Chapter 9: Molecular-dynamics

- Integrate equations of motion--classical!

- Discrete form of Newton's second law

- Forces from interaction potential

$$\vec{F}_i = -\vec{\nabla}_i U\left(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N\right)$$

- For a simple pair potential, we get

$$U\left(\vec{r}_1, \ldots, \vec{r}_N\right) = \frac{1}{2}\sum_{ij} u(r_{ij})$$

Integrating equations of motion

$$F_{i,x} = m_i \frac{dv_{i,x}}{dt} \qquad F_{i,y} = m_i \frac{dv_{i,y}}{dt} \qquad F_{i,z} = m_i \frac{dv_{i,z}}{dt}$$

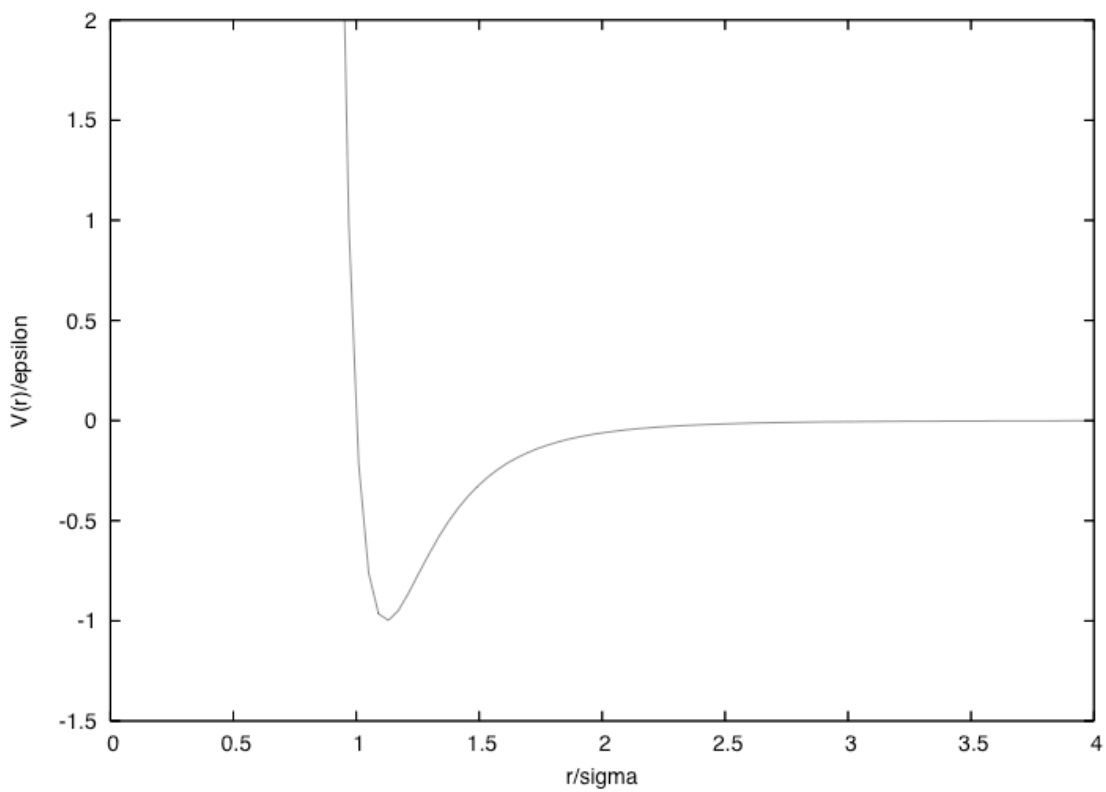
$$\frac{dv_{i,x}}{dt} = \frac{d^2 x_i}{dt^2} \approx \frac{x_i(n+1) - 2x_i(n) + x_i(n-1)}{\Delta t^2}$$

This works out to give the Verlet algorithm,

$$x_i(n+1) = 2x_i(n) - x_i(n-1) + \frac{F_{i,x}}{m_i}\Delta t^2$$

Lennard-Jones potential for noble gas

$$V(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$$



Statistical ensemble

- Newtonian dynamics -----> microcanonical, canonical ensemble

$$P \sim e^{-E/kT}$$

- If we know $U(\mathbf{r}_1, \ldots, \mathbf{r}_N)$, in principle we can compute anything!

….but if it were just that easy I wouldn't have a job!

