Dynamical Nonequilibrium MD: Establishing Benard Convection

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- **Equilibrium vs NEMD**
- **Average in NEMD (Onsager-Kubo)**
- **Case of Benard convection**

with

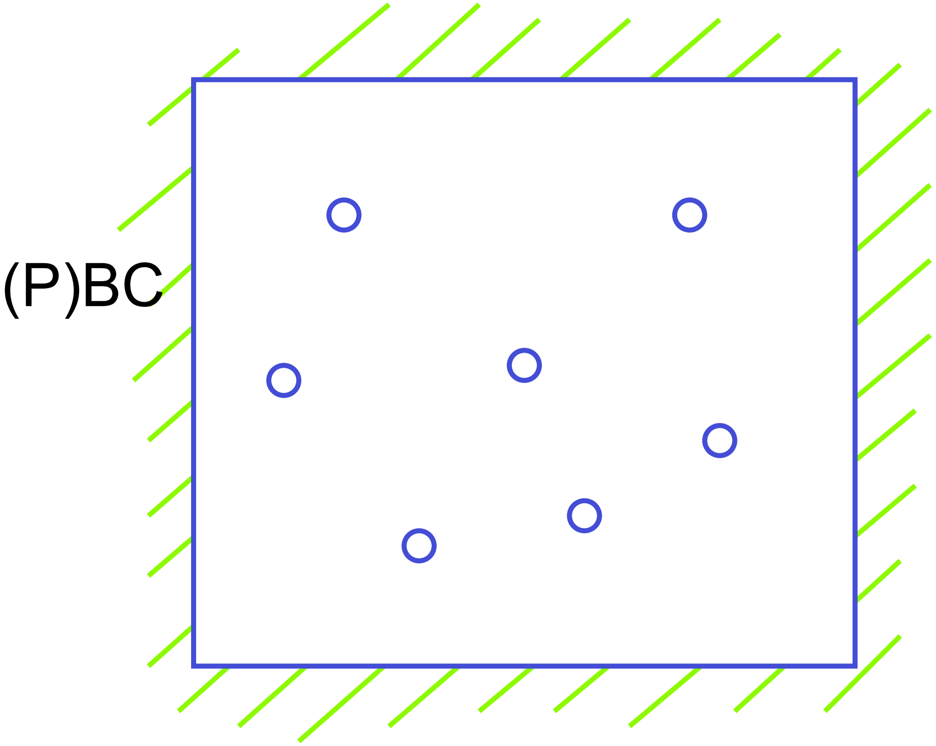
M.L. Mugnai (Rome)

C. Pierleoni (Rome)

S. Caprara (Rome)

M. Mareschal (Brussels)

MD “game” for atoms... (1)



- N point particles
- $\mathcal{V}(r_1, \ldots r_N) = \sum_{i<j} v(r_{ij})$
- Volume $V \Rightarrow \rho = \frac{N}{V}$

$$m\ddot{r} = F\left(\{r\}\right)$$

$$\begin{cases} r(t+h) = -r(t-h) + r(t) + h^2 \frac{F}{m} \\ \dot{r}(t) = \frac{r(t+h) - r(t-h)}{2h} \end{cases}$$

$$h \sim 10\, fs$$

MD “game” for atoms... (2)

Macroscopic properties:

$$O = \left\langle \hat{O} \right\rangle = \lim_{\mathcal{T}\to\infty} \frac{1}{\mathcal{T}} \int_0^{\mathcal{T}} d\tau\, \hat{O}\left(\{r(\tau)\}, \{p(\tau)\}\right) = \int dr dp\, \rho_E(r,p) \hat{O}$$

extension(s)

$$\begin{cases} m\,\ddot{r} = F - \zeta p \\ \dot{\zeta} = \nu^2 \left(\frac{K(t)}{K_0} - 1 \right) \end{cases} \Rightarrow \rho(r,p;\zeta) \Rightarrow \rho_E(r,p') \propto e^{-\beta H}$$

Nose’ Hoover thermostat

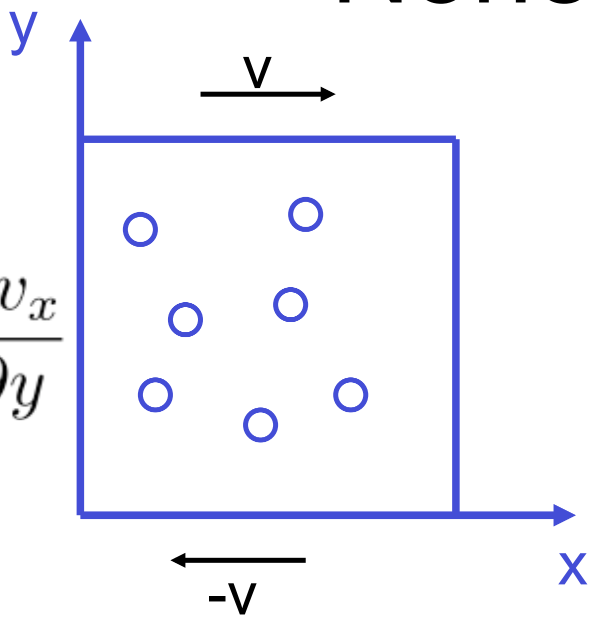
barostat

....

Nonequilibrium

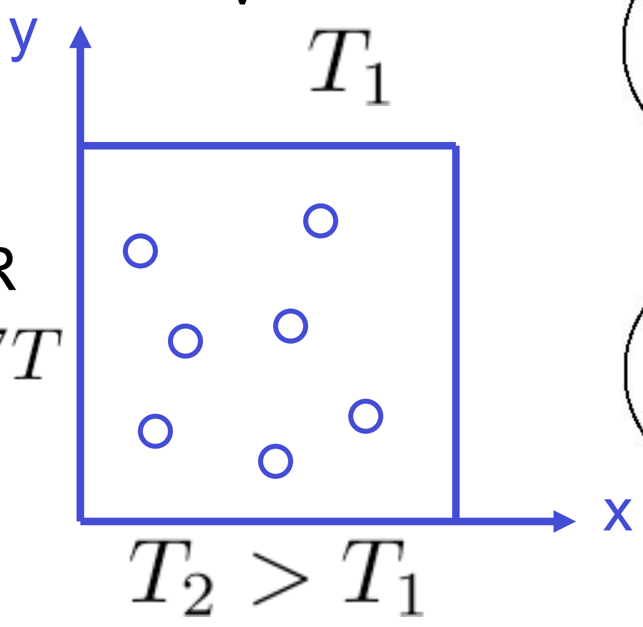
SHEAR

$$J_{xy} = \eta \frac{\partial v_x}{\partial y}$$



FOURIER

$$J_Q = \lambda \nabla T$$



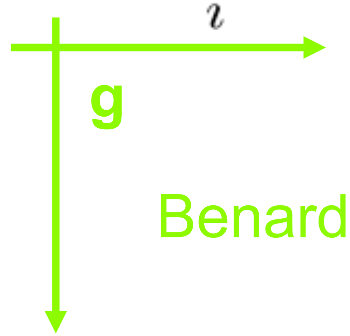
classical field

$$\rho(r,t) = \langle \hat{\rho}(r) \rangle_{ne}$$

$$\hat{\rho}(r) = \sum_i m_i \delta(r - r_i)$$

$$\mathbf{v}(r,t) = \frac{\langle p(r) \rangle_{ne}}{\rho(r,t)}$$

$$\hat{p} = \sum_i p_i \delta(r - r_i)$$



Benard's cells

H
Y
D
R
O
D
Y
N
A
M
I
C
S

NEMD (1)

- Produce an instantaneous fluctuation of a given property and follow its relaxation to equilibrium (Onsager's idea)

Assume that a given, time-dependent external local field $\Psi(x,t)$ is coupled to our system via a suitable local property

$$A\left(x \middle| \{r_j, p_j\}_{j=1,N}\right) = \sum_i A_i\left(\{r_j, p_j\}_{j=1,N}\right)\delta(x - r_i)$$

- The total hamiltonian of the system is $\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_P$

$\mathcal{H}_0$ standard equilibrium hamiltonian

$$\mathcal{H}_P = -\int dx A(x)\Psi(x,t) = -\sum_i A_i(r,p)\underline{\Psi(r_i,t)}$$

$$= -g\left(\sum_i A_i\varphi_i\right)\chi(t) = -gh_P\chi(t)$$

$$\boxed{\Psi(r,t) = g\varphi(r)\chi(t)}$$

NEMD (2)

PERTURBED SYSTEM:

- Equations of motion

$$\begin{cases} \dot{r} = \frac{\partial H_0}{\partial p} + \frac{\partial H_p}{\partial p} = \frac{\partial H_0}{\partial p} - g\frac{\partial h_p}{\partial p} \\ \dot{p} = -\frac{\partial H_0}{\partial r} - \frac{\partial H_p}{\partial r} = F + g\frac{\partial h_p}{\partial r}\chi(t) \end{cases}$$

- Liouville equation

$$\frac{\partial \rho}{\partial t} = iL\rho = iL_0\rho + iL_p\rho = \{H_0, \rho\} + \{H_p, \rho\}$$

with

$$\rho(r, p, t) = S^\dagger(t)\rho(r, p, t = 0)$$

$$S_1^\dagger(t) = S_0^\dagger + \int_{-\infty}^{t} d\tau S^\dagger(t - \tau)iL_p(\tau)S_0^\dagger(\tau)$$

an observable O of the system evolves with

$$O(t) \equiv O(r(t), p(t)) = S(t)O$$

NEMD (2)

PERTURBED SYSTEM:

- Equations of motion

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with

$$\rho(r, p, t) = S^{\dagger}(t)\rho(r, p, t = 0)$$

$\rho(r, p, t = 0) = \rho_0(r, p)$ is an initial distribution obtained from a stationary state, possibly but not necessarily from an equilibrium state

Dynamical NEMD (1) [Ciccotti, Jacucci '75]

