beta\gamma} e^{\beta\Delta E_i})$$

This is a very general result and very important since it connects the microscopic dynamics of atom hopping with a thermodynamical quantity, the chemical potential, μ. Recall we had established that $\mu = -2\gamma$, so

$$\langle R_j \rangle = e^{-\beta\gamma}$$

Remember, the hopping rate of an adatom was 1. Our calculation shows that the average hopping rate can be quite a bit smaller than the adatom hopping rate.

Using the Grand Partition Function

Krug et al use $\Xi(\mu_e)$ instead of Z and they compute

$$\begin{aligned}
\langle R_i \rangle &= \frac{1}{\Xi(\mu_e)} \sum_h R_i e^{-\beta H(h)} \\
&= e^{-\beta\gamma} \frac{1}{\Xi(\mu_e)} \sum_h e^{\beta \Delta H_i} e^{-\beta H(h)} \\
&= e^{-\beta\gamma} \frac{1}{\Xi(\mu_e)} \sum_h e^{-\beta H(h(i))} \\
&= e^{-\beta\gamma} \frac{\Xi'(\mu_e)}{\Xi(\mu_e)} \\
&= e^{-\beta\gamma} \qquad \text{same result}
\end{aligned}$$

where $\Xi'(\mu_e)$ is the value of the grand partition function with one less atom. One can show $\Xi(\mu_e) = \Xi'(\mu_e)$.

Proof that $\Xi(\mu_e) = \Xi'(\mu_e)$

Proof 1. The first way is to notice that since there is no mass constraint, all the possible states will be summed over where or not an atom is removed or not.

Proof 2. Use:

- The grand potential: $\mathcal{A} = -k_B T \log \Xi(\mu_e)$
- The free energy $F = -k_B T \log Z$
- and relationship $\mathcal{A} = F - \mu N$.

This means that

$$-k_B T \log \Xi(\mu_e) = F - \mu_e N \quad \text{and} \quad -k_B T \log \Xi'(\mu_e) = F' - \mu_e (N-1)$$

Take the difference

$$-k_B T \log \Xi(\mu_e) + k_B T \log \Xi'(\mu_e) = (F - \mu_e N) - (F' - \mu_e (N-1))$$

so

$$-k_B T \left(\log \Xi(\mu_e) - \log \Xi'(\mu_e) \right) = F - F' - \mu_e$$

But $F - F' = \mu_e$. So it follows that $\Xi(\mu_e) = \Xi'(\mu_e)$

Film Evolution

- $P = P(h,t)$ is the probability of the film taking on the configuration h at time t
- $P(h,t) = P(h_1, h_2, ..., h_M, t)$
- $h \in Z^M \quad$ where $\quad Z = \{..., -2, -1, 0, 1, 2, ...\}$
- $\sum_h P(h,t) = 1$
- The equation that describes the time evolution of $P(h,t)$ is called the master equation
- If one performed large number of ensembles of kinetic Monte Carlo simulations and computed a probability density function from them, its time evolution would be predicted by the master equation

The Master Equation

The master equation takes the form

$$\frac{\partial P}{\partial t} = RHS$$

Here we will derive RHS for our KMC model. Consider the contribution, $T_{i,i+1}$ to RHS due to contributions for hops between sites i and $i+1$ where i and $i \pm 1$ are not boundary sites.

The hopping rate at site i depends on h_i, h_{i+1},h_{i-1} we write

$$R_i = R_i(h_{i-1}, h_i, h_{i+1})$$

Contribution from an atom hop from i to $i+1$

Piece 1 - atom hops into h

$$+\tfrac{1}{2}\underbrace{P(...,h_i+1,h_{i+1}-1,...)}_{\text{after the hop}\Rightarrow P(h,t)}R_i(h_{i-1},h_i+1,h_{i+1}-1)$$

Piece 2 - atom hops from h

$$-\tfrac{1}{2}P(...,h_i,h_{i+1},...)R_i(h_{i-1},h_i,h_{i+1})$$

Contribution from an atom hop from $i+1$ to i

Piece 1 - atom hops into h

$$+\tfrac{1}{2}\underbrace{P(...,h_i-1,h_{i+1}+1,...)}_{\text{after the hop}\Rightarrow P(h,t)}R_{i+1}(h_i-1,h_{i+1}+1,h_{i+1})$$

Piece 2 - atom hops from h

$$-\tfrac{1}{2}P(...,h_i,h_{i+1},...)R_{i+1}(h_i,h_{i+1},h_{i+2})$$

Contribution from an atom hops between i to $i+1$

$$
\begin{aligned}
T_{i,i+1} = \quad & \tfrac{1}{2} P(..., h_i + 1, h_{i+1} - 1, ...) R_i(h_{i-1}, h_i + 1, h_{i+1} - 1) \\
+ \quad & \tfrac{1}{2} P(..., h_i - 1, h_{i+1} + 1, ...) R_{i+1}(h_i - 1, h_{i+1} + 1, h_{i+2}) \\
- \quad & \tfrac{1}{2} P(..., h_i, h_{i+1}, ...) R_i(h_{i-1}, h_i, h_{i+1}) \\
- \quad & \tfrac{1}{2} P(..., h_i, h_{i+1}, ...) R_{i+1}(h_i, h_{i+1}, h_{i+2})
\end{aligned}
$$

We also have

$$T_{0,1} = 0 \quad \text{and} \quad T_{M,M+1} = 0$$

since no atoms can hop between these sites.

The Master Equation

The master equation is then

$$\frac{\partial P}{\partial t} = \sum_{i=1}^{M-1} T_{i,i+1}$$

This can be written in the following form

$$\frac{\partial P(h,t)}{\partial t} = \sum_{h'} P(h',t)T(h',h) - P(h,t)T(h,h')$$

where h' is any configuration that is one hop away from h and $T(h,h')$ is the transition rate between h and h'.

Transition Rates and Detailed balance

Suppose there is transition between sites i and $i+1$ then
$h' = \{.., h_i - 1, h_{i+1} + 1, ...\}$ or $h' = \{.., h_i + 1, h_{i+1} - 1, ...\}$.

Consider the case $h' = \{.., h_i - 1, h_{i+1} + 1, ...\}$, then

$$T(h, h') = \frac{1}{2} e^{-\beta\gamma} e^{\beta(H(h) - H(h(i))}$$

and

$$T(h', h) = \frac{1}{2} e^{-\beta\gamma} e^{\beta(H(h') - H(h'(i+1)))}$$

Notice

$$e^{-\beta H(h)} T(h, h') = \frac{1}{2} e^{-\beta\gamma} e^{-\beta H(h(i))}$$

and

$$e^{-\beta H(h')} T(h', h) = \frac{1}{2} e^{-\beta\gamma} e^{-\beta H(h'(i+1))}$$

Now

$$h(i) = \{..., h_i - 1, h_{i+1}, ...\} \quad \text{and} \quad h'(i+1) = \{..., h_i - 1, h_{i+1}, ...\}$$

Since $h(i) = h'(i+1)$ it follows,

$$e^{-\beta H(h)} T(h, h') = e^{-\beta H(h')} T(h', h)$$

This is detailed balance.

Now consider the case $h' = \{..., h_i + 1, h_{i+1} - 1, ...\}$ then

$$T(h, h') = \frac{1}{2} e^{-\beta\gamma} e^{\beta(H(h) - H(h(i+1))}$$

and

$$T(h', h) = \frac{1}{2} e^{-\beta\gamma} e^{\beta(H(h') - H(h'(i)))}$$

Now

$$h(i+1) = \{..., h_i, h_{i+1} - 1, ...\} \quad \text{and} \quad h'(i) = \{..., h_i, h_{i+1} - 1, ...\}$$

so again it follows

$$e^{-\beta H(h)} T(h, h') = e^{-\beta H(h')} T(h', h)$$

Equilibrium Solution of the Master Equation

The master equation is

$$\frac{\partial P(h,t)}{\partial t} = \sum_{h'} P(h',t)T(h',h) - P(h,t)T(h,h')$$

where the transition rates satisfied detailed balance

$$e^{-\beta H(h)}T(h,h') = e^{-\beta H(h')}T(h',h)$$

It follows that $P_{eq}(h) = Z^{-1}e^{-\beta H(h)}$ is a solution of the master equation.

Long Time Behavior of the Master Equation

It also follows that for any normalized initial condition $P(h,0)$ that

$$\lim_{t\to\infty} P(h,t) = Z^{-1}e^{-\beta H(h)}$$

To prove this result we will use a Lyapunov function, sometimes called the relative entropy, namely

$$\mathcal{L} = \sum_h P(h,t)\log\frac{P(h,t)}{P_{eq}(h)}$$

One can prove that $\mathcal{L} \geq 0$ with $\mathcal{L} = 0$ if and only if $P = P_{eq}$.

Now we will compute $\dot{\mathcal{L}}$ and show that it is less than zero for all $P \neq P_{eq}$ which implies the claim above.

$$\begin{aligned}\frac{d}{dt}\mathcal{L} &= \sum_h \left(1+\log\frac{P(h,t)}{P_{eq}(h)}\right)\frac{\partial P(h,t)}{\partial t} \\ &= \sum_{h,h'} \left(1+\log\frac{P(h,t)}{P_{eq}(h)}\right)\left(P(h',t)T(h',h)-P(h,t)T(h,h')\right)\end{aligned}$$

Notice that sum is over h and h' and that for each term in the sum,

$$\left(1+\log\frac{P(h,t)}{P_{eq}(h)}\right)\left(P(h',t)T(h',h)-P(h,t)T(h,h')\right)$$

there is a corresponding term,

$$\left(1+\log\frac{P(h',t)}{P_{eq}(h')}\right)\left(P(h',t)T(h,h')-P(h',t)T(h',h)\right)$$

and when these are added one finds

$$\left(\log\frac{P(h,t)/P_{eq}(h)}{P(h',t)/P_{eq}(h')}\right)\left(P(h',t)T(h',h)-P(h,t)T(h,h')\right).$$

Therefore

$$\frac{d}{dt}\mathcal{L}$$

$$= \sum_{\substack{h,h' \\ \text{distinct pairs}}} \left(\log \frac{P(h,t)/P_{eq}(h)}{P(h',t)/P_{eq}(h')} \right) (P(h',t)T(h',h) - P(h,t)T(h,h'))$$

$$= \sum_{\substack{h,h' \\ \text{distinct pairs}}} \left(\log \frac{P(h,t)/P_{eq}(h)}{P(h',t)/P_{eq}(h')} \right) \left(\frac{P(h',t)}{P_{eq}(h')} - \frac{P(h,t)}{P_{eq}(h)} \right) P_{eq}(h)T(h,h')$$

The last simplification comes from using detailed balance.

Since

$$(\log x - \log y)(x - y) \geq 0 \quad \text{for all} \quad x > 0 \quad y > 0$$

then it follows that each term on the rhs of $\dot{\mathcal{L}} \leq 0$. Therefore

$$\frac{d}{dt}\mathcal{L} \leq 0$$

Furthermore, $\dot{\mathcal{L}} = 0$, only if $P(h,t) = P_{eq}(h)$. Therefore $\mathcal{L}$ decreases in time for all $P(h,t) \neq P_{eq}(h)$. Since $\mathcal{L} \geq 0$ with $\mathcal{L} = 0$ only when $P(h,t) = P_{eq}(h)$, it follows that

$$\lim_{t \to \infty} P(h,y) = P_{eq}(h)$$

Proof that $\mathcal{L} \geq 0$ with $\mathcal{L} = 0$ iff $P = P_{eq}$.

We start with Jensen's inequality. Suppose X is random variable and $f(x)$ is convex function ($f''(x) > 0$). Then

$$E[f(X)] \geq f(E[X]) \quad \text{or} \quad \int f(x)p(x)dx \geq f\left(\int xp(x)dx\right)$$

where $p(x)$ is the pdf of X.

Consider a new random variable $Y = p(X)/q(X) > 0$ where $q(X) > 0$ and $\int q(x)dx = 1$

Now, $-\log x$ is convex and by Jensen's inequality $E[-\log(Y)] \geq -\log(E(Y))$.