Challenges:

- We usually *do not* know interactions accurately
- Timescales, length scales usually are ~ns, nm …
- Problems of interest often on scales of ~ μs, μm **and beyond!**

Monte-Carlo for d=2 Ising model

The Hamiltonian is given by,

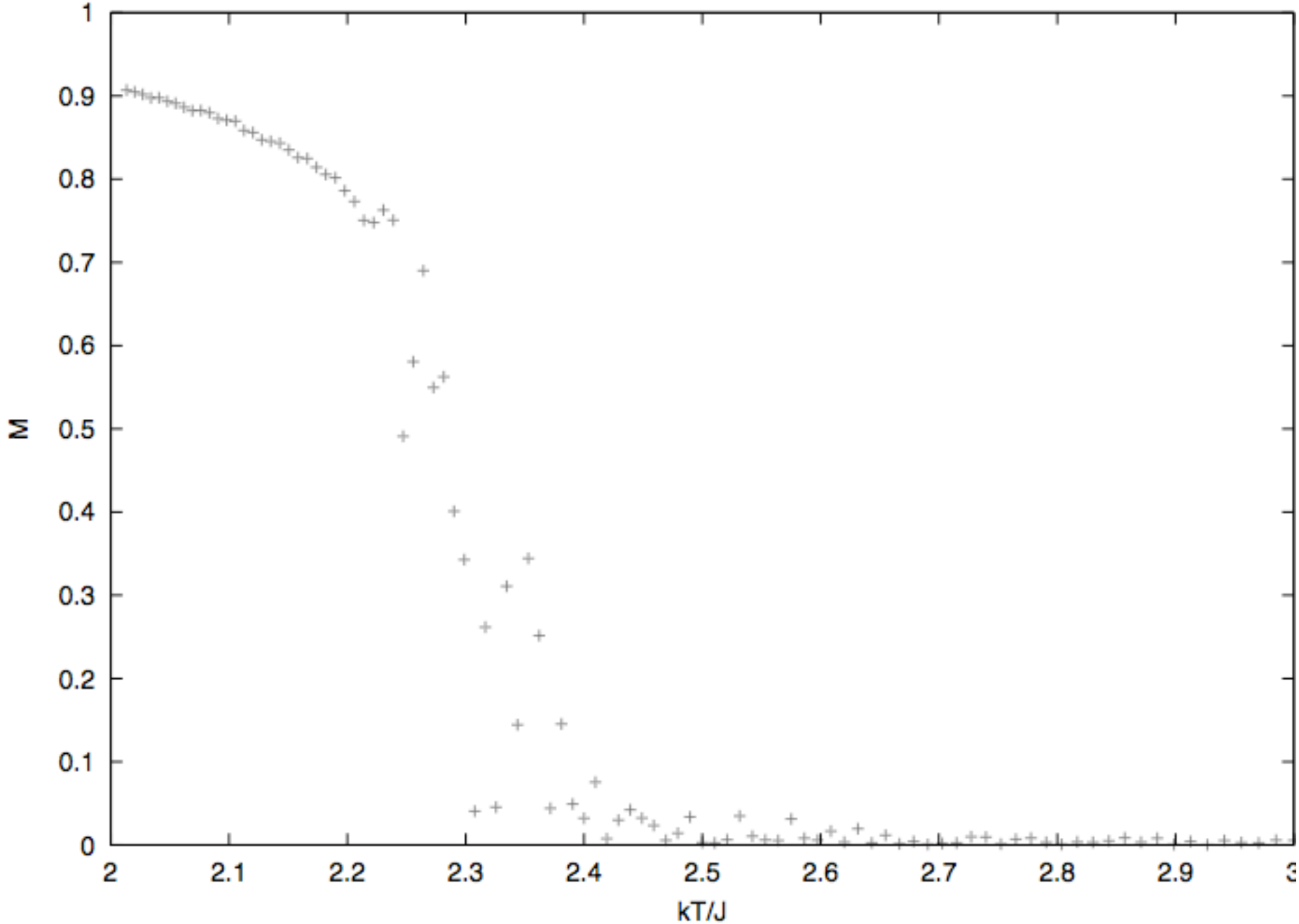
$$H_\Omega = -\frac{1}{2} J \sum_{i=1}^{N} \sum_{j=1}^{N} S_{ij} \left(S_{i+1,j} + S_{i-1,j} + S_{i,j+1} + S_{i,j-1} \right)$$