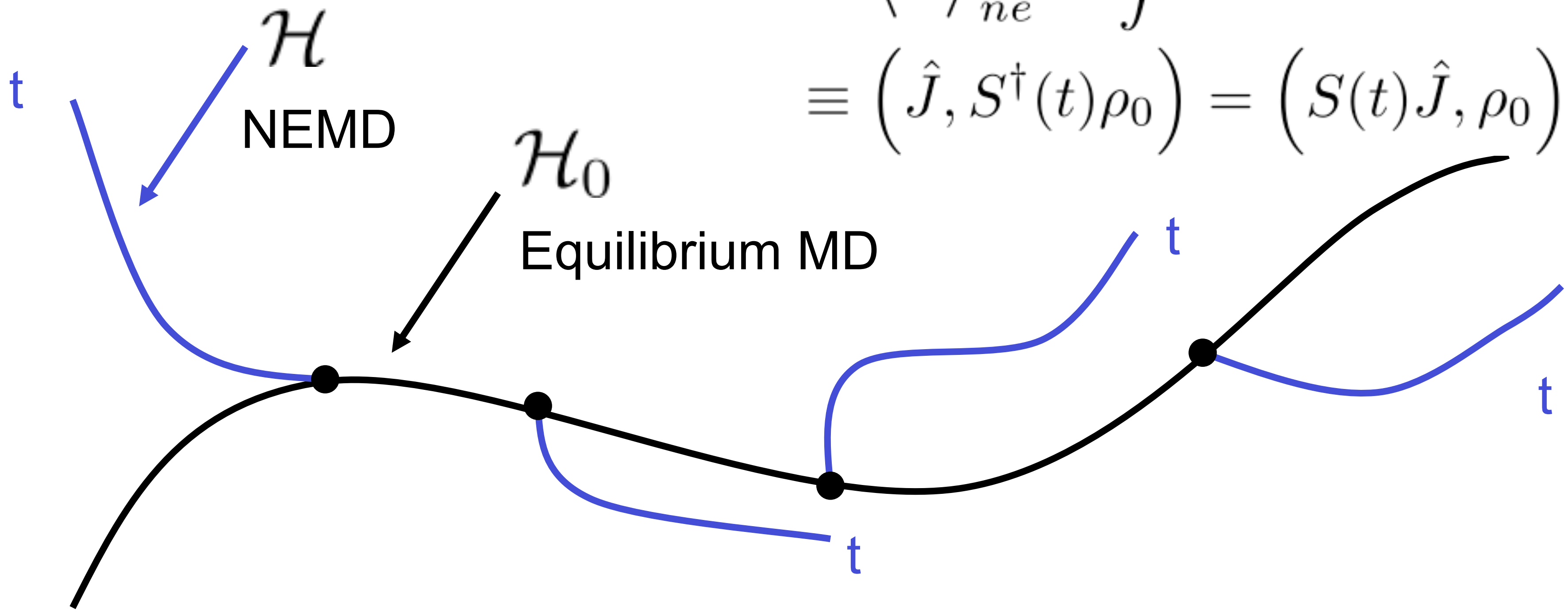
The NE average of a given observable

$$\frac{d\hat{J}}{dt} = -iL\hat{J} \quad , \quad \hat{J}(t) = S(t)\hat{J}$$

can be obtained via an EQUILIBRIUM AVERAGE as follows

(Onsager-Kubo equation) $J(t) = \left\langle \hat{J} \right\rangle_{ne}^{t} = \int d\Gamma \hat{J} \rho(t)$

$$\equiv \left(\hat{J}, S^{\dagger}(t)\rho_0 \right) = \left(S(t)\hat{J}, \rho_0 \right)$$



Dynamical NEMD (2) [Ciccotti, Jacucci '75]

Direct calculation of nonequilibrium response:

$$\langle O \rangle_{ne}(t) \equiv \left(O, S^\dagger(t,0)\rho_0\right) = \left(S(t,0)O, \rho_0\right) \equiv \langle S(t,0)O \rangle_0$$

response (only strong P)

also if

$$\langle O \rangle_0 = \langle S_0(t,0)O \rangle_0 = 0$$

$$\langle O \rangle_{ne}(t) = \langle S(t,0)O - S_0(t,0)O \rangle_0$$

response by subtraction (P ⟶ 0)

Dynamical NEMD (3) [Ciccotti, Jacucci '75]

$$S(t,0)O \equiv \tilde{O}(t)$$
$$S_0(t,0)O \equiv O(t)$$

$$Var[\tilde{O}(t) - O(t)] =$$
$$= Var[\tilde{O}(t)] + Var[O(t)] - 2Cov[\tilde{O}(t), O(t)]$$

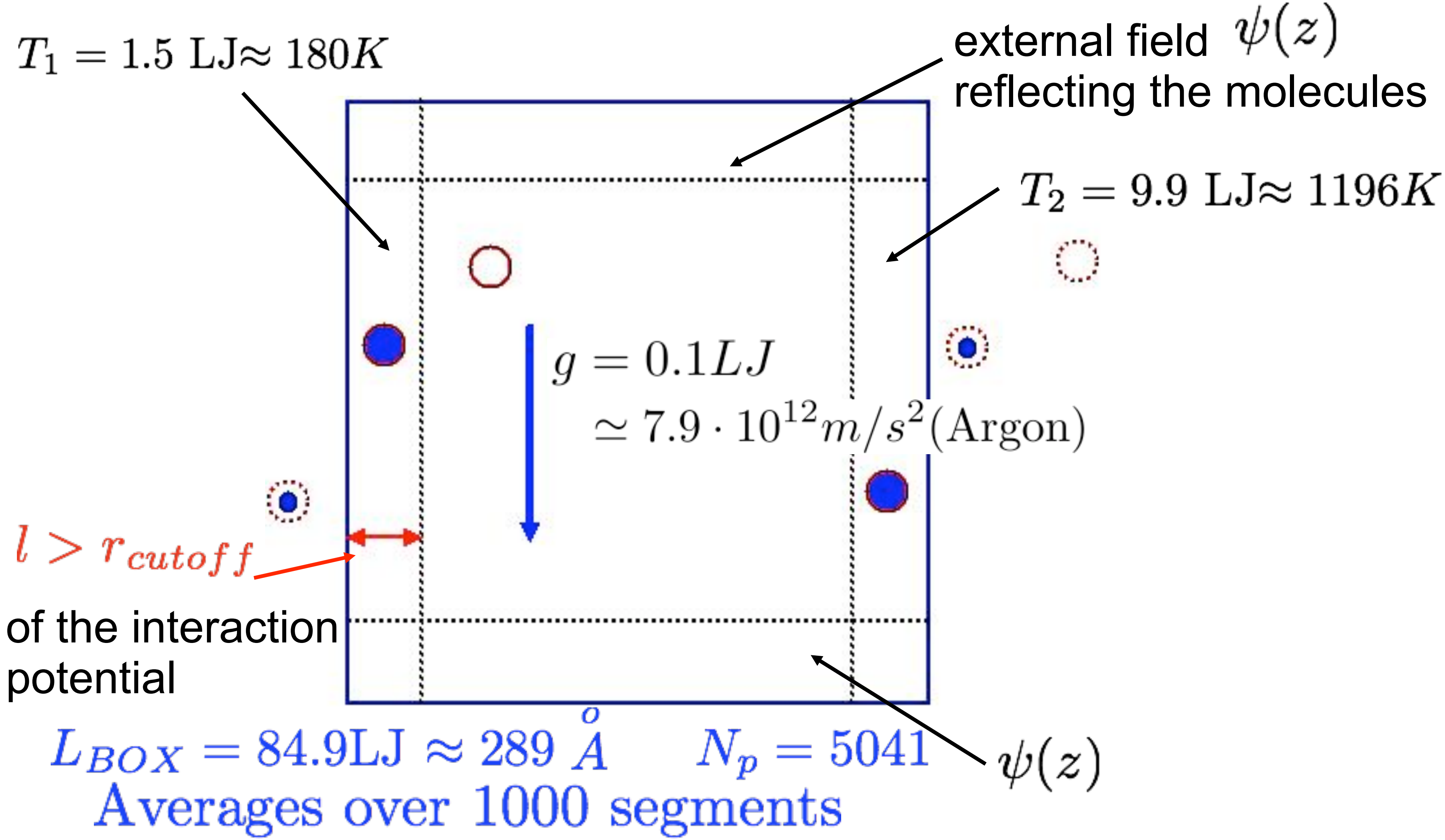
with $Cov\left[\widetilde{O}(t), O(t)\right] = \left(Var\left[\widetilde{O}(t)\right] Var\left[O(t)\right]\right)^{1/2} c(t)$