But

$$E[-\log(Y)] = -\int \log(p(x)/q(x))p(x)dx$$

and

$$E(Y) = \int q(x)dx = 1$$

Therefore we have

$$\mathcal{L} = \int \log(p(x)/q(x))p(x)dx \geq 0$$

Now for $\mathcal{L} = 0$ it must be true that $p(x)/q(x) = 1$ for all x.
Therefore $p(x) = q(x)$.

So far we have learned that any initial condition for the film will result in the film relaxing to the Boltzmann distribution,

$$\begin{aligned} \lim_{t\to\infty} P(h,t) = P_{eq}(h) &= Z^{-1} e^{-H(h)/k_B T} \\ &= Z^{-1} \exp\left(-\frac{\beta\gamma}{4} \sum_{i=1}^{M} |h_i - h_{i-1}| \right) \end{aligned}$$

One can use this to establish that

$$\langle h_i \rangle \to 0 \quad \text{as} \quad t \to \infty$$

How natural question to ask is: exactly how does $\langle h_i \rangle \to 0$?

This question, not surprising, has a long history. For the most part, insight has been provided by continuum theory.

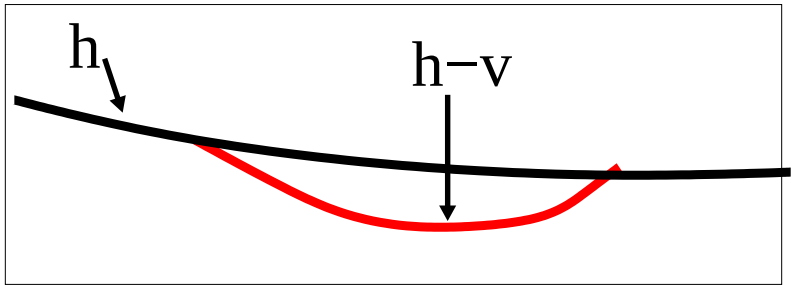
Outline of what is next

- Discuss the continuum formulation of film relaxation.
- Discuss the connection between KMC and continuum formulation.
- Derive a continuum model for the KMC dynamics invoking the notation of local equilibrium.

Continuum Model

- Film is assumed to be in:
  - mechanical equilibrium (for strained systems)
  - local thermodynamic equilibrium
- Free Energy: F= Surface energy
- $F = \int \gamma ds$
- $F = F[h]$; $h = h(x,t)$ where h is the film profile

The Chemical Potential



μ = F - F(one surface atom removed)

$$\mu(x) = F(h) - F(h - v(x,\cdot)) \approx \int \frac{\delta F}{\delta h} v(x,x')dx'$$

$$\approx \frac{\delta F}{\delta h} \int v(x,x')dx'$$

$$\approx v_a \frac{\delta F}{\delta h}(x)$$

v_a is the atomic volume

Drift Speed

$$V = \frac{D\mathcal{F}}{k_B T} \qquad \text{(Einstein)}$$

- V is the drift speed
- $\mathcal{F}$ is the thermodynamic driving force.
- D is the surface diffusivity
- $k_B T$ is the thermal energy

Continuum Model

- $\mathcal{F} = -\dfrac{\partial \mu}{\partial s}$ (Thermodynamic Force)
- Surface Flux of Atoms: $j = \nu V$
- $$= -\frac{\nu D}{k_B T}\frac{\partial \mu}{\partial s}$$
- Mass Conservation: $\dfrac{\partial h}{\partial t} + v_a \dfrac{\partial j}{\partial s} = 0$

where s is arc length and ν is the number density of surface atoms.

Film Dynamics

- $\mu = v_a \dfrac{\delta F}{\delta h} = v_a \kappa \gamma$ (Herring, 1951)
- $h_t = \dfrac{v_a^2 \gamma \nu D}{k_B T} \dfrac{\partial^2 \kappa}{\partial s^2}$ (Mullins, 1957)
- This the basic mathematical description of surface diffusion
- small slope approximation: $h_t = -B h_{xxxx}$

Connection Between

Continuum Mechanics

and Kinetic Monte Carlo

Statistical Mechanics of KMC

- Consider Film in Thermodynamic Equilibrium
- Free Energy $F = -k_B T \log Z$ where $Z = \sum_{\text{states}} e^{-U(\text{state})/\text{k}_\text{B}\text{T}}$
- Ensemble Avera $\langle g \rangle \equiv \frac{1}{Z} \sum_{\text{states}} g e^{-U(\text{state})/\text{k}_\text{B}\text{T}}$
- $\mu = F - F_p = k_B T \log \langle \exp\left[(U - U_p)/k_B T\right] \rangle$ (Chemical Potential)
- $R_p = \omega \exp\left[(U - U_p)/k_B T\right]$ (Hopping Rate)
- $\Rightarrow \langle R \rangle = \omega e^{\mu/k_B T}$ (Ensemble Averaged Hopping Rate)

Local Thermodynamic Equilibrium

- $\Rightarrow \langle R \rangle(x) = \omega e^{\mu(x)/k_B T}$
- Fick's Law: $j = -M\ell \dfrac{\partial \langle R \rangle}{\partial s}$
- M depends on the details of the hopping rules and ℓ is the atomistic length
- $j = -\dfrac{M\ell \langle R \rangle}{k_B T} \dfrac{\partial \mu}{\partial s}$
- $D = M\ell^2 \langle R \rangle$
- $\Rightarrow j = -\dfrac{\nu D}{k_B T} \dfrac{\partial \mu}{\partial s}, \quad \nu = \ell^{-1}$ (same as continuum)

Comment

It is interesting to note that in this and many continuum models the chemical potential plays a key role. However, in Ab Initio Kinetic Monte Carlo and in Molecular Dynamics the chemical potential does not make an explicit appearance. The reason it appears in our KMC model (and others like it) is because it was convenient to define a transition state with an atom removed from the system. The success of continuum models, suggests that using $E_0 + \Delta E$ to approximate an energy barrier must be quite reasonable.

Plan

Next we will attempt to derive a closed model for the time evolution for $\langle h_i \rangle$ from the master equation. To begin we must write the master equation in a different form.

But first some notation

$$D_j^- F = F(..., h_j, ...) - F(..., h_j - 1, ...)$$

and

$$D_j^+ F = F(..., h_j + 1, ...) - F(..., h_j, ...)$$

then

$$D_{j+1}^- [D_j^+ F] = D_{j+1}^- [F(..., h_j + 1, ...) - F(..., h_j, ...)]$$

therefore

$$D^-_{j+1}[D^+_j F]$$

$$= F(..., h_j + 1, h_{j+1}, ...) - F(..., h_j, h_{j+1}, ...)$$
$$\quad -F(..., h_j + 1, h_{j+1} - 1, ...) + F(..., h_j, h_{j+1} - 1, ...)$$

$$= -F(..., h_j + 1, h_{j+1} - 1, ...) + D^+_j F + F(..., h_j, h_{j+1} - 1, ...)$$

$$= -F(..., h_j + 1, h_{j+1} - 1, ...) + D^+_j F - D^-_{j+1} F + F(..., h_j, h_{j+1}, ...)$$

Consequently we have

$$F(..., h_j + 1, h_{j+1} - 1, ...) = F + D_j^+ F - D_{j+1}^- F - D_{j+1}^- [D_j^+ F]$$

In a similar way, we have

$$F(..., h_j - 1, h_{j+1} + 1, ...) = F + D_{j+1}^+ F - D_j^- F - D_{j+1}^+ [D_j^- F]$$

Note: these formulas are akin to a discrete form of a Taylor series.

The Master Equation Again

$$\frac{\partial P(h,t)}{\partial t} = \frac{1}{2}\sum_{i=1}^{M-1} P(...,h_i+1,h_{i+1}-1,...)R_i(h_{i-1},h_i+1,h_{i+1}-1)$$

$$+P(...,h_i-1,h_{i+1}+1,...)R_{i+1}(h_i-1,h_{i+1}+1,h_{i+2})$$

$$-P(...,h_i,h_{i+1},...)R_i(h_{i-1},h_i,h_{i+1})$$

$$-P(...,h_i,h_{i+1},...)R_{i+1}(h_i,h_{i+1},h_{i+2})$$

Using previous identities we can rewrite the master equation as

$$\frac{\partial P(h,t)}{\partial t} = \frac{1}{2}\sum_{i=1}^{M-1} D_j^+(PR_j) - D_{j+1}^-(PR_j) - D_{j+1}^-[D_j^+(PR_j)]$$
$$+D_{j+1}^+(PR_{j+1}) - D_j^-(PR_{j+1}) - D_{j+1}^+[D_j^-(PR_{j+1})]$$

Moments of the Master Equation

First we make the following definition

$$\langle h_k \rangle = \sum_h h_k P(h_1, h_2, ..., h_M)$$

from which we see

$$\begin{aligned} \frac{\partial \langle h_k \rangle}{\partial t} &= \sum_h h_k \frac{\partial P}{\partial t}(h_1, h_2, ..., h_M) \\ &= \sum_h h_k L P \end{aligned}$$

In what follows we shall assume that

$$\lim_{h_k \to \pm\infty} P = 0 \quad \text{for all} \quad k$$

Summation by Parts

One can use summation by parts to show the following

$$\sum_{h_j=-\infty}^{\infty} h_j D_j^+ P = -\sum_{h_j=-\infty}^{\infty} P(...,h_j,...)$$

$$\sum_{h_j=-\infty}^{\infty} h_j D_j^- P = -\sum_{h_j=-\infty}^{\infty} P(...,h_j,...)$$

$$\sum_{h_j=-\infty}^{\infty} h_k D_j^- P = 0 \quad \text{if} \quad k \neq j$$

$$\sum_{h_{j+1}=-\infty}^{\infty} \sum_{h_j=-\infty}^{\infty} h_j D_{j+1}^- [D_j^+ P] = 0$$

Moment Computation

$$\frac{d\langle h_k \rangle}{dt} = \frac{1}{2} \sum_{i=1}^{M-1} \sum_{h} h_k \left(D_j^+(PR_j) - D_{j+1}^-(PR_j) - D_{j+1}^-[D_j^+(PR_j)] \right.$$
$$\left. + D_{j+1}^+(PR_{j+1}) - D_j^-(PR_{j+1}) - D_{j+1}^+[D_j^-(PR_{j+1})] \right)$$

We now apply summation by parts to obtain

$$\frac{d\langle h_k\rangle}{dt} = \frac{1}{2}\Delta_k\langle R\rangle$$

where

$$\Delta_k\langle R\rangle \equiv \begin{cases} -\langle R_1\rangle + \langle R_2\rangle & k = 1 \\ \langle R_{k-1}\rangle - 2\langle R_k\rangle + \langle R_{k+1}\rangle & 1 < k < M \\ \langle R_{M-1}\rangle - \langle R_M\rangle & k = M \end{cases}$$

Note this system is not closed since we do not have an expression of the form $\langle R_k\rangle = \mathcal{R}_k(\langle h_1\rangle, \langle h_2\rangle, ...\langle h_M\rangle)$

Closure

- The closure of the model we propose here is based on the observation that the average film profile evolves on a much slower time scale than $1/\langle R \rangle_{eq}$.
- To estimate $\langle R_k \rangle$ we propose to do the following. We will modify the KMC hopping rates in such a way that an average film profile can be prescribed.
- This prescribed film profile is now the equilibrium profile for the film.
- One now computes the equilibrium values of the new hopping rates.
- These should be a good approximation of the hopping rates of the original system.

Modifying the KMC rates for a prescribed film profile

Recall the hopping rates of our model were $R_i = e^{-\beta\gamma} e^{\beta \Delta H_i}$

We modify $H(h)$ to

$$H_L(h) = H(h) - \sum_{i=1}^{M} (h_i - h_{i-1}) m_i$$

where m_i are user specified.