The Weiss theory in d=2 gives $k_B T_c = 4J$

The exact relation from Onsager is $k_B T_c = 2.2692J$

In project 4, we can come close to the exact result using Metroplis Monte Carlo

I ran for a 100x100 spin lattice


1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
M
2
2.1
2.2
2.3
2.4
2.5
2.6
2.7
2.8
2.9
3
kT/J

Monte-Carlo for d=2 Ising model

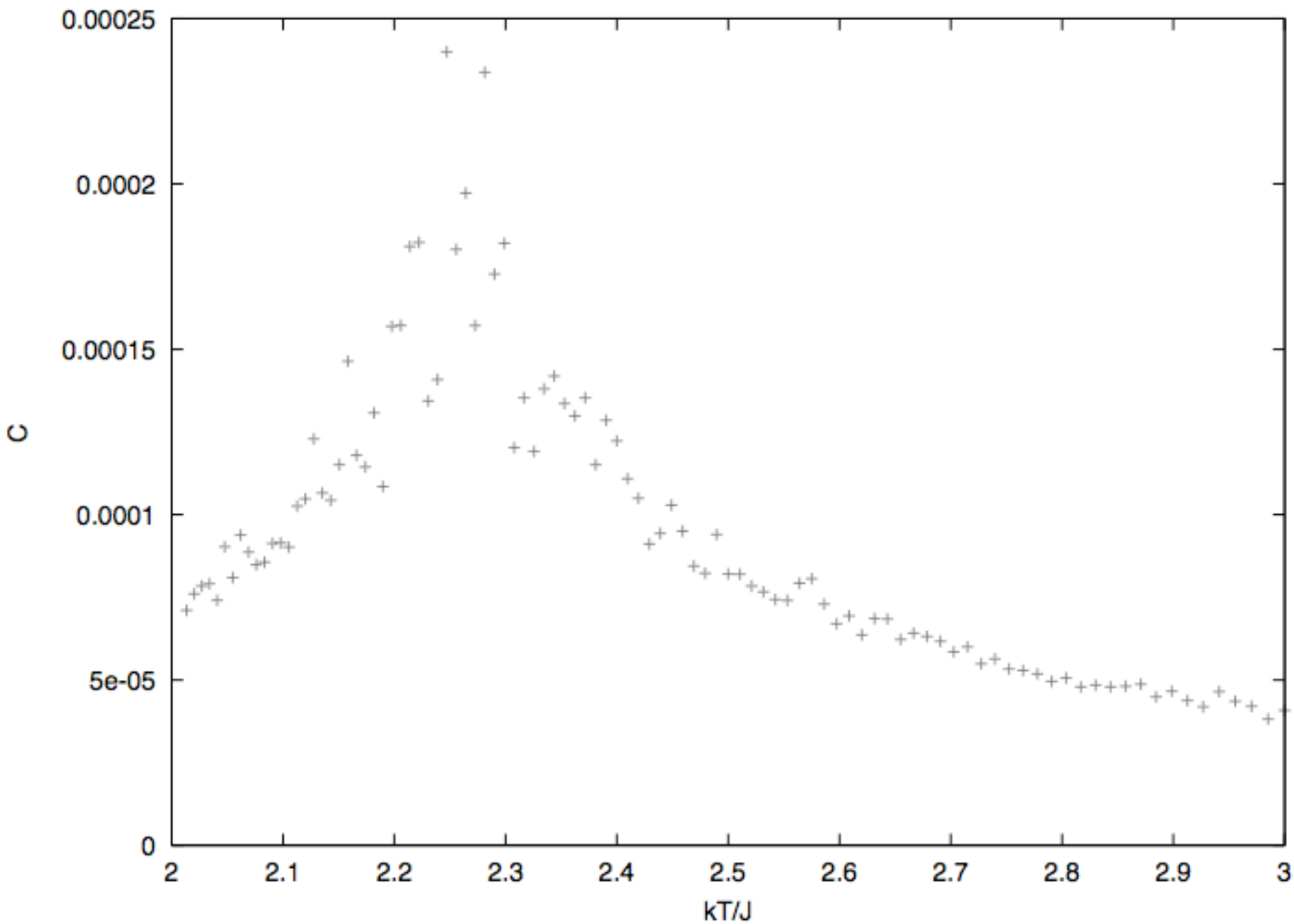
We showed, starting with the free-energy, that

$$\chi = \frac{1}{k_B T}\left[\langle M^2\rangle - \langle M\rangle^2\right]$$

$$C = \frac{1}{k_B T^2}\left[\langle H_\Omega^2\rangle - \langle H_\Omega\rangle^2\right]$$