$$c(t), \text{correlation coefficient} : |c| \leq 1$$

$$c(t = 0^+) \sim 1$$

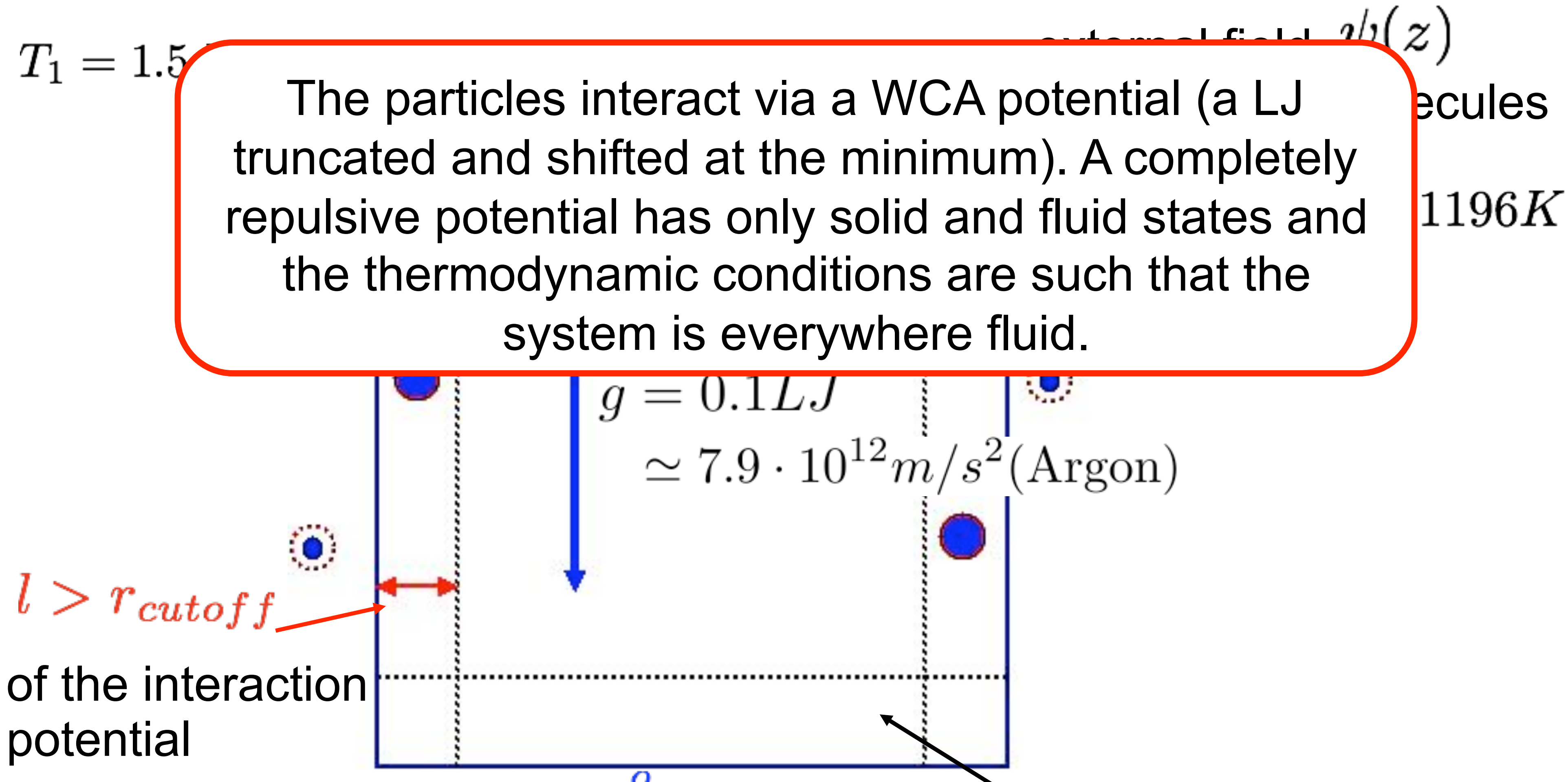
$$\text{Var}\left[\widetilde{O}(t) - O(t)\right] = \mathcal{O}(P^2) \quad \text{if } t \sim 0$$

Benard simulation setting



Benard simulation setting

The particles interact via a WCA potential (a LJ truncated and shifted at the minimum). A completely repulsive potential has only solid and fluid states and the thermodynamic conditions are such that the system is everywhere fluid.



$L_{BOX} = 84.9\text{LJ} \approx 289\ \mathring{A} \qquad N_p = 5041$

Averages over 1000 segments

Benard simulation setting

$T_1 = 1.5$ … external field $\psi(z)$ … ecules … $1196K$

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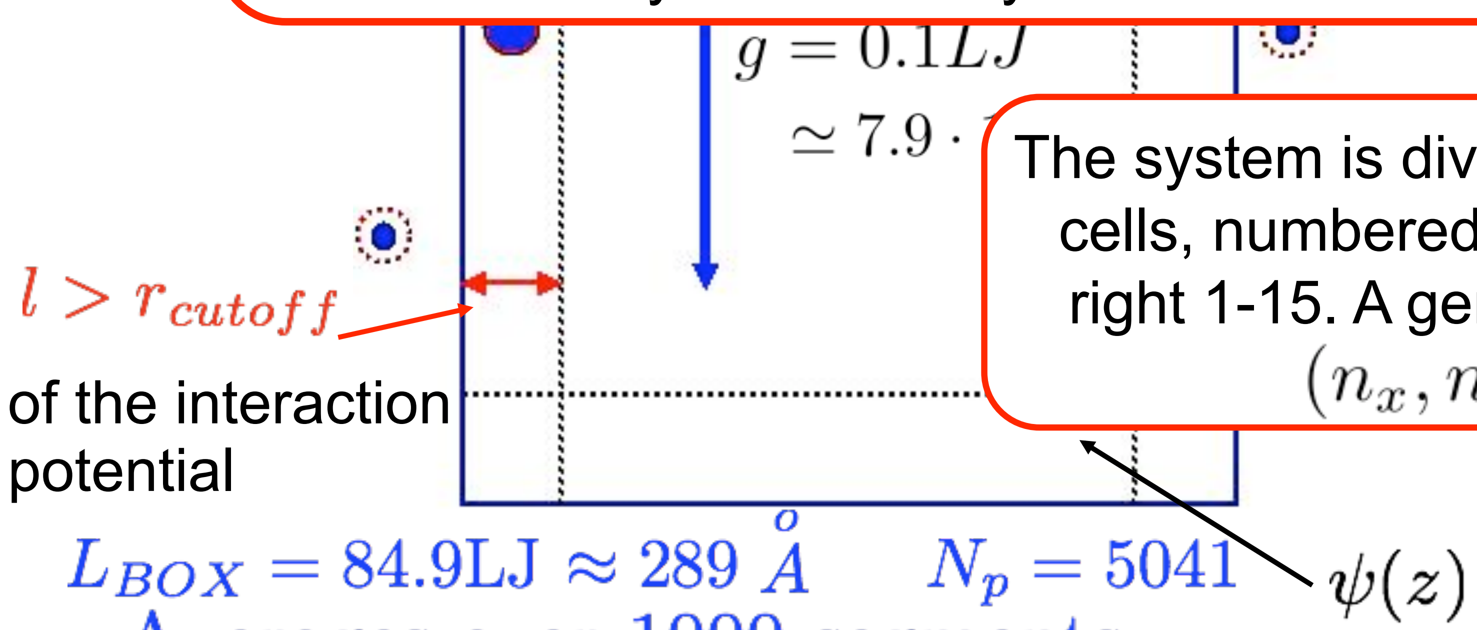

The system is divided in 15*15 cells, numbered from left to right 1-15. A generic cell is (n_x, n_y)