The new hopping rates are $\tilde{R}_i = e^{-\beta\gamma} e^{\beta \Delta H_{L\,k}}$

These new rates also satisfy detailed balance.

Therefore this modified system will converge to the Boltzmann distribution which is now

$$P_{leq} = \frac{1}{\Xi_L} e^{-\beta H_L(h)}$$

where

$$\Xi_L = \sum_h \exp\left(\sum_{i=1}^{M} -\theta|h_i - h_{i-1}| + \beta m_i(h_i - h_{i-1})\right)$$

In equilibrium the ensemble average of a quantity is

$$\langle g \rangle_L = \frac{1}{\Xi_L} \sum_h g e^{-\beta H_L(h)}$$

Our plan is as follows

1. Find $m_1, m_2, ..., m_M$ so that $\langle h_k \rangle_L$ can be arbitrarily specified.
2. Find $\langle R_k \rangle_L$.
3. Use $\langle R_k \rangle_L$ in place of $\langle R_k \rangle$ to close the system equations for $\frac{d}{dt}\langle h_k \rangle$.

Remark

- P_{leq} is called a local Boltzmann or Maxwellian distribution.
- The concept of a local Maxwellian is well known in the kinetic theory of gases.
- In that setting it used to close the set of equations that arise when taking moments of the Boltzmann equation.

Calculation of Ξ_L

Notice as long as $|m| < \theta/\beta$ then

$$\sum_{k=-\infty}^{\infty} e^{-\theta|k|+\beta m k} = \frac{\sinh\theta}{\cosh\theta - \cosh\beta m}$$

Therefore we find, provided that $|m_i| < \gamma/2$,

$$\Xi_L = \prod_{i=1}^{M} \frac{\sinh\theta}{\cosh\theta - \cosh\beta m_i} \tag{2}$$

where $\theta = \frac{\beta\gamma}{2}$.

Determination of m_i

$$
\begin{aligned}
\langle h_k - h_{k-1} \rangle_L &= \frac{1}{\Xi_L} \sum_h (h_k - h_{k-1}) e^{-\beta H_L(h)} \\
&= \frac{1}{\Xi_L} \sum_h (h_k - h_{k-1}) \exp\left(-\beta H(h) + \beta \sum_{i=1}^{M} (h_i - h_{i-1}) m_i \right) \\
&= \frac{1}{\beta \Xi_L} \frac{\partial}{\partial m_k} \sum_h \exp\left(-\beta H(h) + \beta \sum_{i=1}^{M} (h_i - h_{i-1}) m_i \right) \\
&= \frac{1}{\beta \Xi_L} \frac{\partial}{\partial m_k} \Xi_L \\
&= \frac{\sinh \beta m_k}{\cosh \theta - \cosh \beta m_k}
\end{aligned}
$$

Therefore by choosing m_k one can prescribe the average profile of the film. On the other hand, one can instead prescribe the average profile of the film which determines $\langle h_k - h_{k-1} \rangle_L$ and solve the above equation for m_k. Doing so one finds

$$m_k = k_B T \, G(\langle h_k - h_{k-1} \rangle_L)$$

where

$$G(x) = \mathrm{sgn}(x) \cosh^{-1} \left[\frac{x^2 \cosh\theta - \sqrt{1 + x^2 \sinh^2 \theta}}{x^2 - 1} \right]$$

Local Chemical potential

We note that H_L can be rewritten, using summation by parts as

$$H_L = H + \sum_{i=1}^{M} (m_{i+1} - m_i) h_i$$

provided we take $m_{M+1} = 0$.

Now define the local chemical potential as

$$\mu_i = -(m_{i+1} - m_i) \tag{3}$$

so

$$H_L = H(h) - \sum_{i=1}^{M} \mu_i h_i$$

Prescribed Profile

Now suppose we consider the following problem. We prescribe an average height profile $\bar{h}_i$ $i = 1, 2, ..., M$. Then we calculate

$$m_i = k_B T \, G(\bar{h}_i - \bar{h}_{i-1}) \quad \text{for} \quad i = 1, ..., M$$

and set $m_{M+1} = 0$. We then use these value to calculate μ_i These values of μ_i are used in H_L. We now consider a KMC simulation where the rates are determined using H_L. Then, in equilibrium we have

$$\langle h_i \rangle_L = \overline{h}_i$$

and

$$\langle R_i \rangle_L = e^{-\beta\gamma} e^{\beta\mu_i}$$

Proofs

$$
\begin{aligned}
\langle h_k - h_{k-1} \rangle_L &= \frac{1}{\Xi_L} \sum_h (h_k - h_{k-1}) e^{-\beta H_L(h)} \\
&= \frac{\sinh \beta m_k}{\cosh \theta - \cosh \beta m_k} \\
&= \frac{\sinh(G(\overline{h}_k - \overline{h}_{k-1}))}{\cosh \theta - \cosh(G(\overline{h}_k - \overline{h}_{k-1}))} \\
&= \overline{h}_k - \overline{h}_{k-1}
\end{aligned}
$$

Therefore, $\langle h_k \rangle_L = \overline{h}_k$

Proofs

$$\begin{aligned}
\langle R_k \rangle_L &= \frac{1}{\Xi_L} \sum_h R_k e^{-\beta H_L(h)} \\
&= \frac{1}{\Xi_L} \sum_h e^{-\beta\gamma} e^{\beta \Delta H_k} e^{-\beta H_L(h)} \\
&= \frac{e^{-\beta\gamma}}{\Xi_L} \sum_h e^{\beta(H(h) - H(h(k)))} e^{-\beta H_L(h)}
\end{aligned}$$

Proofs

$$\text{Recall: } H_L(h) = H(h) - \sum_{i=1}^{M} \mu_i h_i$$

$$\begin{aligned}
\langle R_k \rangle_L &= \frac{e^{-\beta\gamma}}{\Xi_L} \sum_h e^{\beta(H(h)-H(h(k)))} e^{-\beta H_L(h)} \\
&= \frac{e^{-\beta\gamma}}{\Xi_L} \sum_h e^{-\beta H(h(k)) + \beta \sum_{i=1} h_i \mu_i} \\
&= \frac{e^{-\beta\gamma}}{\Xi_L} \sum_h e^{\beta\mu_k - \beta H(h(k)) + \beta \sum_{i=1} h_i \mu_i - \beta\mu_k}
\end{aligned}$$

Proofs

$$
\begin{aligned}
\langle R_k \rangle_L &= \frac{e^{-\beta\gamma}}{\Xi_L} \sum_h e^{\beta\mu_k - \beta H(h(k)) + \beta \sum_{i=1} h_i \mu_i - \beta\mu_k} \\
&= \frac{e^{-\beta\gamma}}{\Xi_L} \sum_h e^{\beta(\,\mu_k - H_L(h(k))\,)} \\
&= \frac{e^{-\beta\gamma} e^{\beta\mu_k}}{\Xi_L} \sum_h e^{-H_L(h(k))} \\
&= e^{-\beta\gamma} e^{\beta\mu_k} \frac{\Xi'_L}{\Xi_L} \\
&= e^{-\beta\gamma} e^{\beta\mu_k}
\end{aligned}
$$

The Closed System

Recall we had derived the exact system

$$\frac{d\langle h_k \rangle}{dt} = \tfrac{1}{2}\left(\langle R_{k-1} \rangle - 2\langle R_k \rangle + \langle R_{k+1} \rangle\right) \quad \text{where} \quad k = 1, ..., M$$

with $\langle R_1 \rangle = \langle R_2 \rangle$ and $\langle R_{M+1} \rangle = \langle R_M \rangle$.

Closure Relation:

$$\langle R_i \rangle = \langle R_i \rangle_L = e^{-\beta\gamma} e^{\beta\mu_i}$$

where $\mu_i = -(m_{i+1} - m_i)$ and $m_i = k_B T\, G(\langle h_i \rangle - \langle h_{i-1} \rangle)$

The Closed System

This system can be written as

$$\frac{dy_k}{dt} = \tfrac{1}{2} e^{-\beta\gamma} \left(e^{\beta\mu_{k-1}} - 2e^{\beta\mu_k} + e^{\beta\mu_{k+1}} \right)$$

where $y_k = \langle h_k \rangle$, provided we take:

$$y_0 = 0, \quad y_{M+1} = y_M, \quad \mu_0 = \mu_1, \quad \text{and,} \quad \mu_M = \mu_{M+1}.$$

An Energy Estimate

If we let $\frac{d}{dx}\mathcal{G} = G$ with $\mathcal{G}(0) = 0$ then $\mathcal{G}$ is convex and the quantity

$$U(y) = \sum_{i=1}^{M} \mathcal{G}(y_k - y_{k-1})$$

has the property that $U(y) \geq 0$ with $U(y) = 0$ only if $y = 0$. In addition one can show

$$\frac{d}{dt}U \leq 0$$

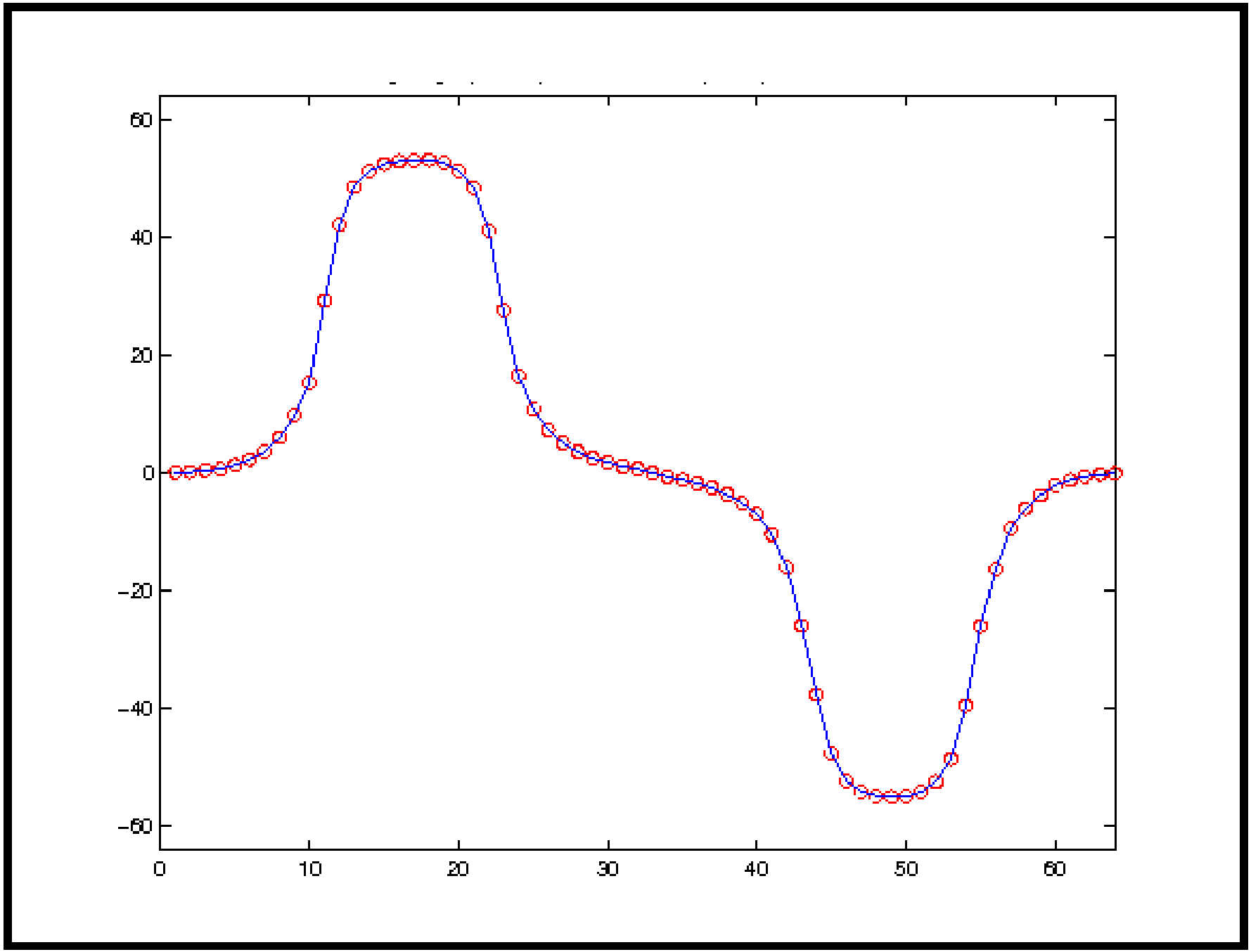
and $\frac{d}{dt}U = 0$ only if $y = 0$.