In experiment and exact theory it is believed that for d=2:

- χ diverges at $T=T_C$ with critical exponent 7/4
- C is discontinuous (not diverging) at $T=T_c$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0.00015
0.0001
5e-05
0
C
2
2.1
2.2
2.3
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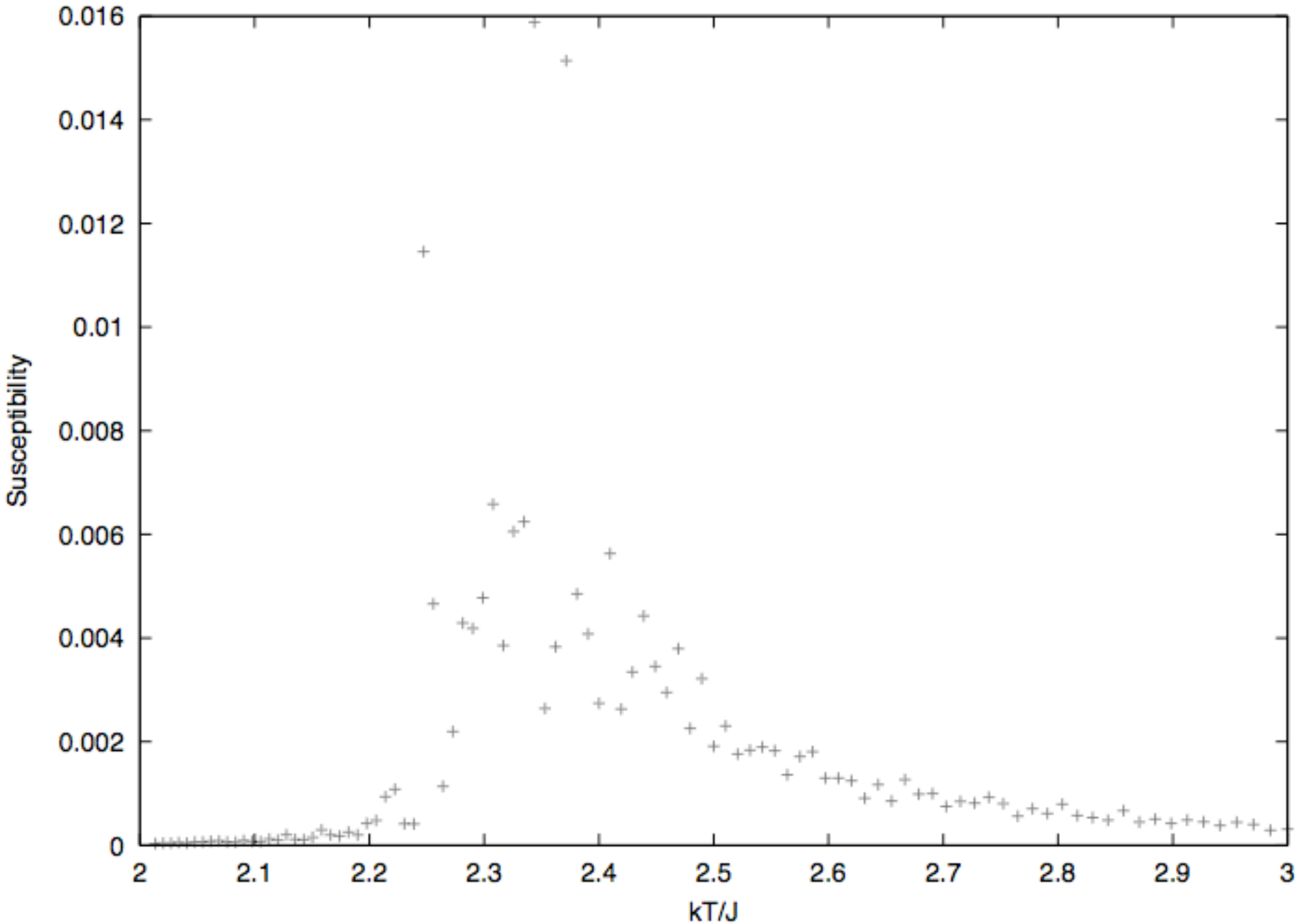
2.6
2.7
2.8
2.9
3
kT/J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0.014
0.012
0.01
0.008
0.006
0.004
0.002
0
Susceptibility
2
2.1
2.2
2.3
2.4
2.5
2.6
2.7
2.8
2.9
3
kT/J