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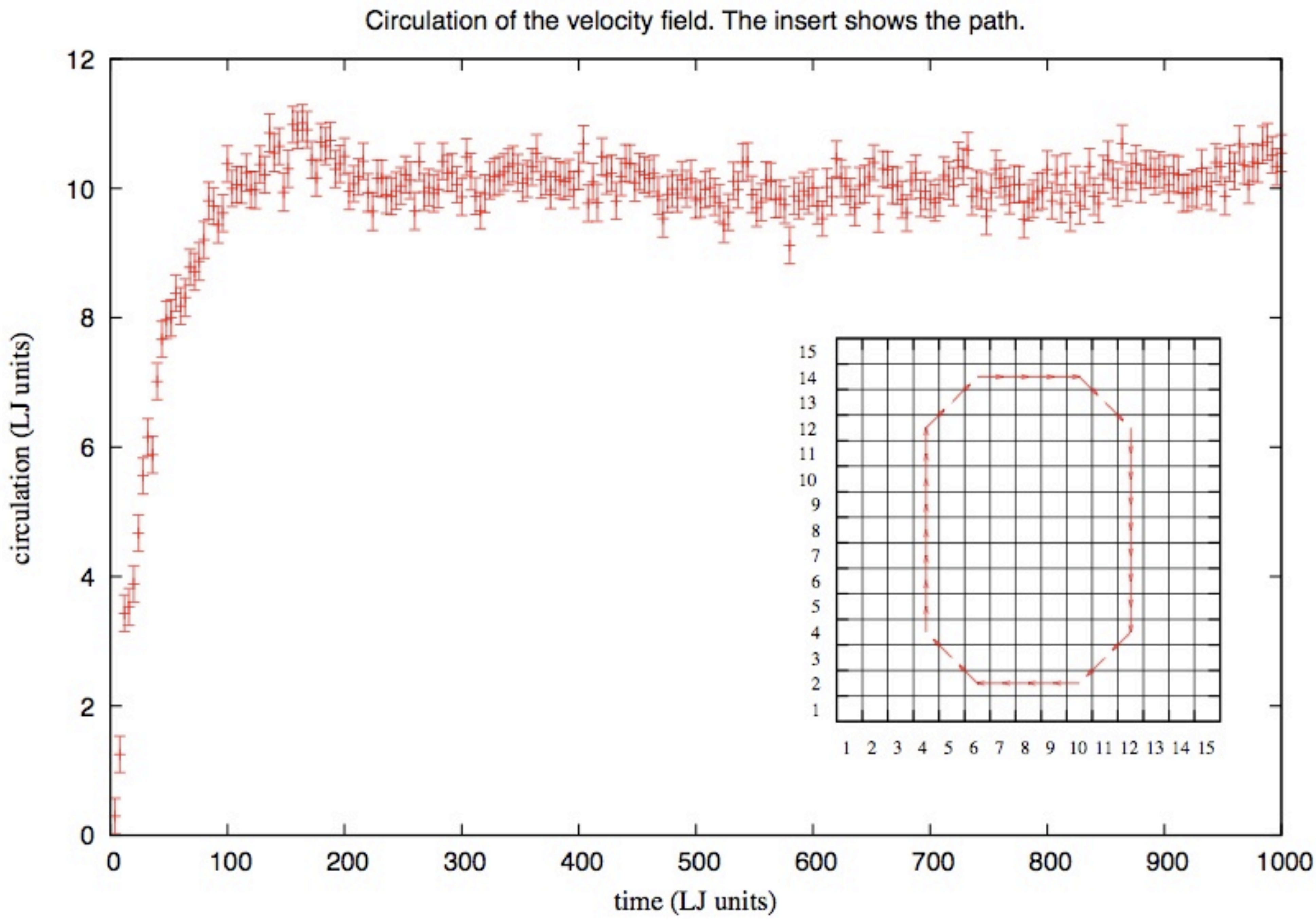
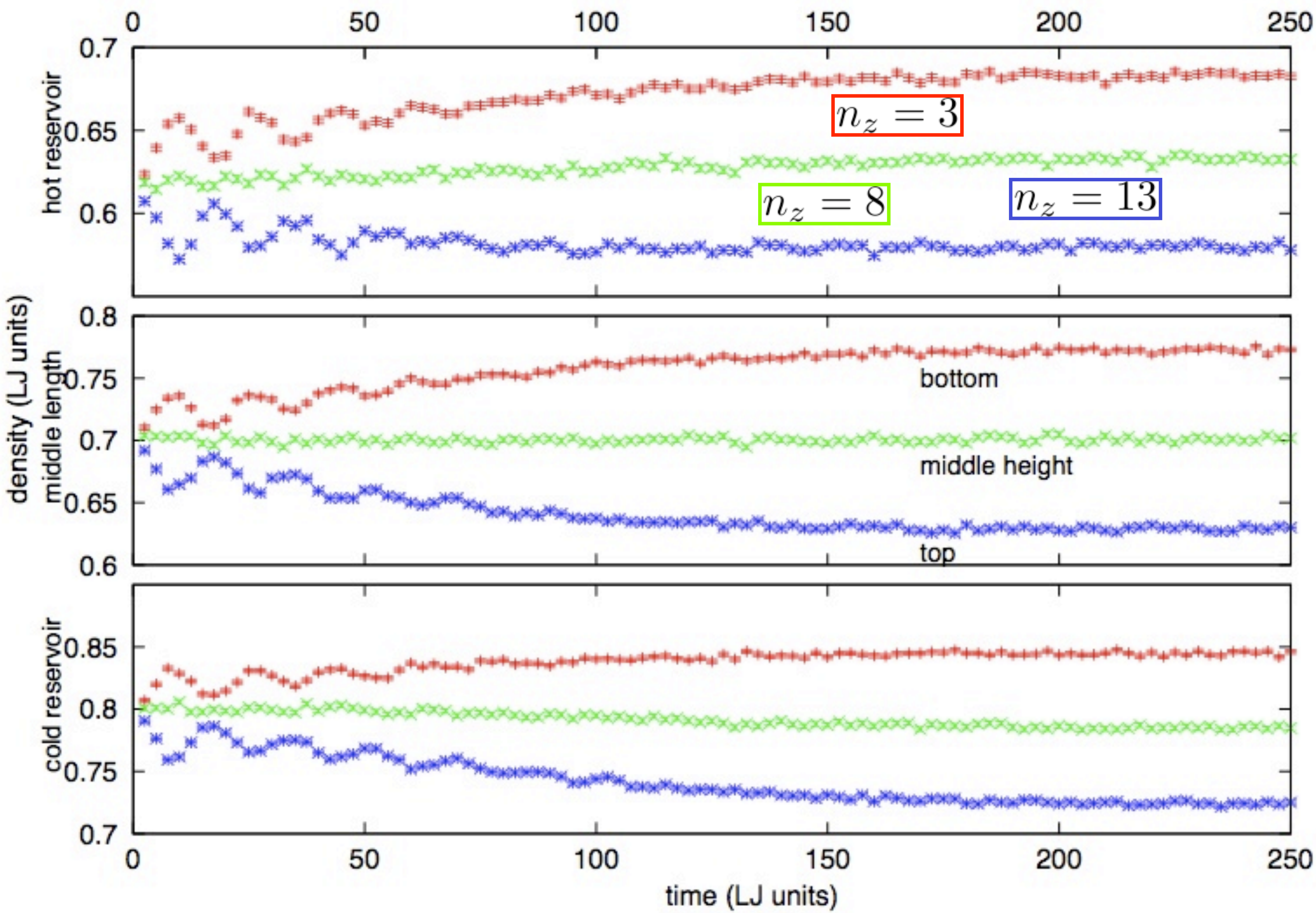
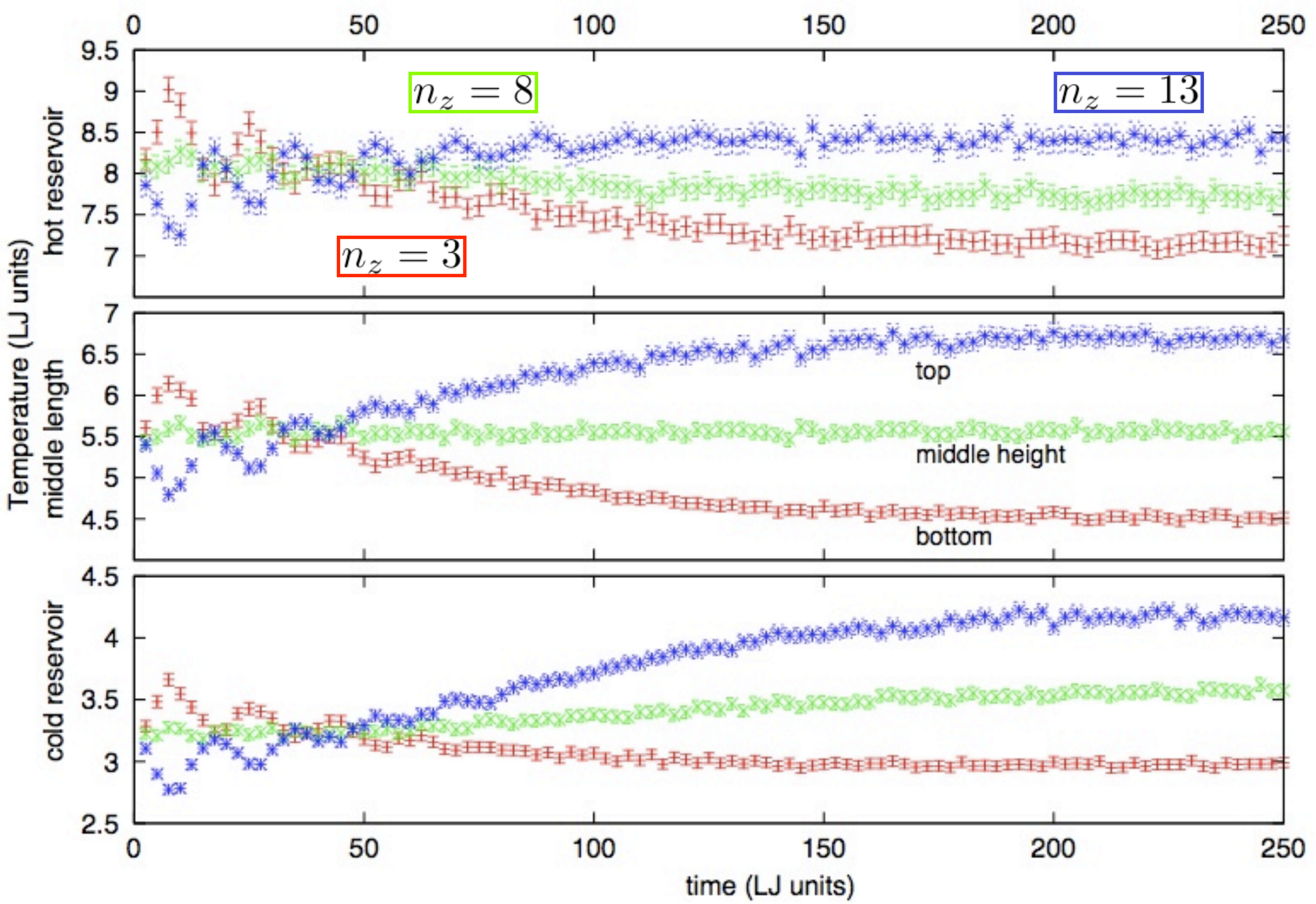
Averages over 1000 segments



Circulation of the velocity field. The insert shows the path.
circulation (LJ units)
time (LJ units)
0
2
4
6
8
10
12
0
100
200
300
400
500
600
700
800
900
1000
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15