Therefore $y \to 0$ as $t \to \infty$

How well does this work ?

Quite well

In the pictures that follow the red dot represents the solution of the closed system and the solid blue line are ensembles of KMC simulations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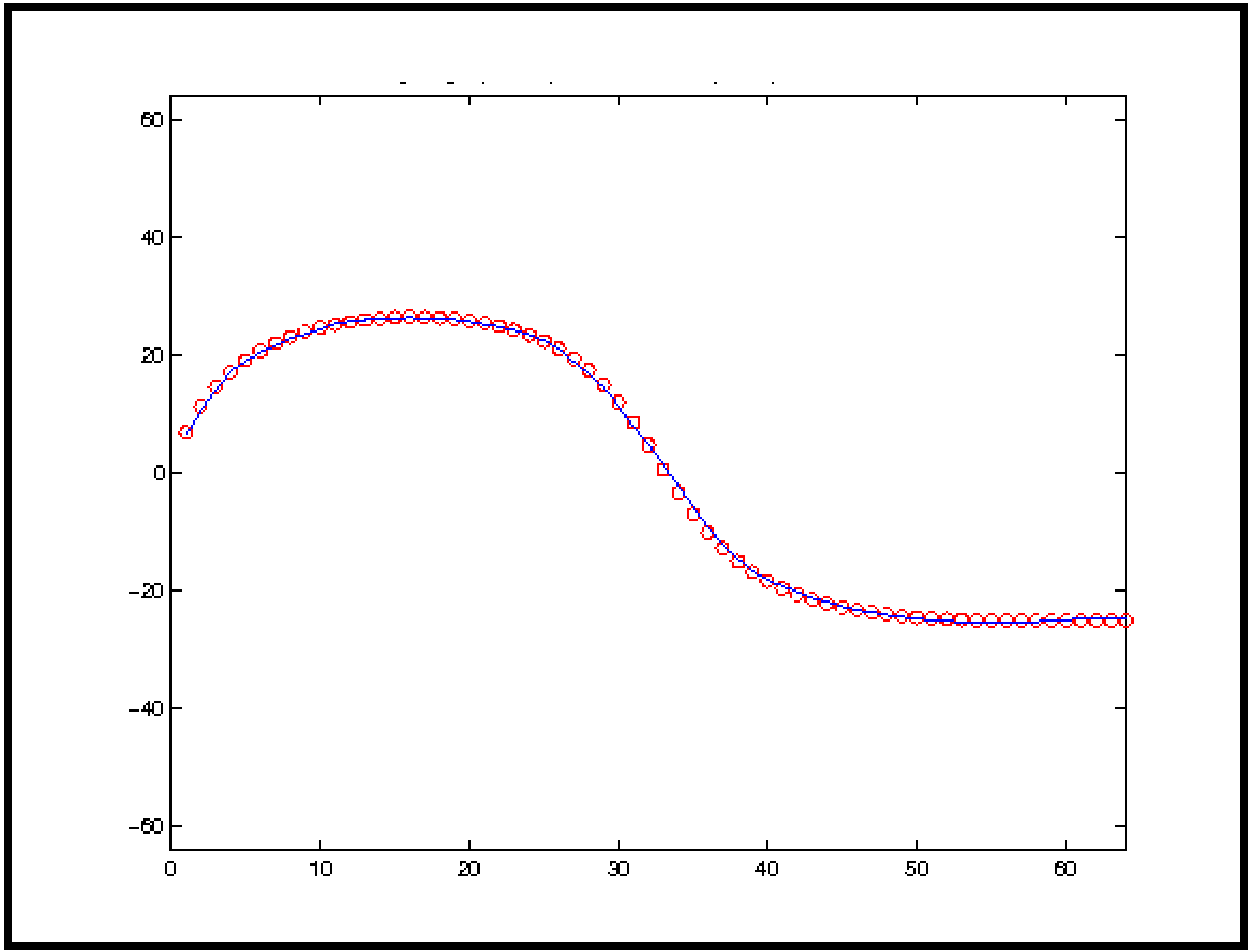