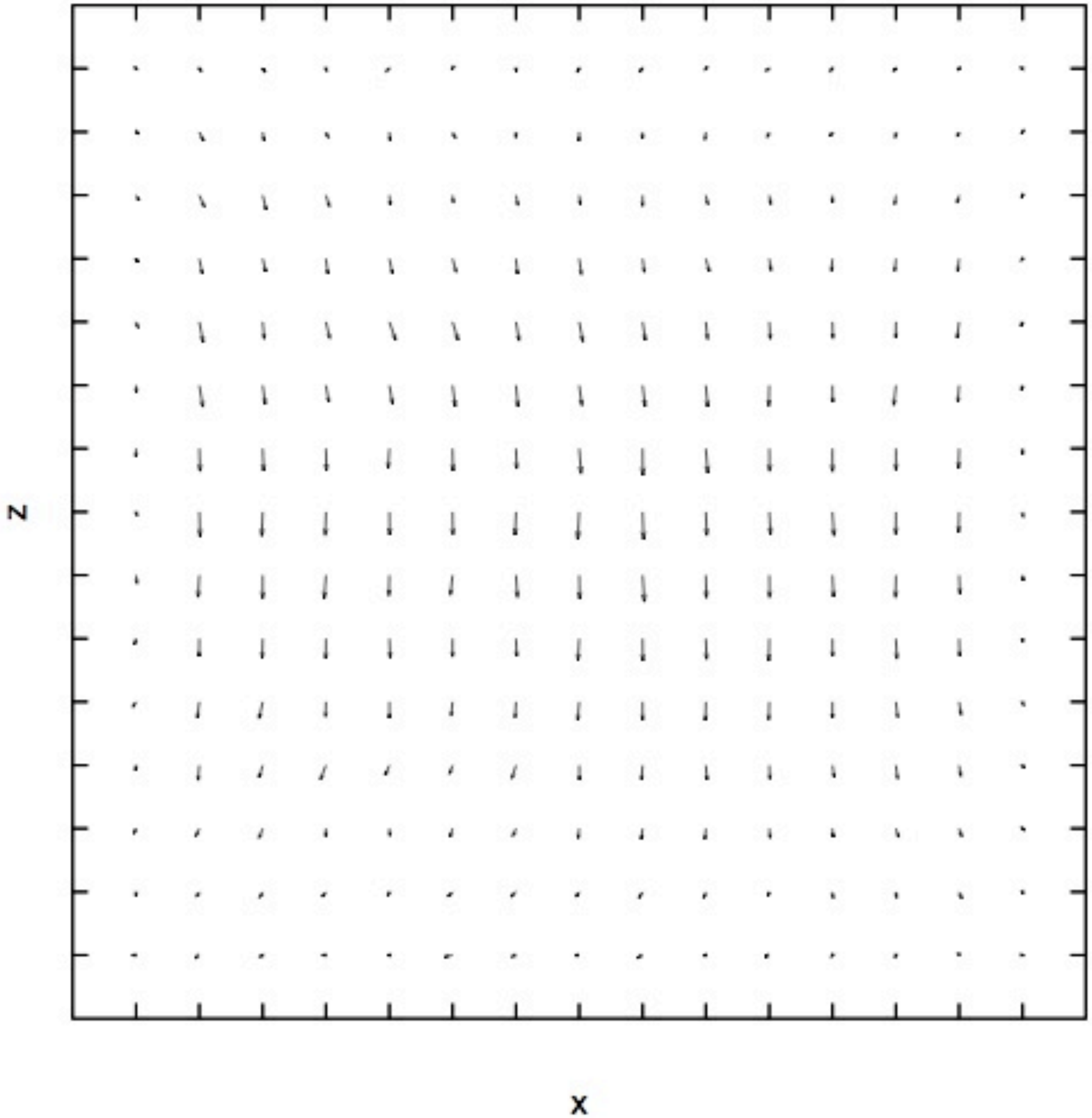


Top $n_x = 3$ Center $n_x = 8$ Bottom $n_x = 13$

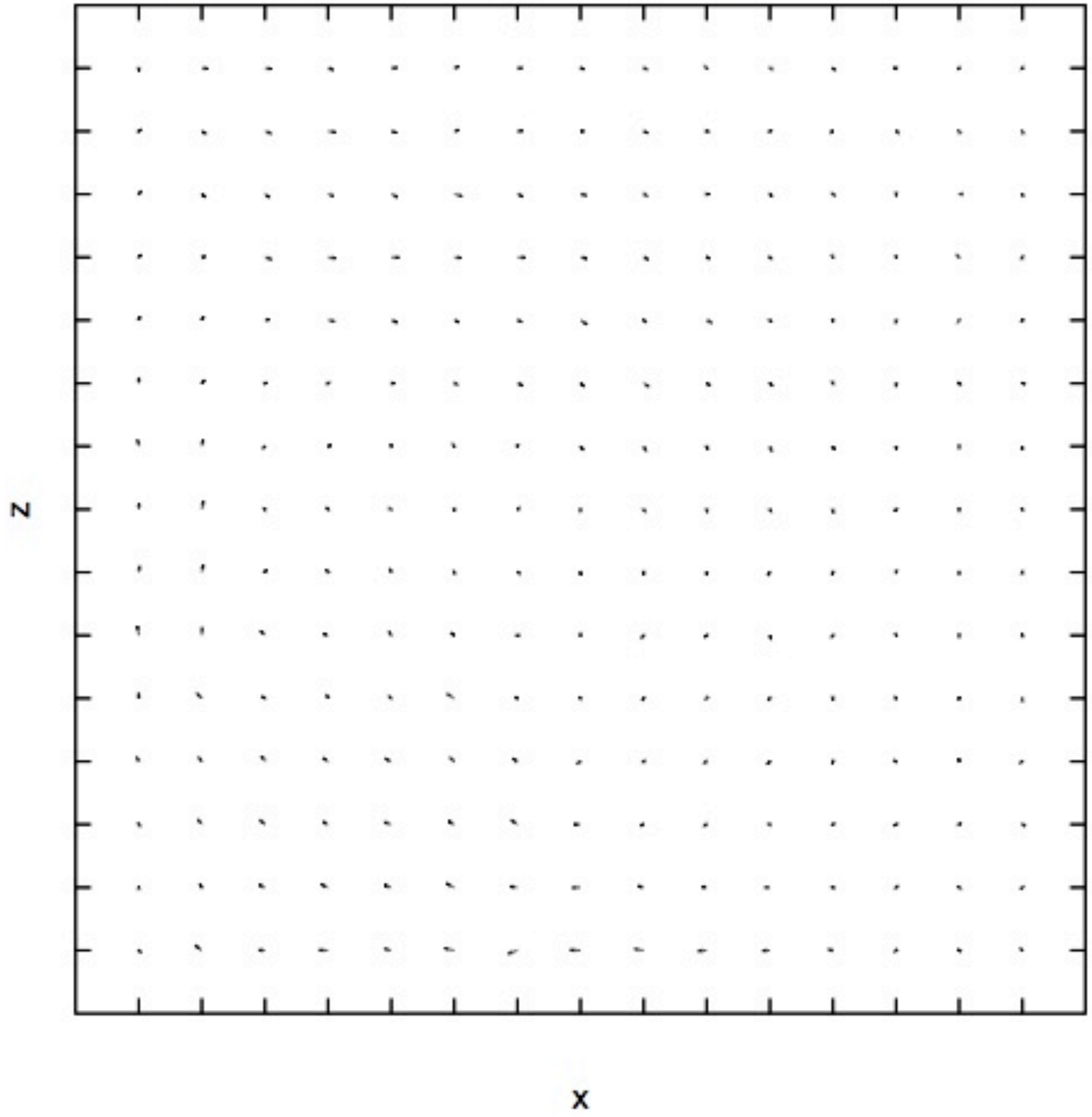


Top $n_x = 3$ Center $n_x = 8$ Bottom $n_x = 13$

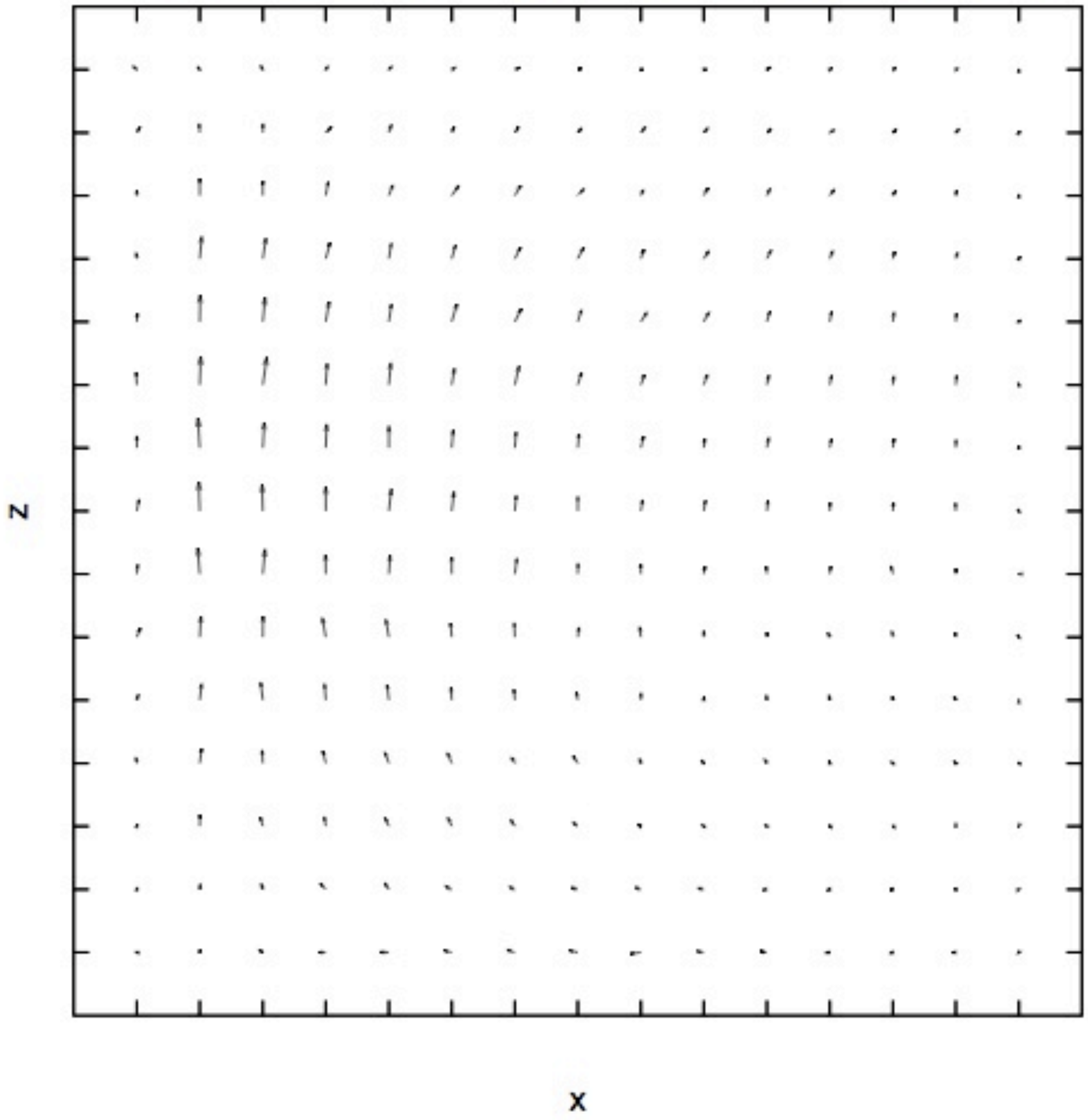
velocity field at about t=T/4 (T=temperature oscillation period)

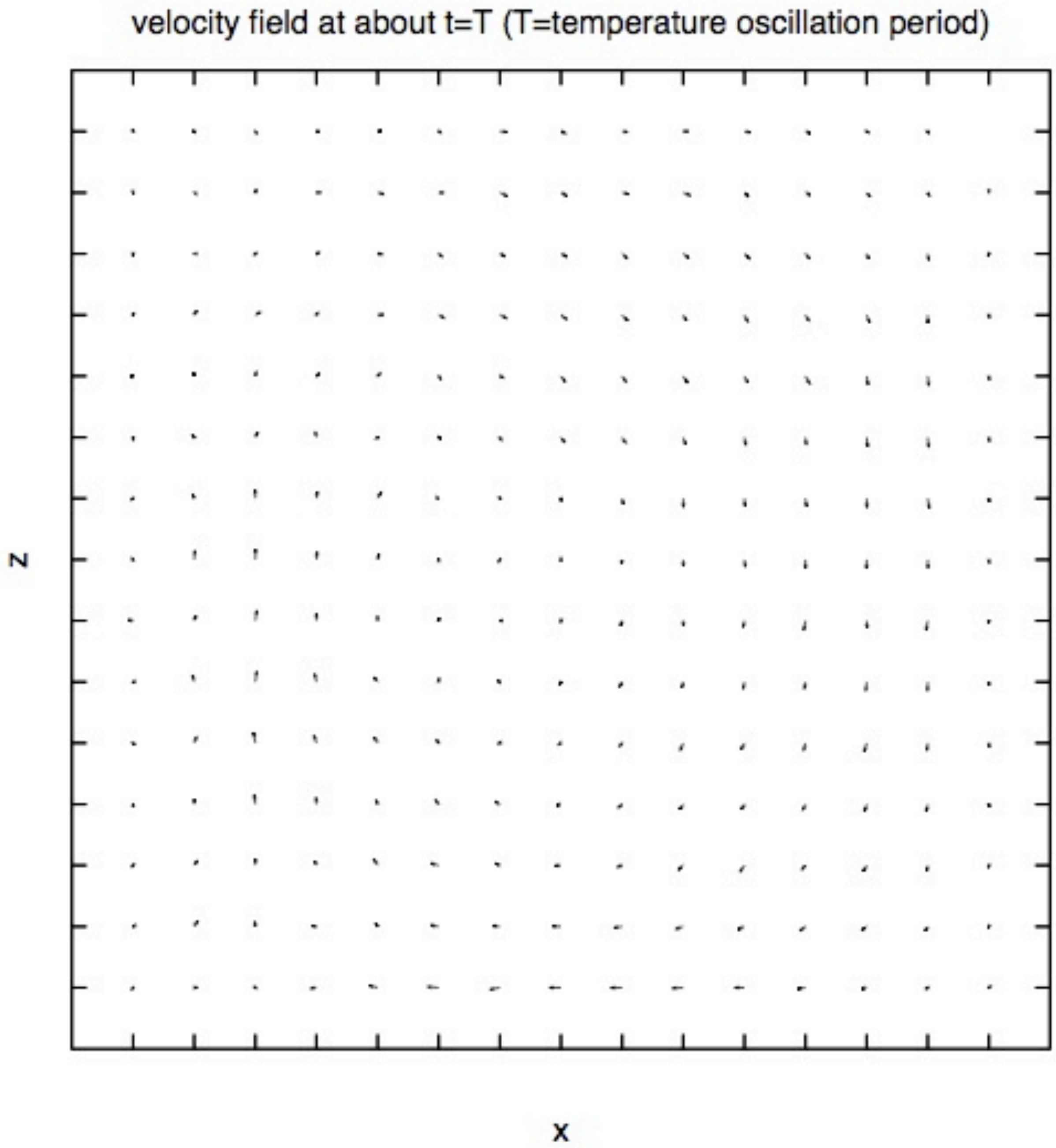


velocity field at about t=T/2 (T=temperature oscillation period)

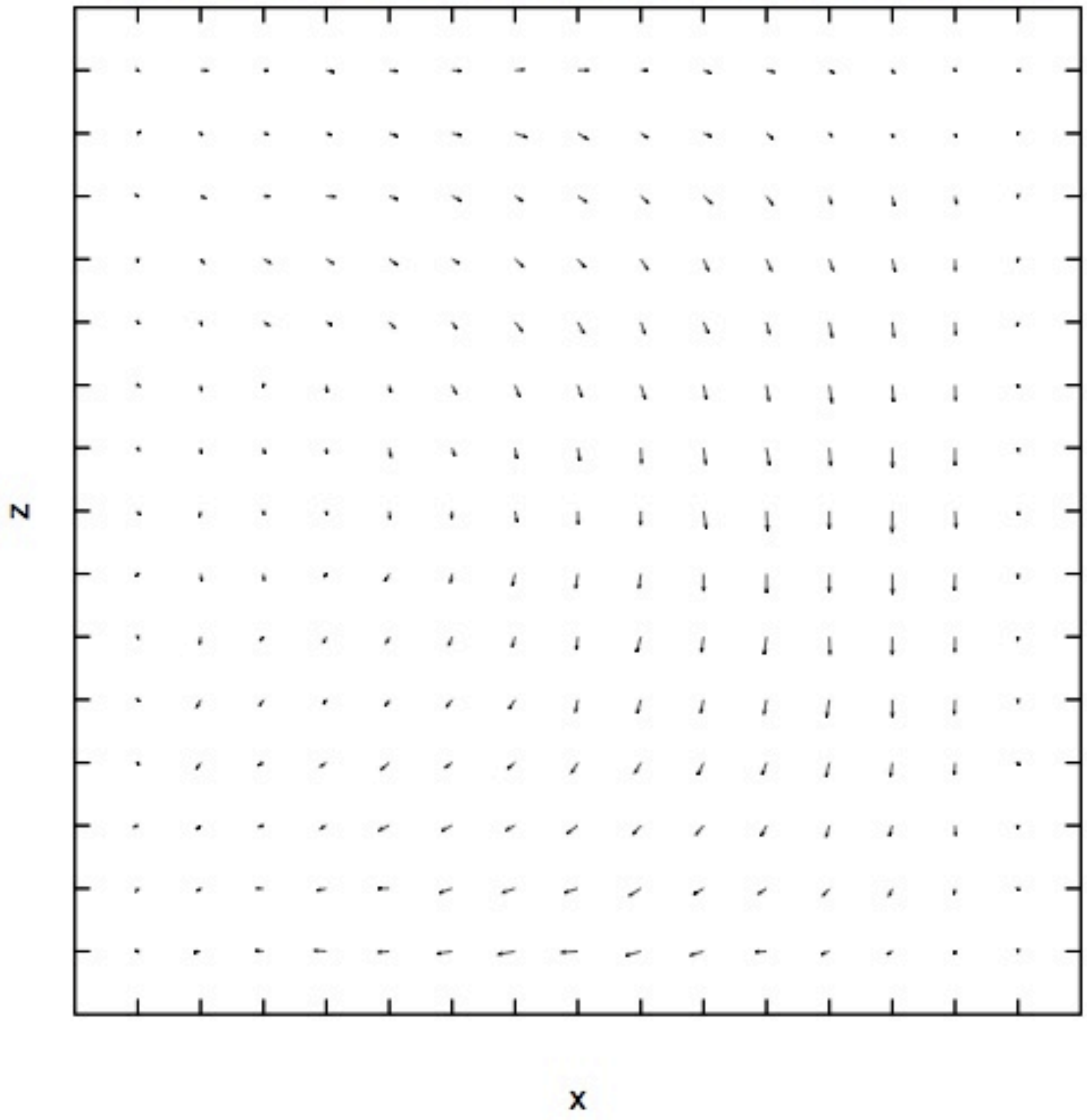


velocity field at about t=3T/4 (T=temperature oscillation period)