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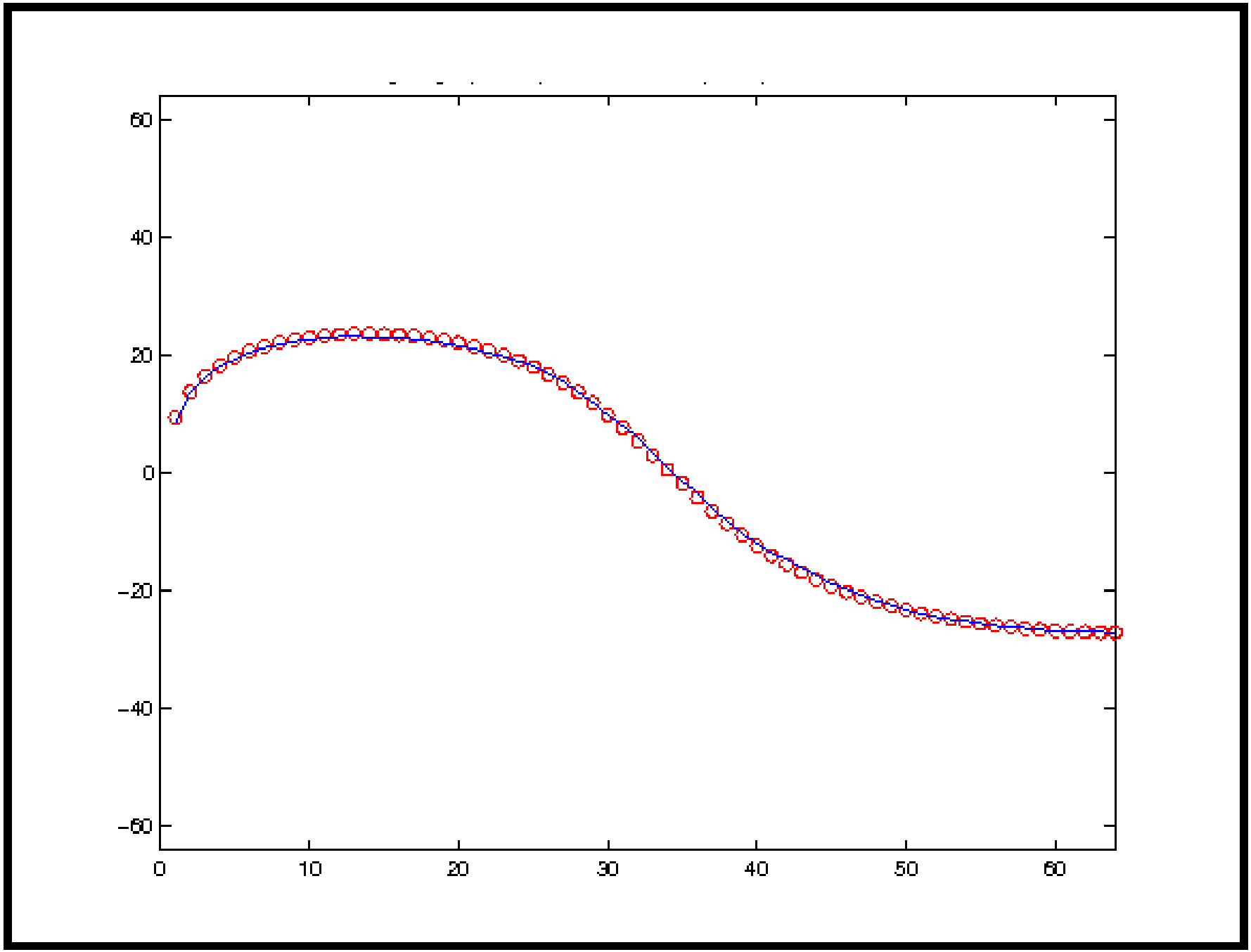
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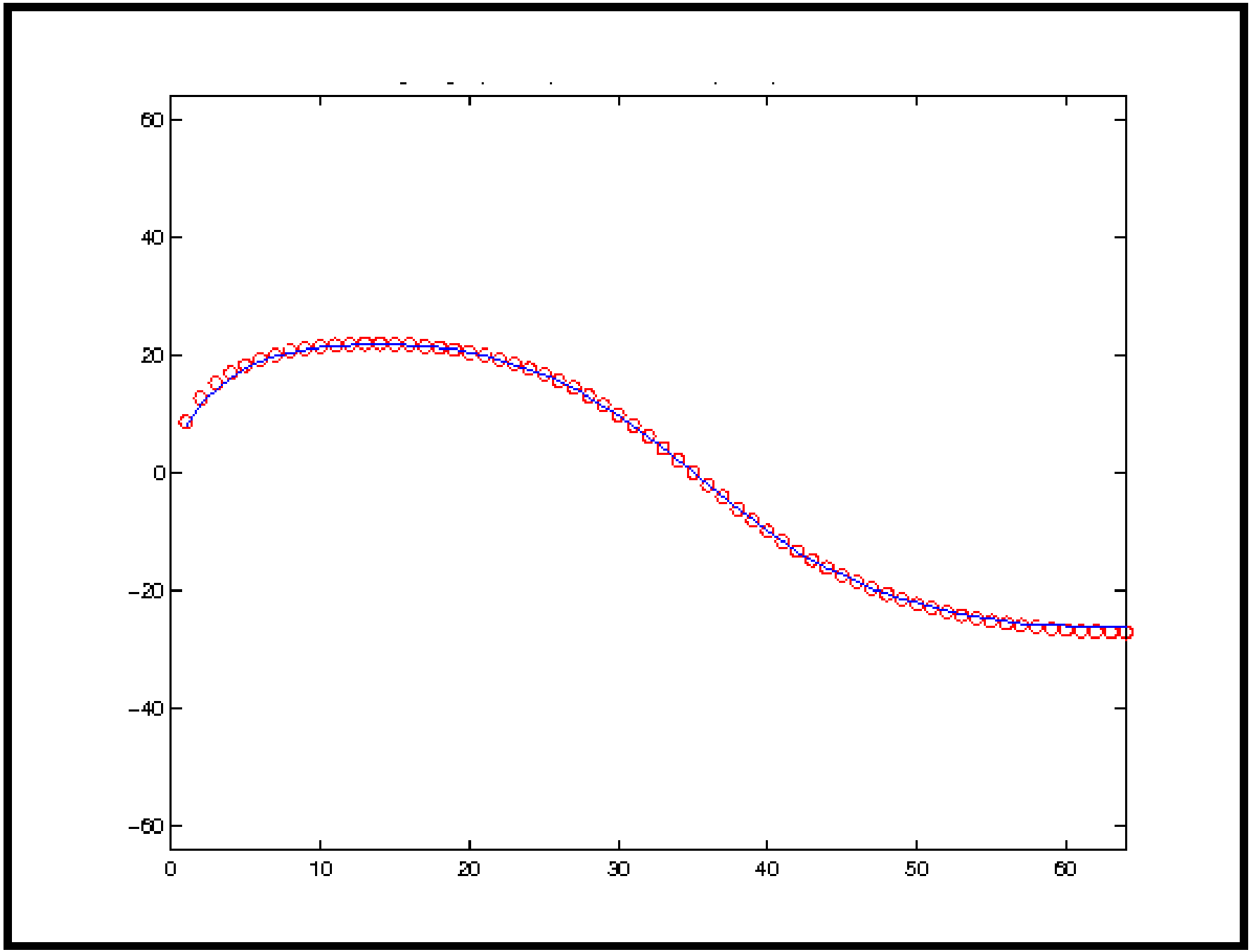
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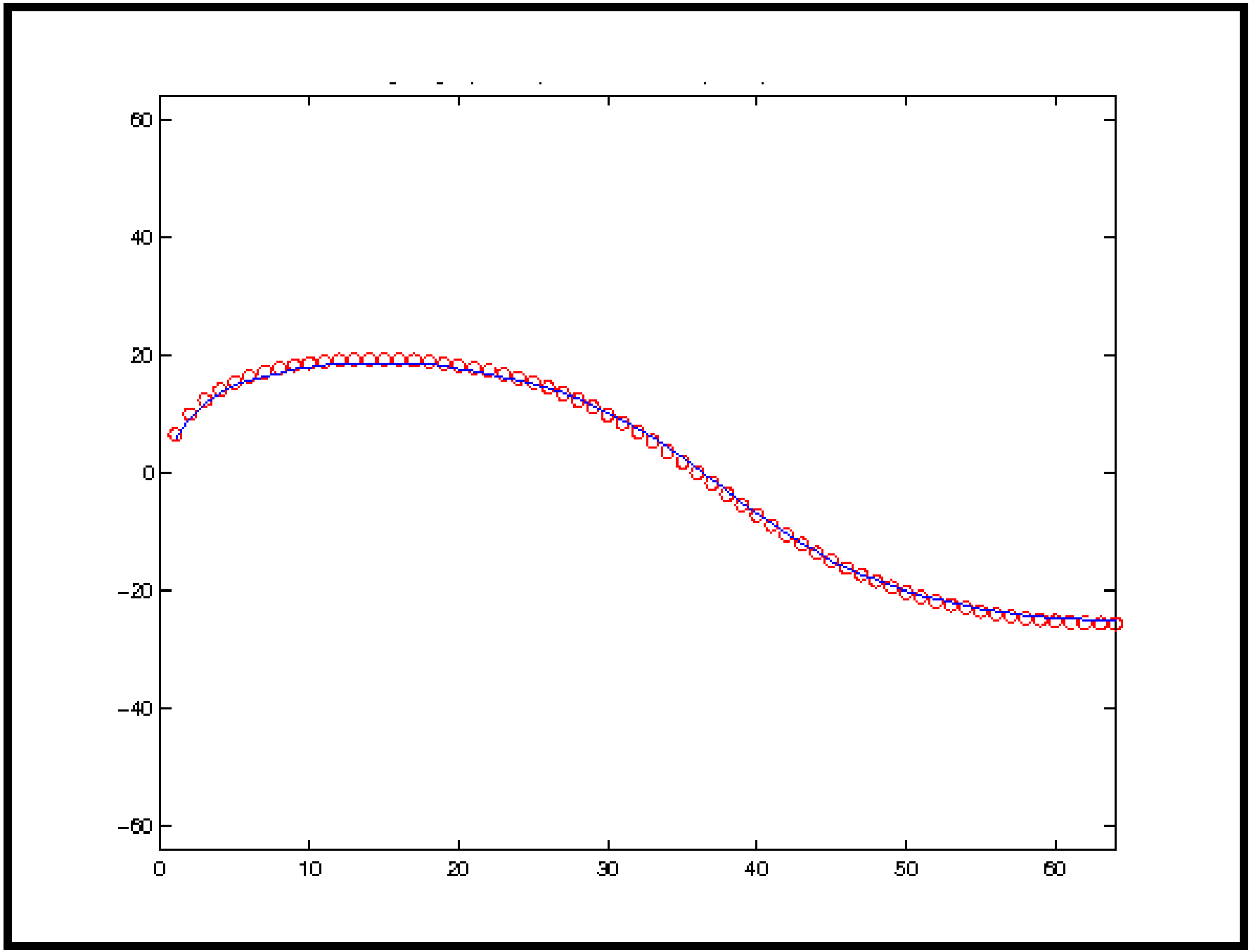