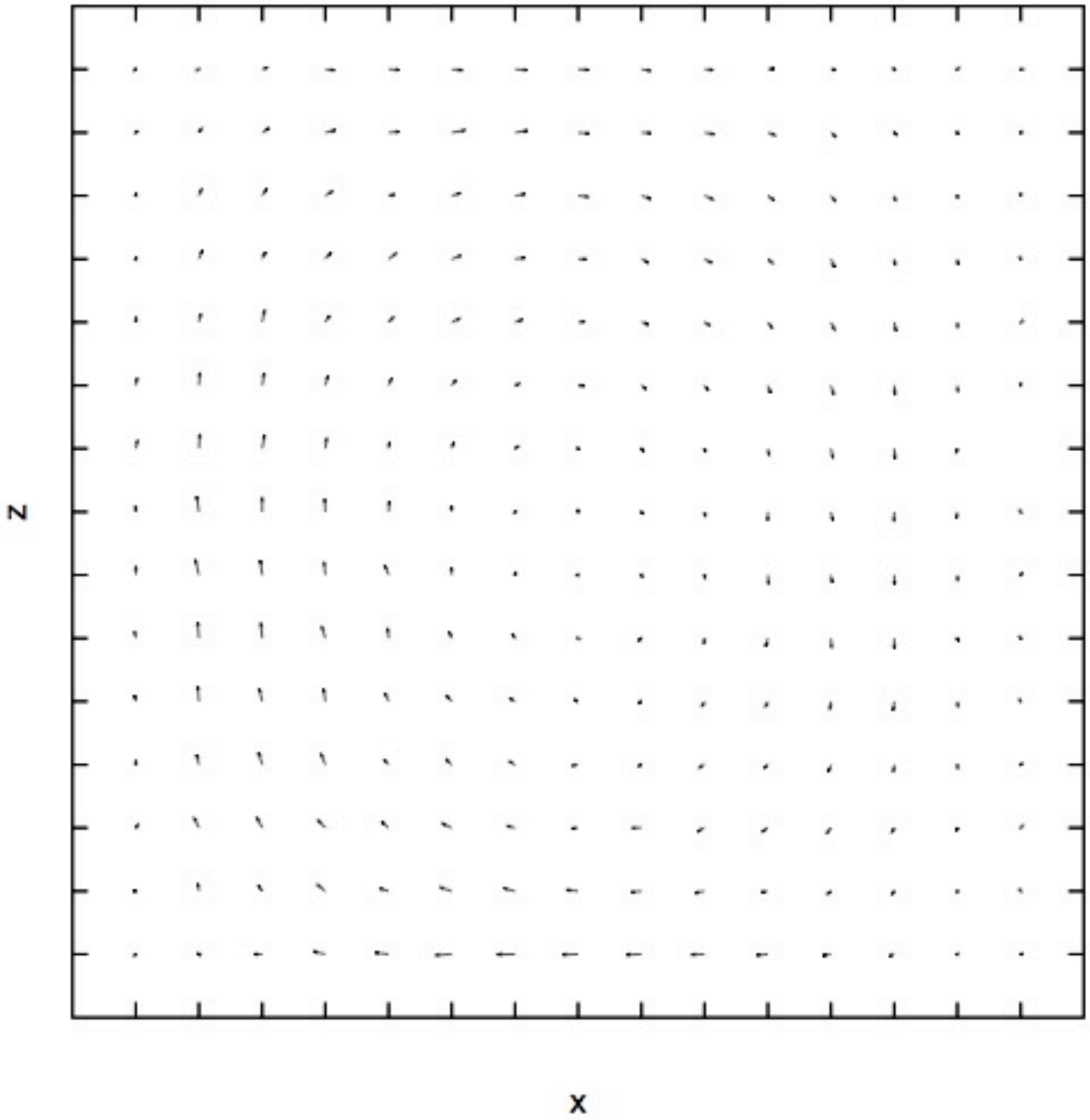



velocity field at about t=T (T=temperature oscillation period)
z
x

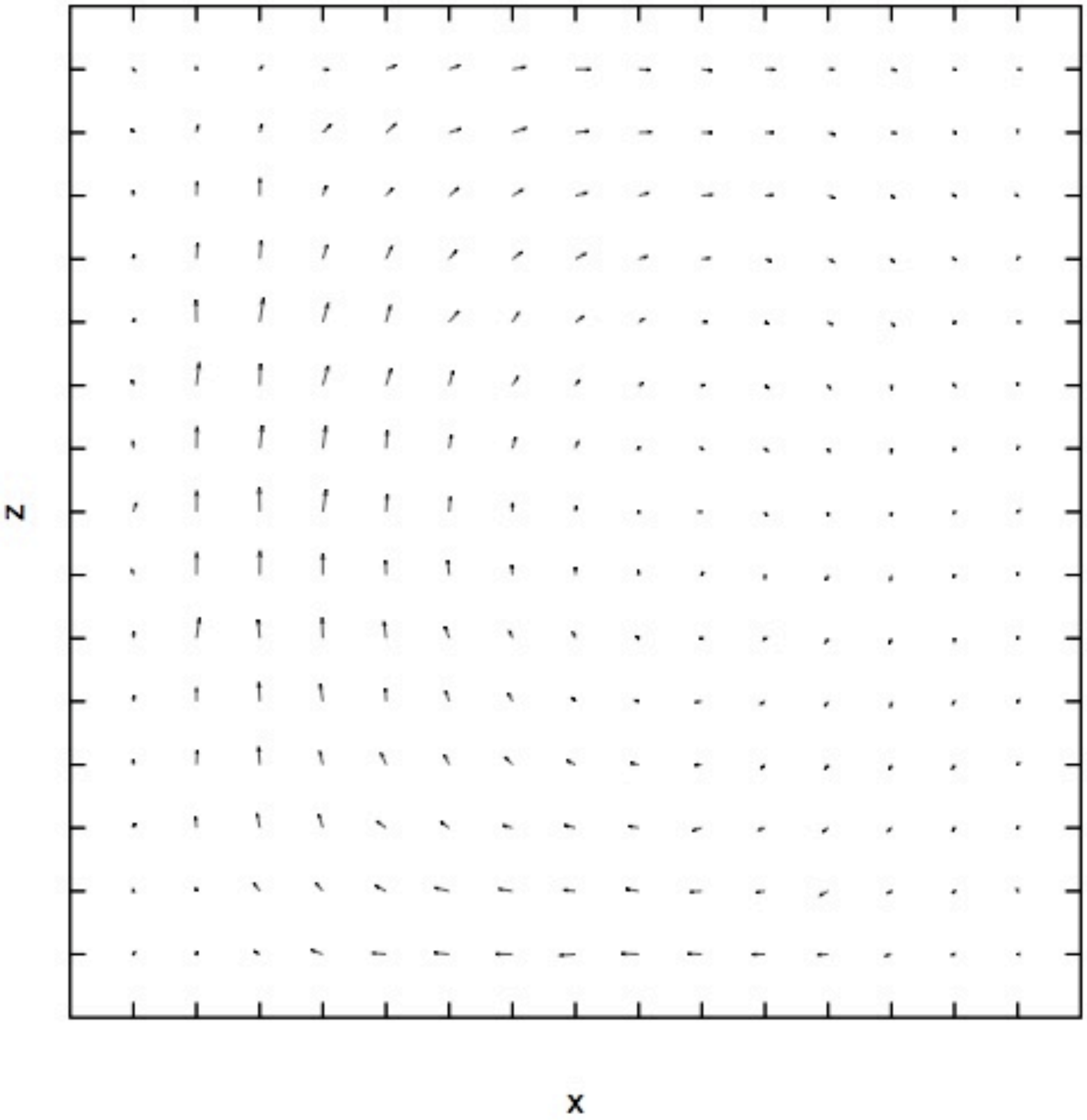
velocity field at about t=5T/4 (T=temperature oscillation period)



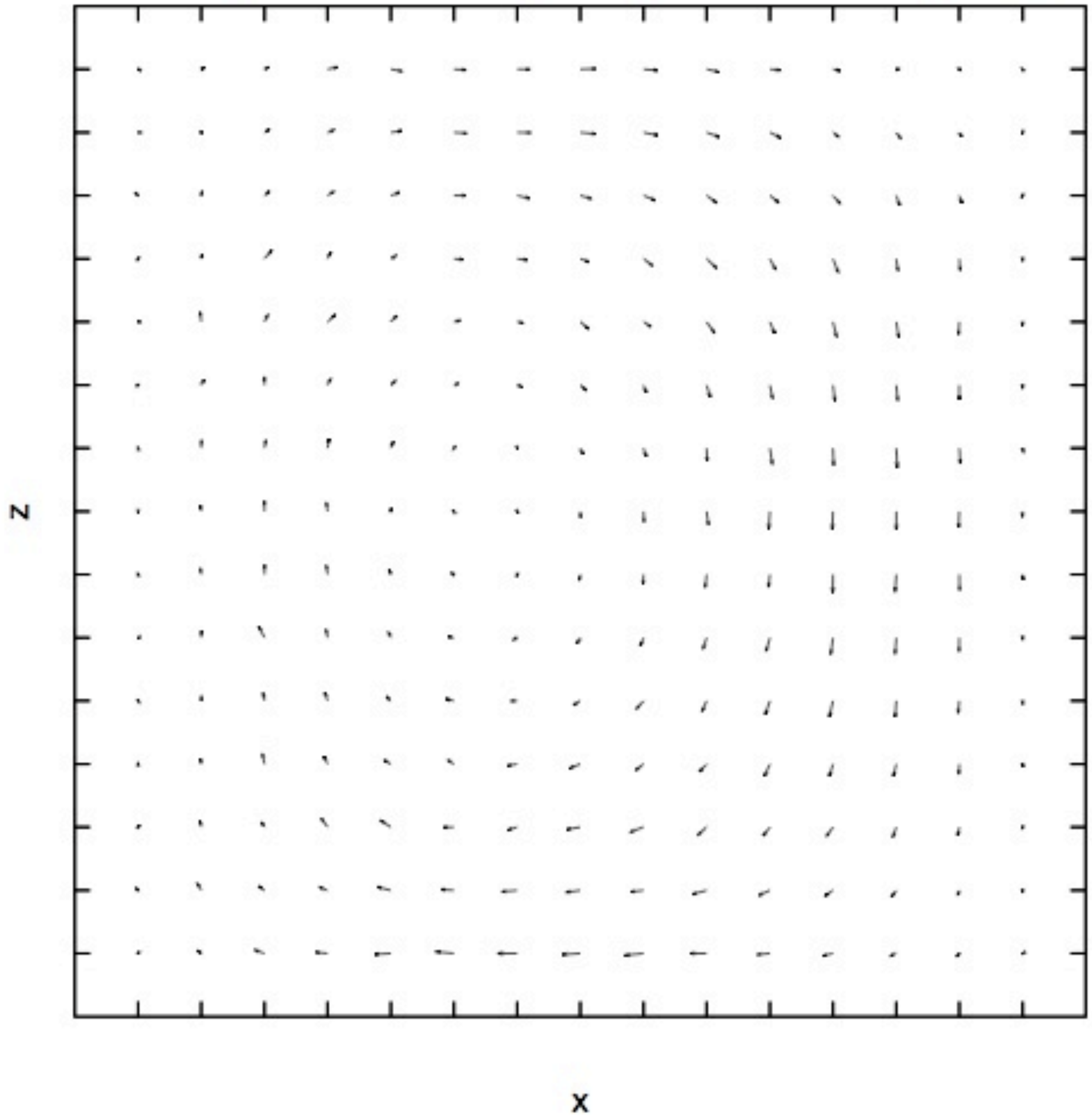
velocity field at about t=6T/4 (T=temperature oscillation period)