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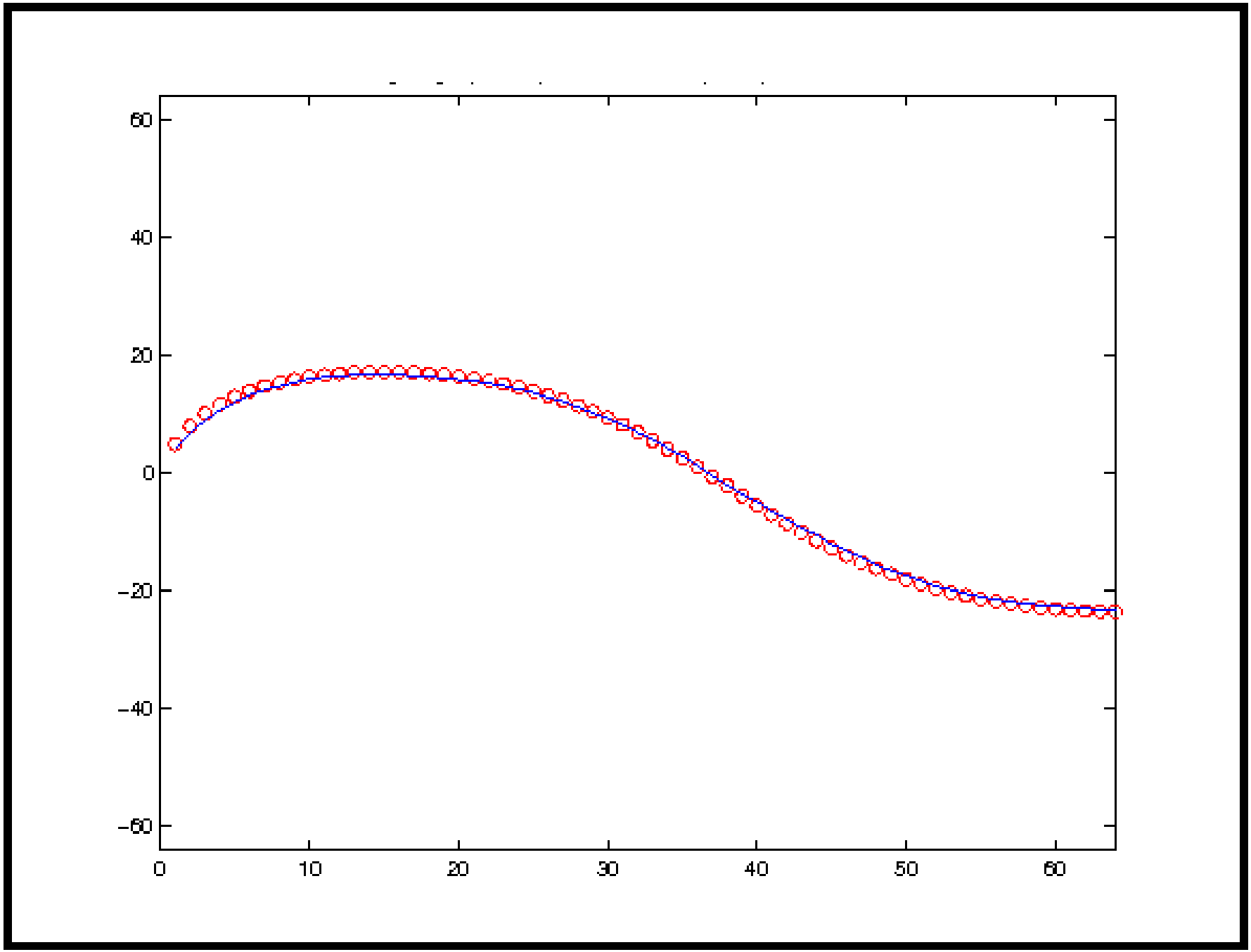
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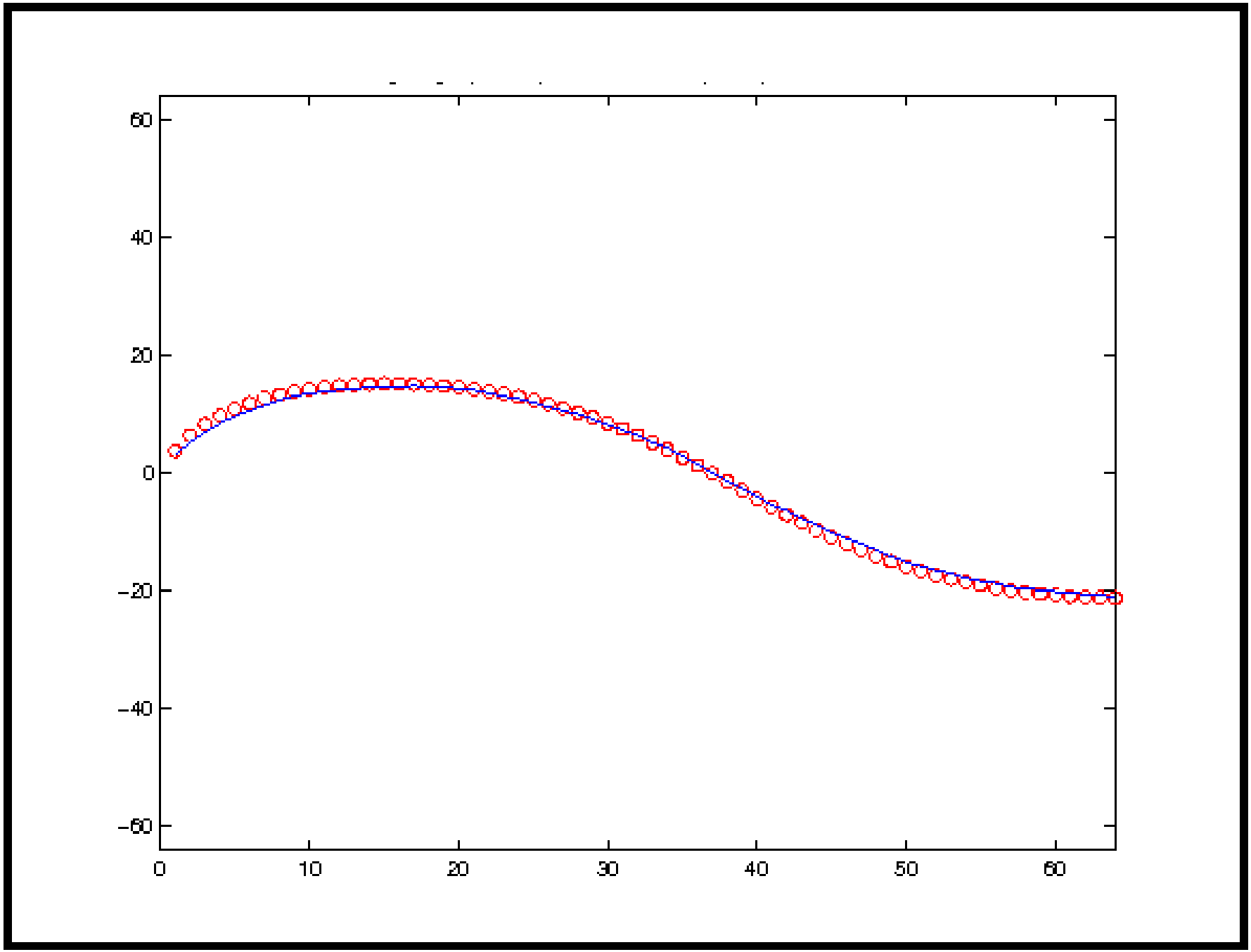
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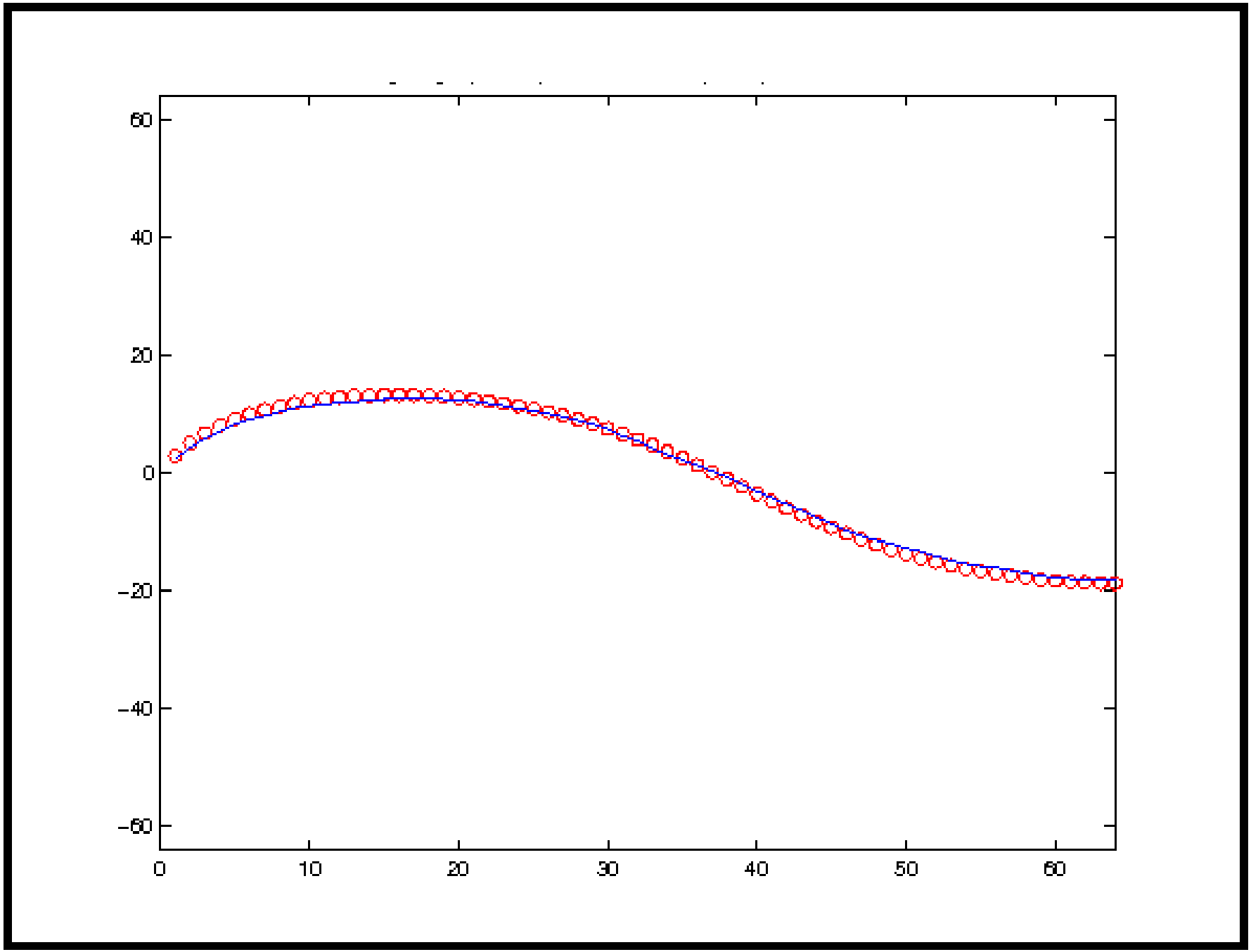
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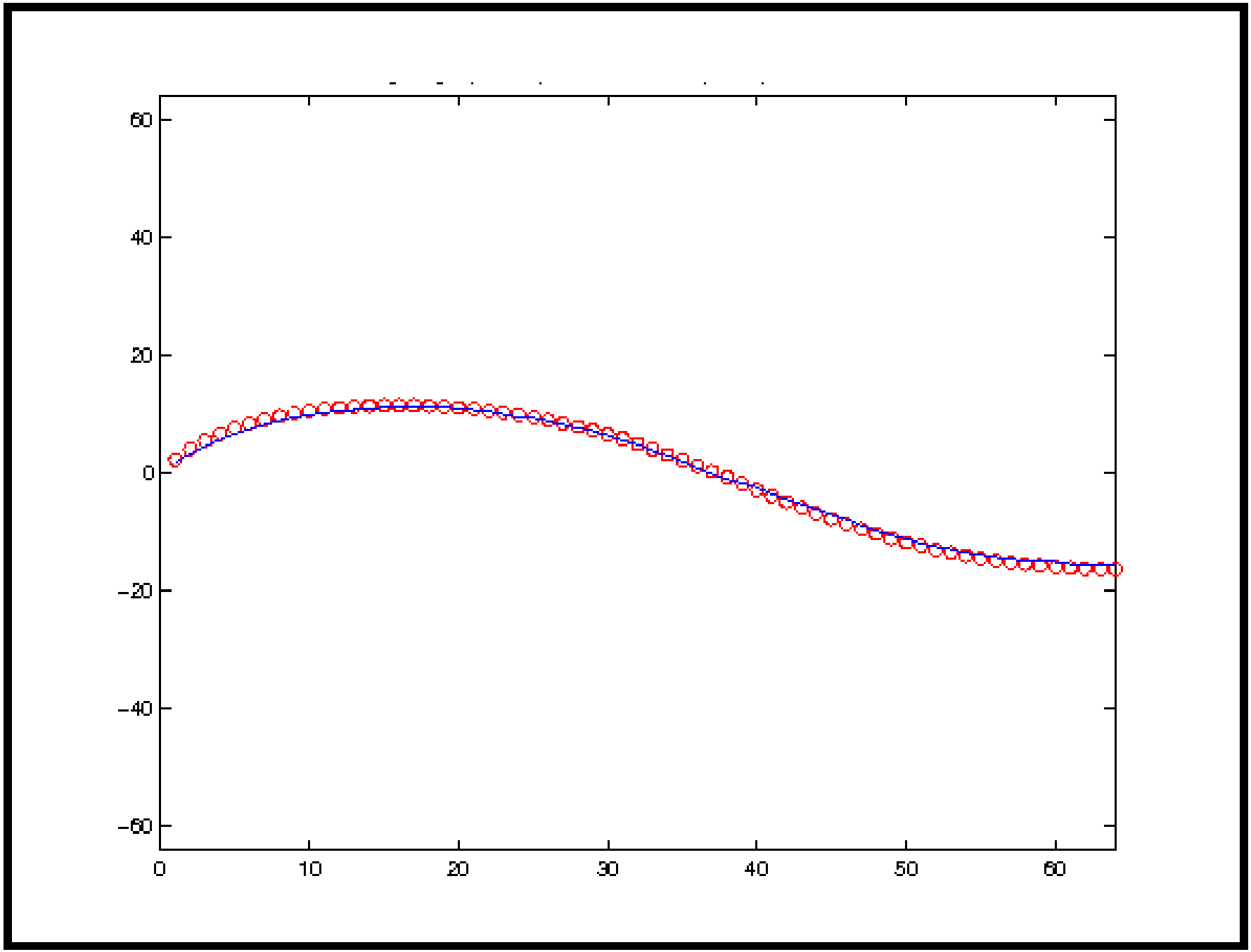
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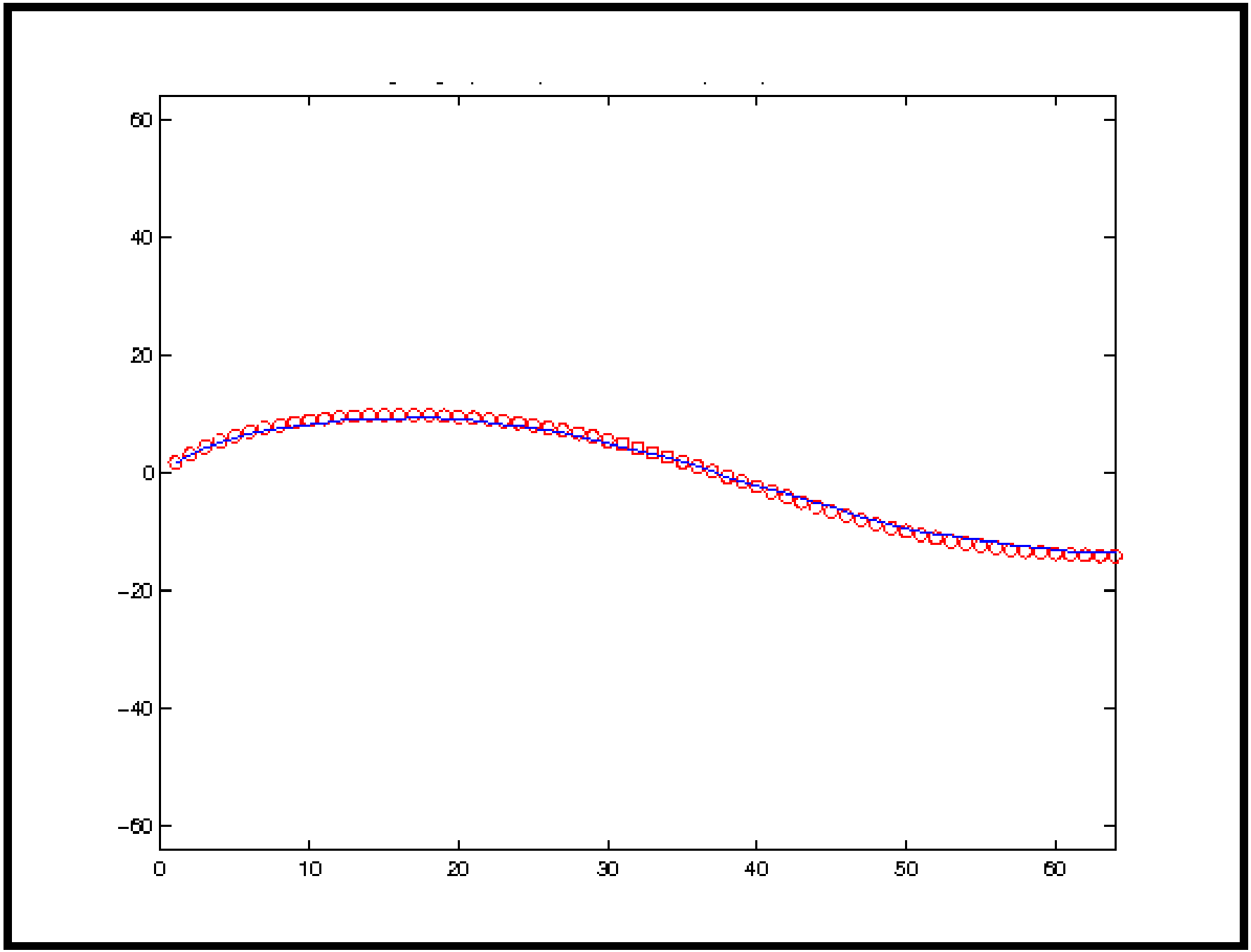
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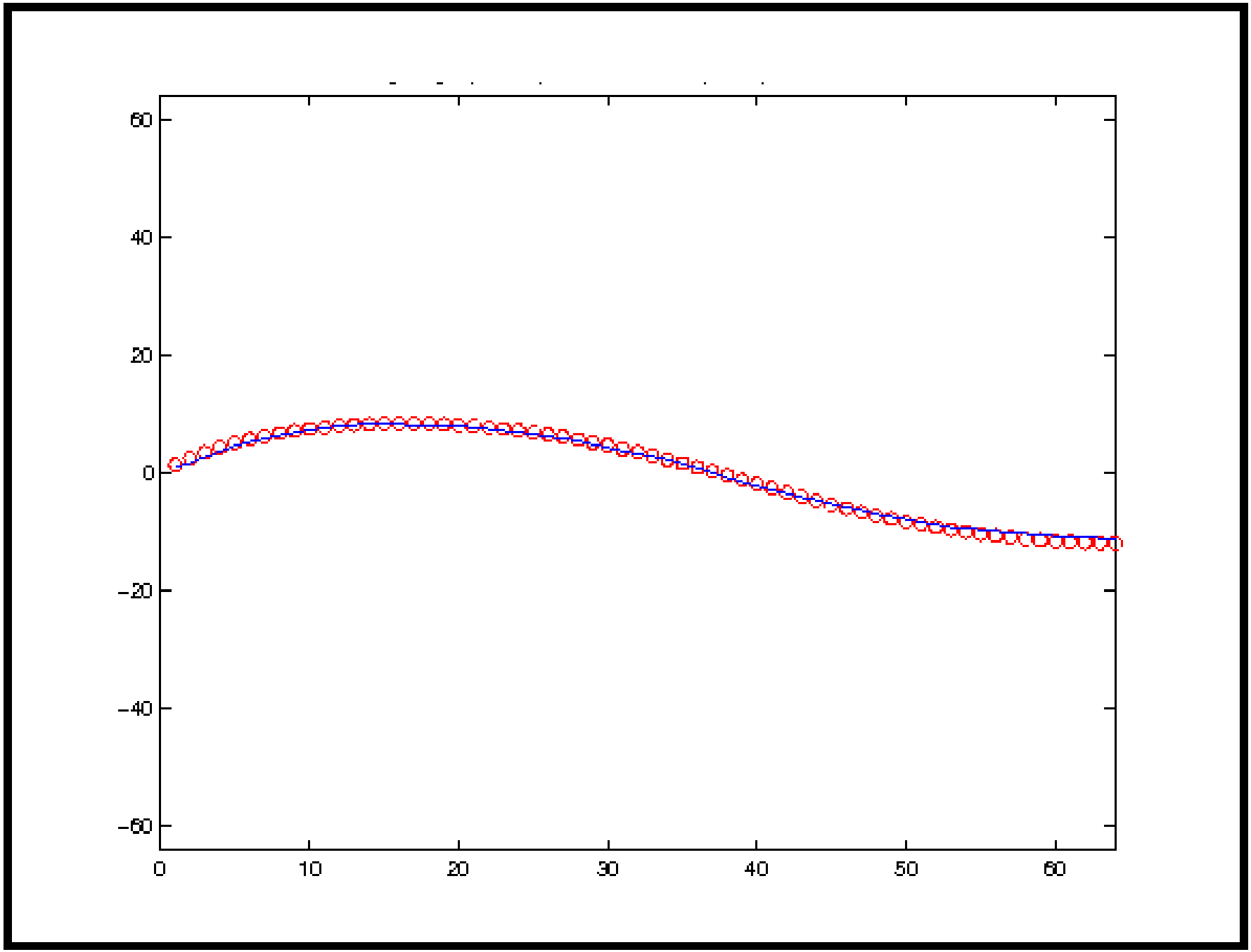
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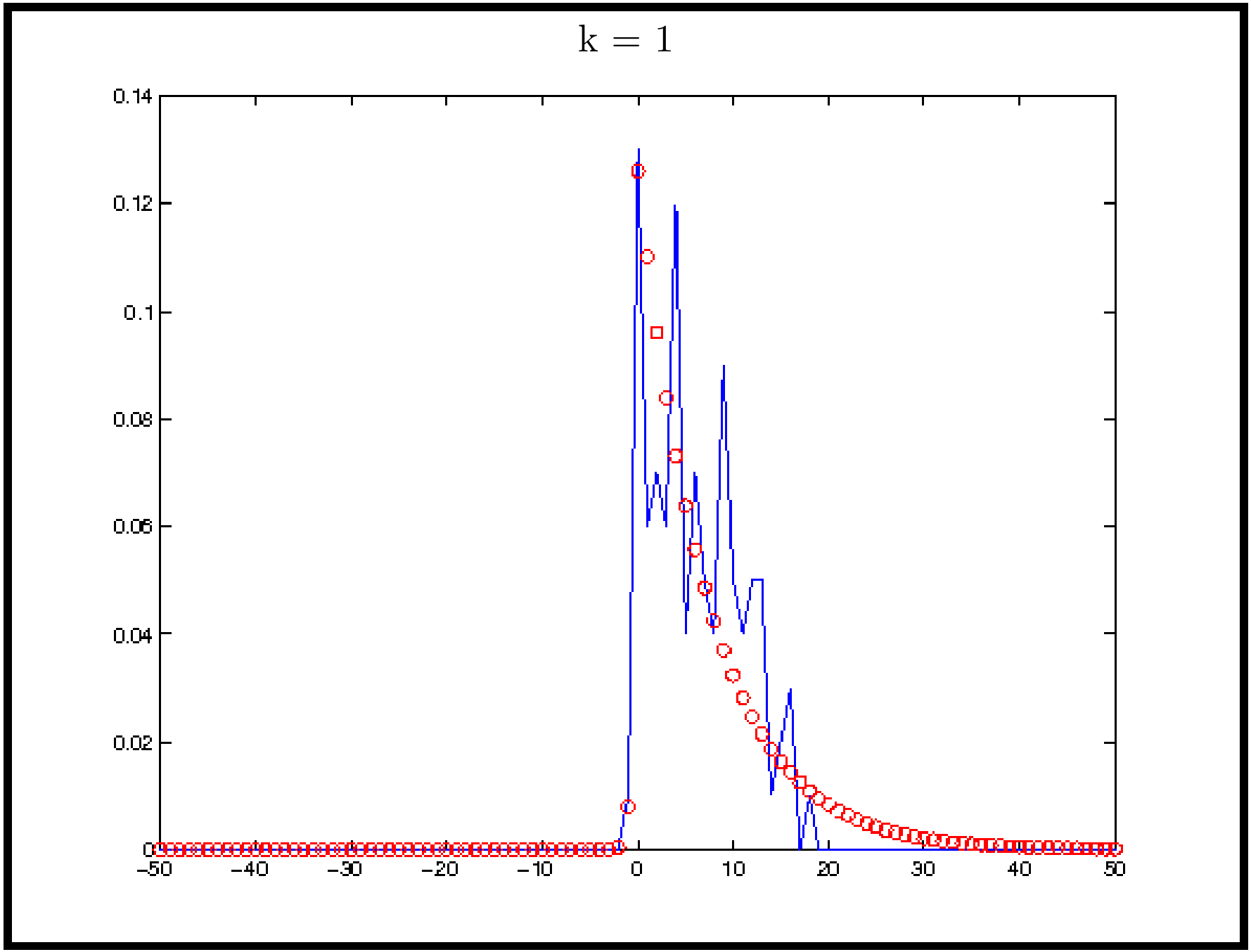
Marginals

Here we consider $Q(g,t)$ instead of $P(h,t)$ and compare the actual marginals

$$Q_k(g_k,t) = \sum_{g_1=-\infty}^{\infty} \cdots \sum_{g_{k-1}=-\infty}^{\infty} \sum_{g_{k+1}=-\infty}^{\infty} \cdots \sum_{g_M=-\infty}^{\infty} Q(g,t)$$

where $g_k = h_k - h_{k-1}$. with the ones computed using Q_{leq}

$$Q_{leq_k}(g_k,t) = \sum_{g_1=-\infty}^{\infty} \cdots \sum_{g_{k-1}=-\infty}^{\infty} \sum_{g_{k+1}=-\infty}^{\infty} \cdots \sum_{g_M=-\infty}^{\infty} Q_{leq}(g,t)$$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0.12
0.1
0.08
0.06
0.04
0.02
0
−50
−40
−30
−20
−10
0
10
20
30
40
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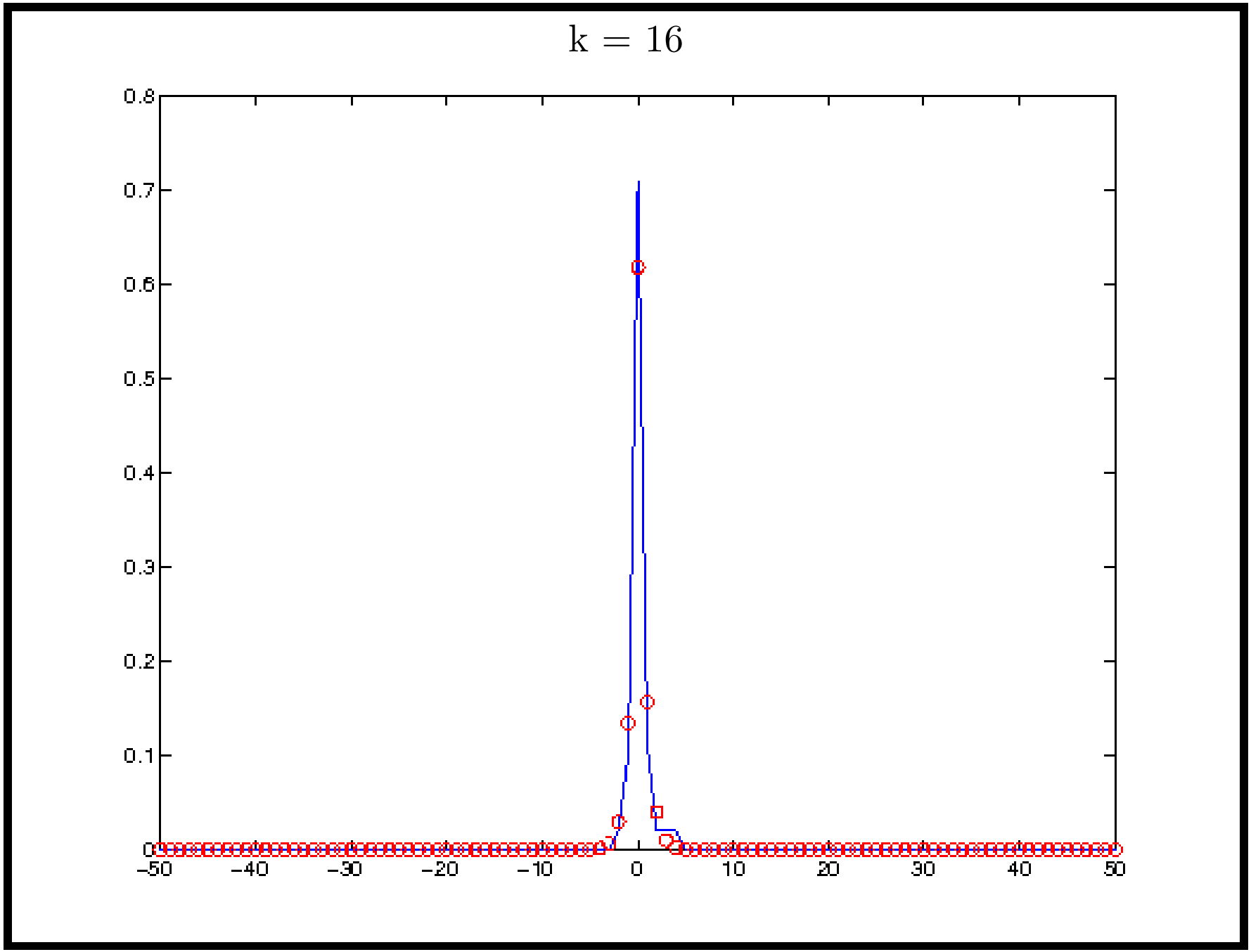
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0.7
0.6
0.5
0.4
0.3
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0.1
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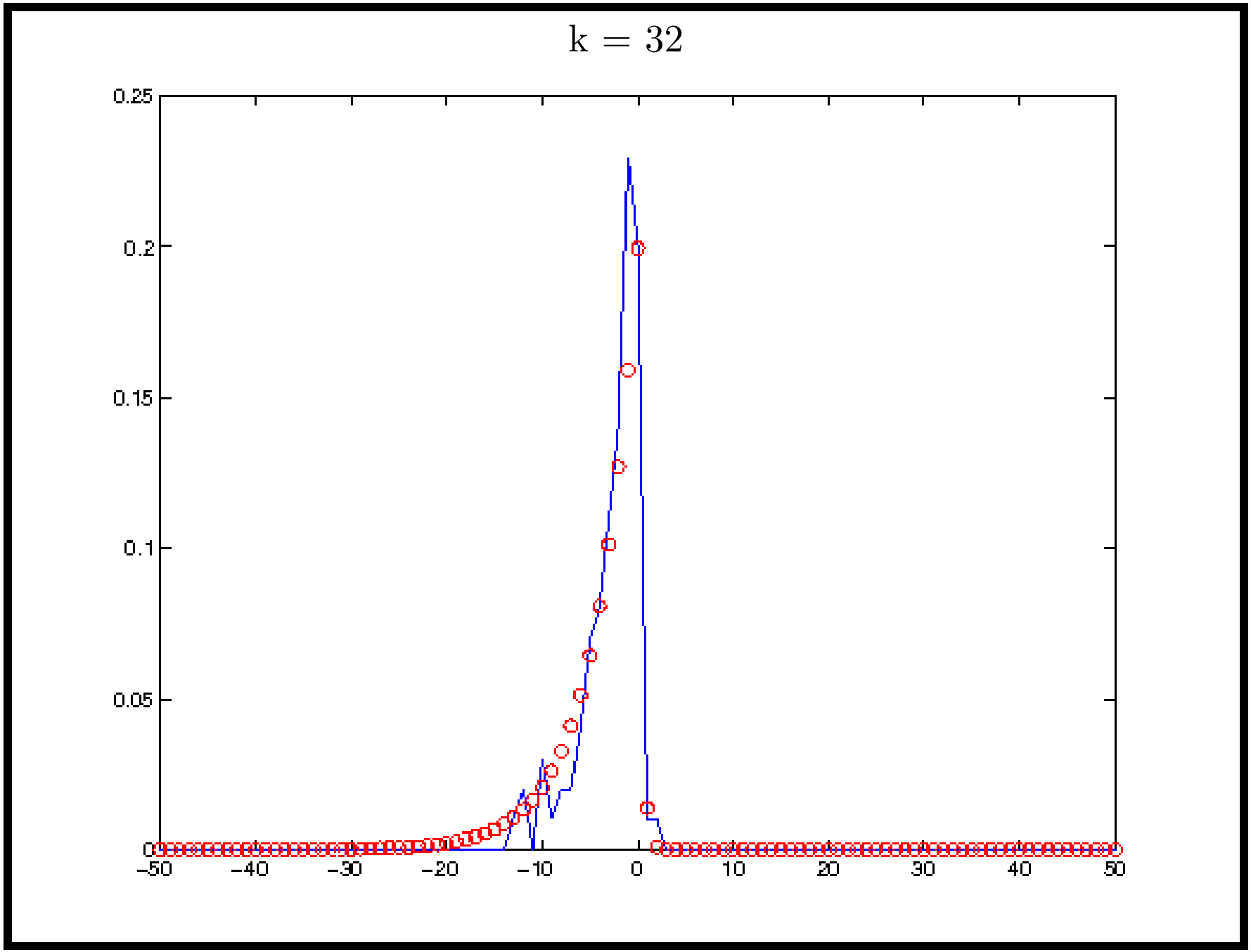
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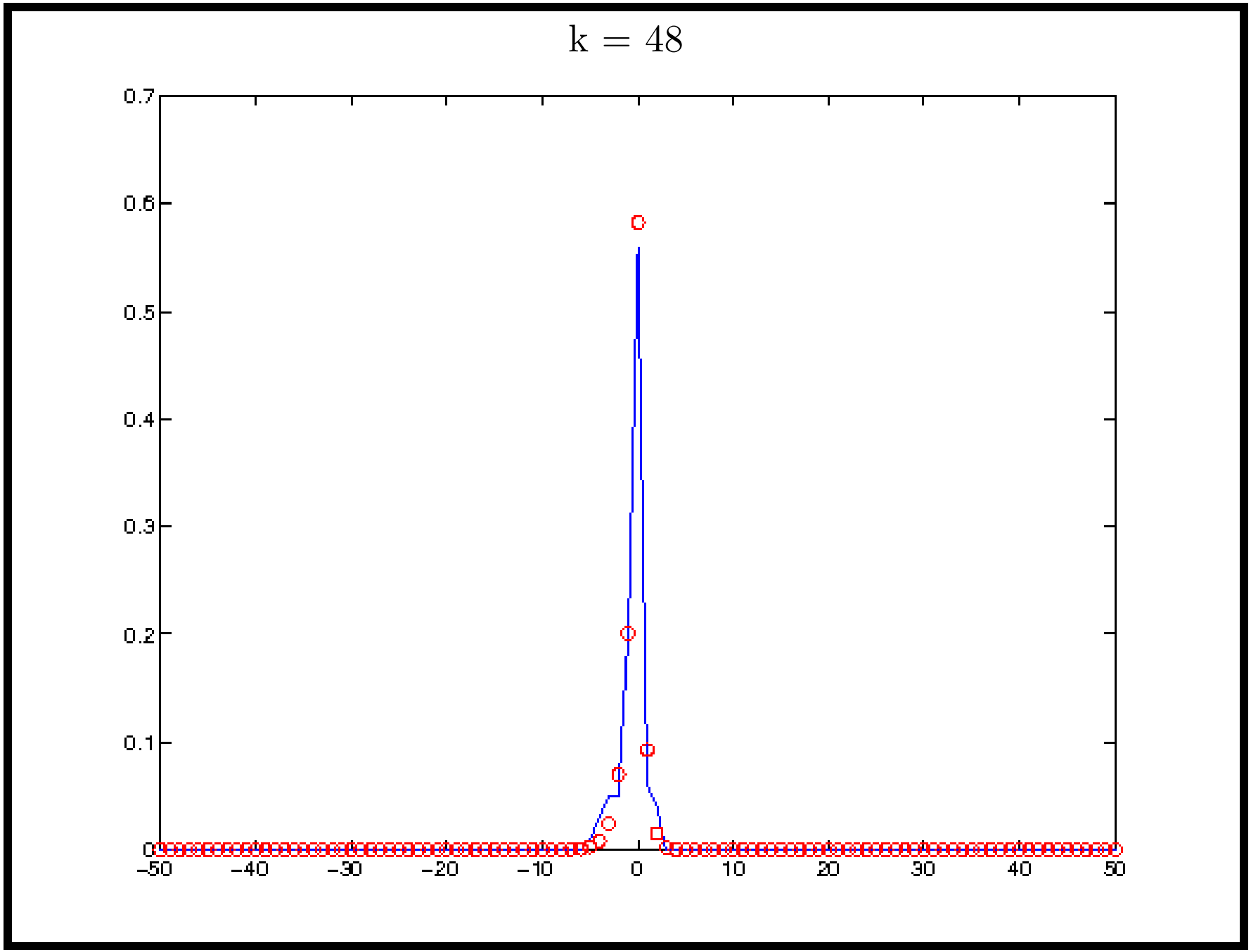
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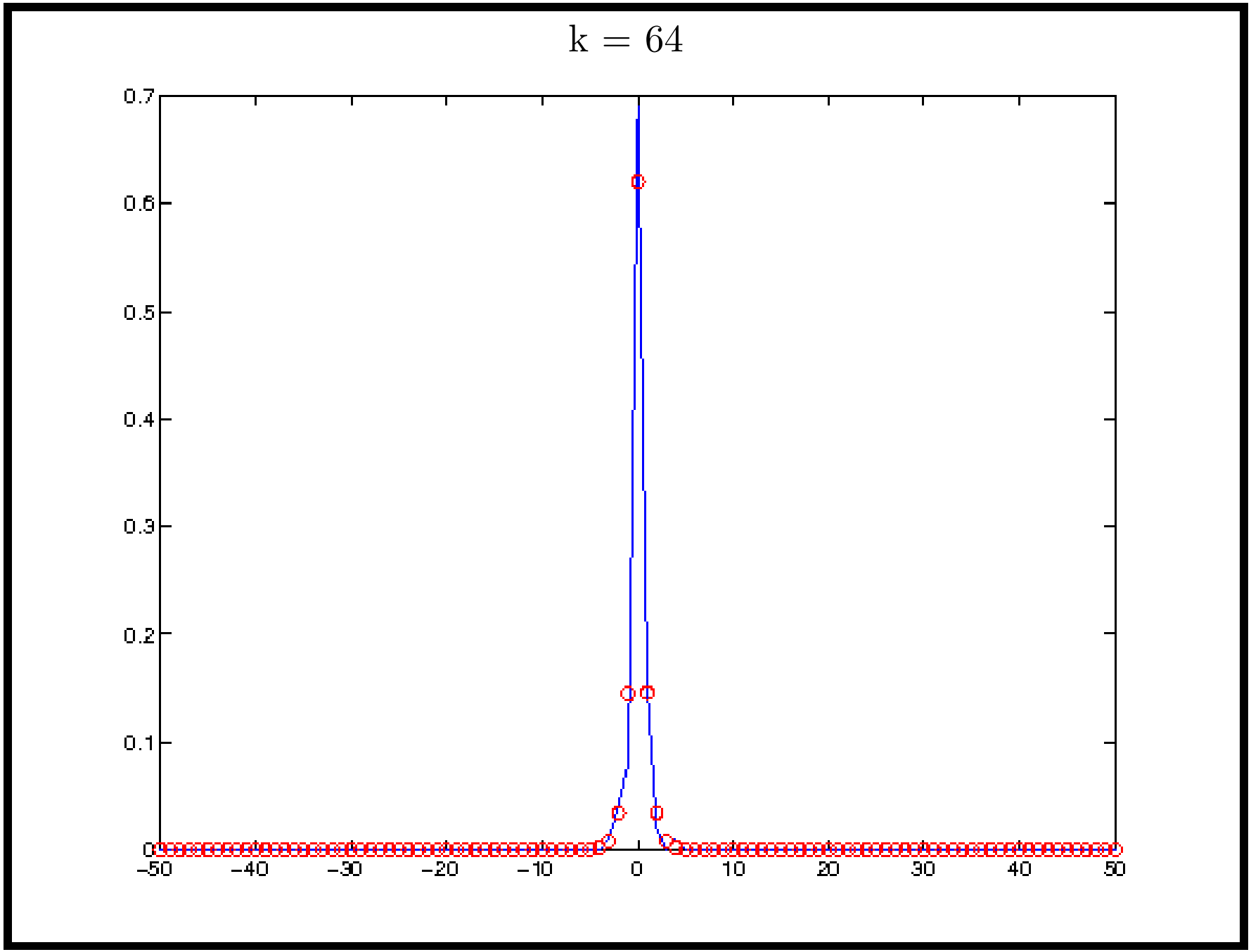
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0.3
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−10
0
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A Continuum Limit

In our model the atomistic scale is taken to be one. For a continuum limit to exist we must suppose that μ_i varies very slowly on the atomistic scale. Consequently there must exist a smooth function $\mu(x)$ such that

$$\mu_i = \mu(i)$$

which means that

$$e^{\beta\mu_{k-1}} - 2e^{\beta\mu_k} + e^{\beta\mu_{k+1}} \approx \partial_{xx} e^{\beta\mu(x)}$$

The smoothness of μ_i implies that y_i is also smooth and we write

$$\frac{\partial y}{\partial t} = \tfrac{1}{2} e^{-\beta\gamma} \partial_{xx}^2 e^{\beta\mu(x)}$$

where

$$\beta\mu(x) = -\partial_x G(y_x) = -G'(y_x) y_{xx}$$

and

$$G'(x) = \frac{\cosh\theta\sqrt{1 + x^2 \sinh^2\theta} - 1}{1 + x^2(\sinh^2\theta + \cosh\theta\sqrt{1 + x^2\sinh^2\theta})}$$

where $\theta = \frac{\beta\gamma}{2}$. This is a fourth order nonlinear diffusion equation.

If we make the small slope approximation one has

$$G'(x) \approx \cosh\theta - 1 \quad \text{and} \quad \beta\mu(x) \approx -(\cosh\theta - 1)y_{xx}.$$

This gives

$$\frac{\partial y}{\partial t} = -By_{xxxx}$$

where

$$B = \tfrac{1}{2}e^{-\beta\gamma}(\cosh\theta - 1)$$