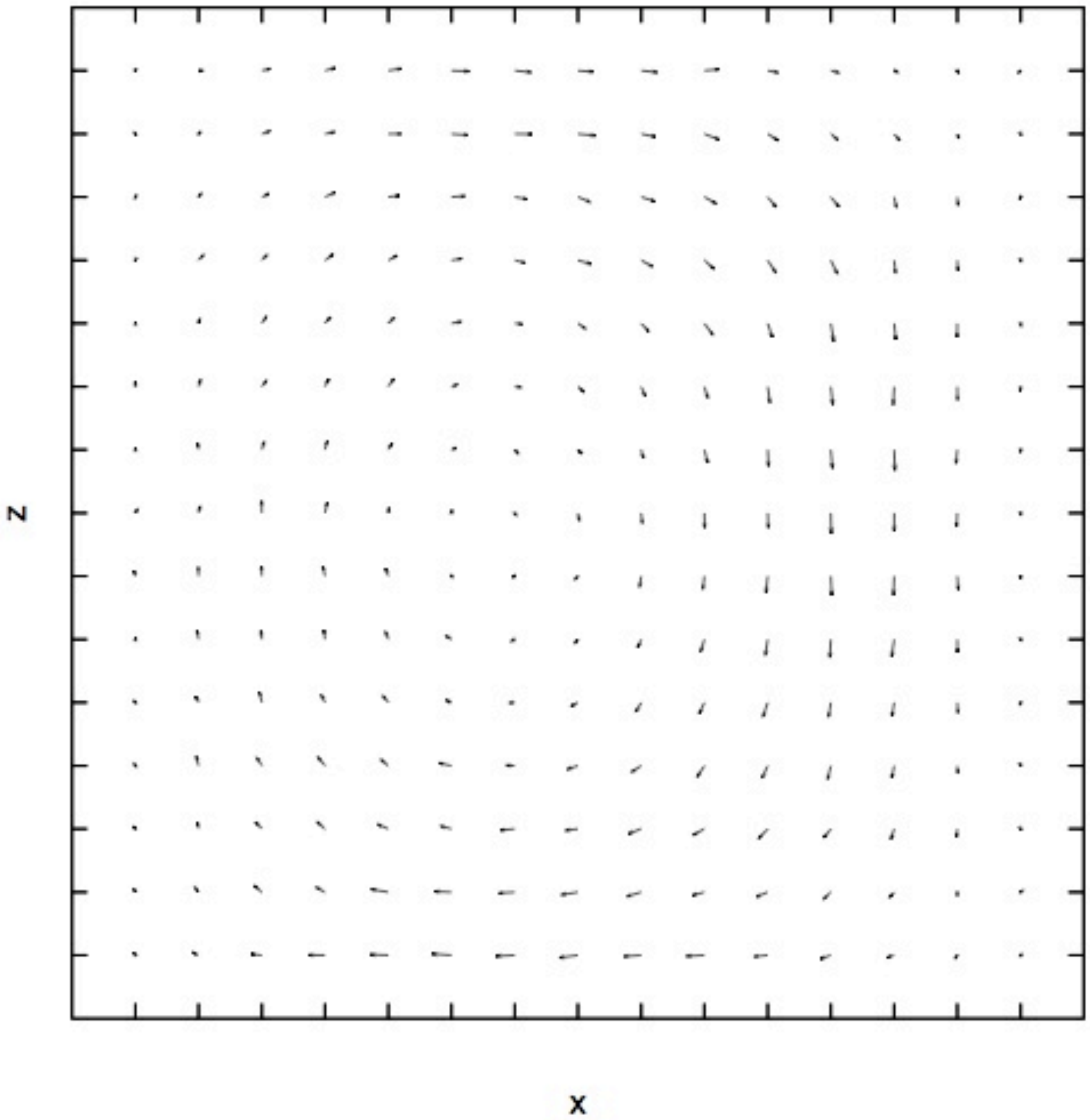
velocity field at about t=7T/4 (T=temperature oscillation period)



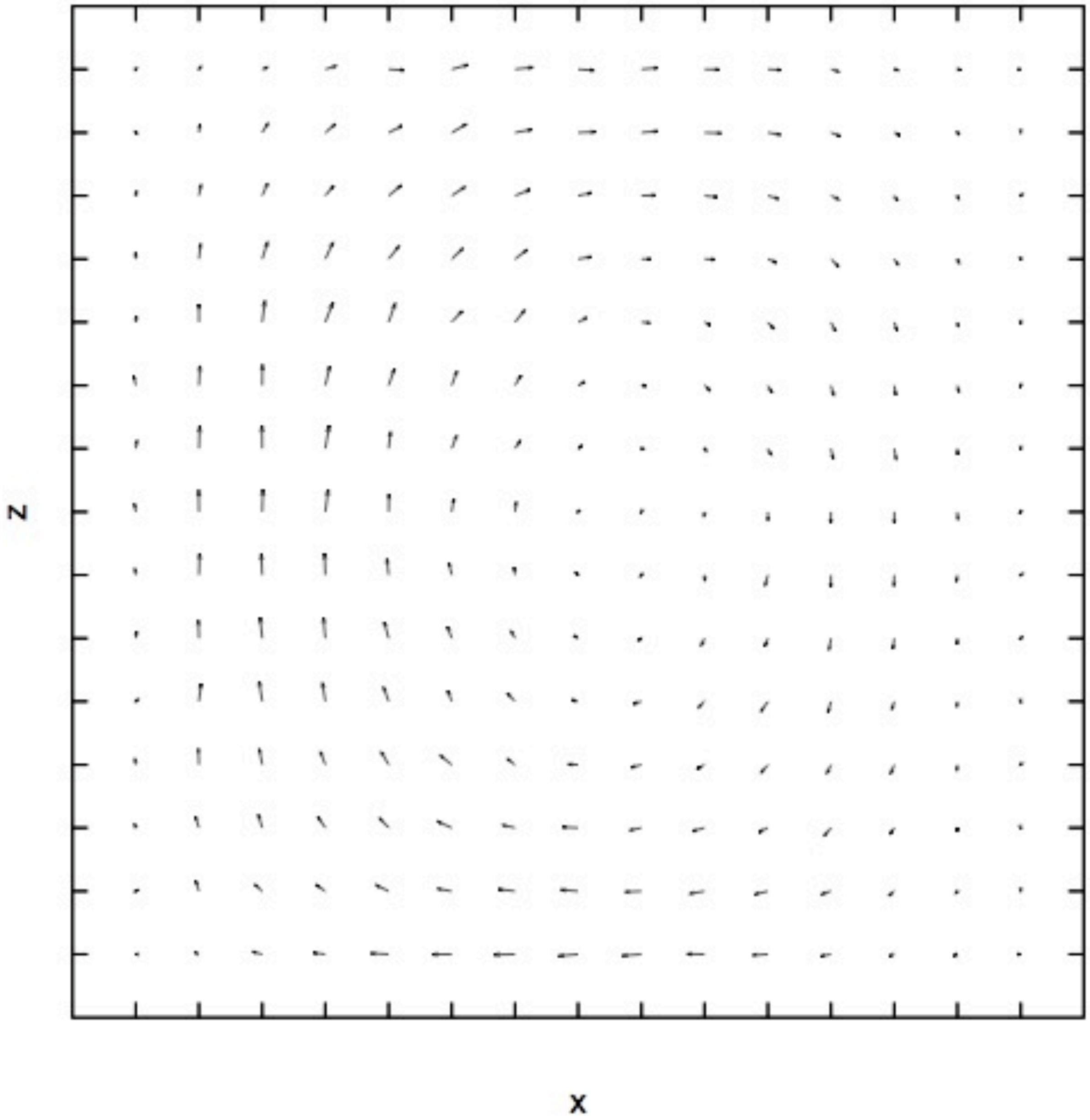
velocity field at about t=2T (T=temperature oscillation period)

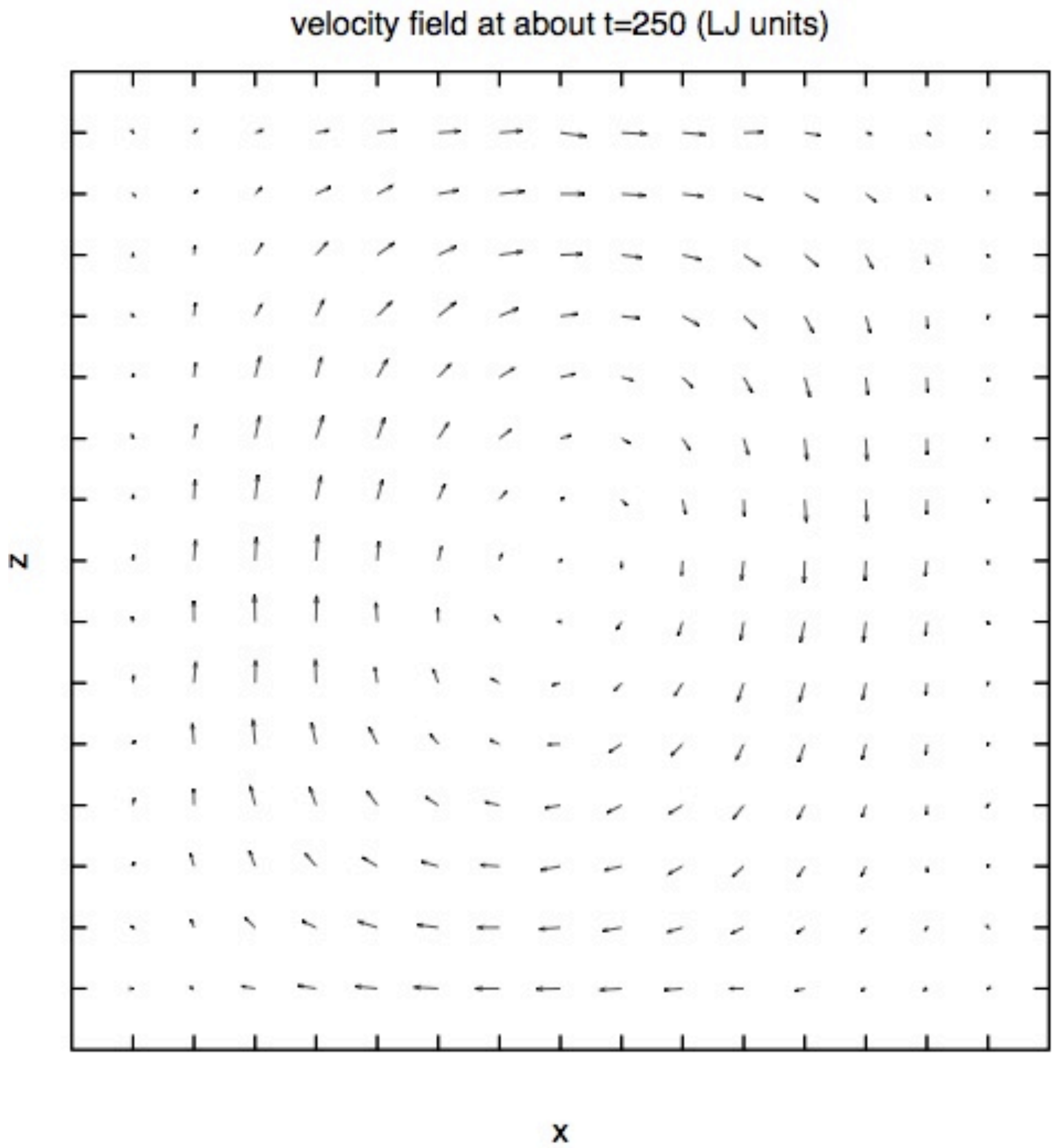


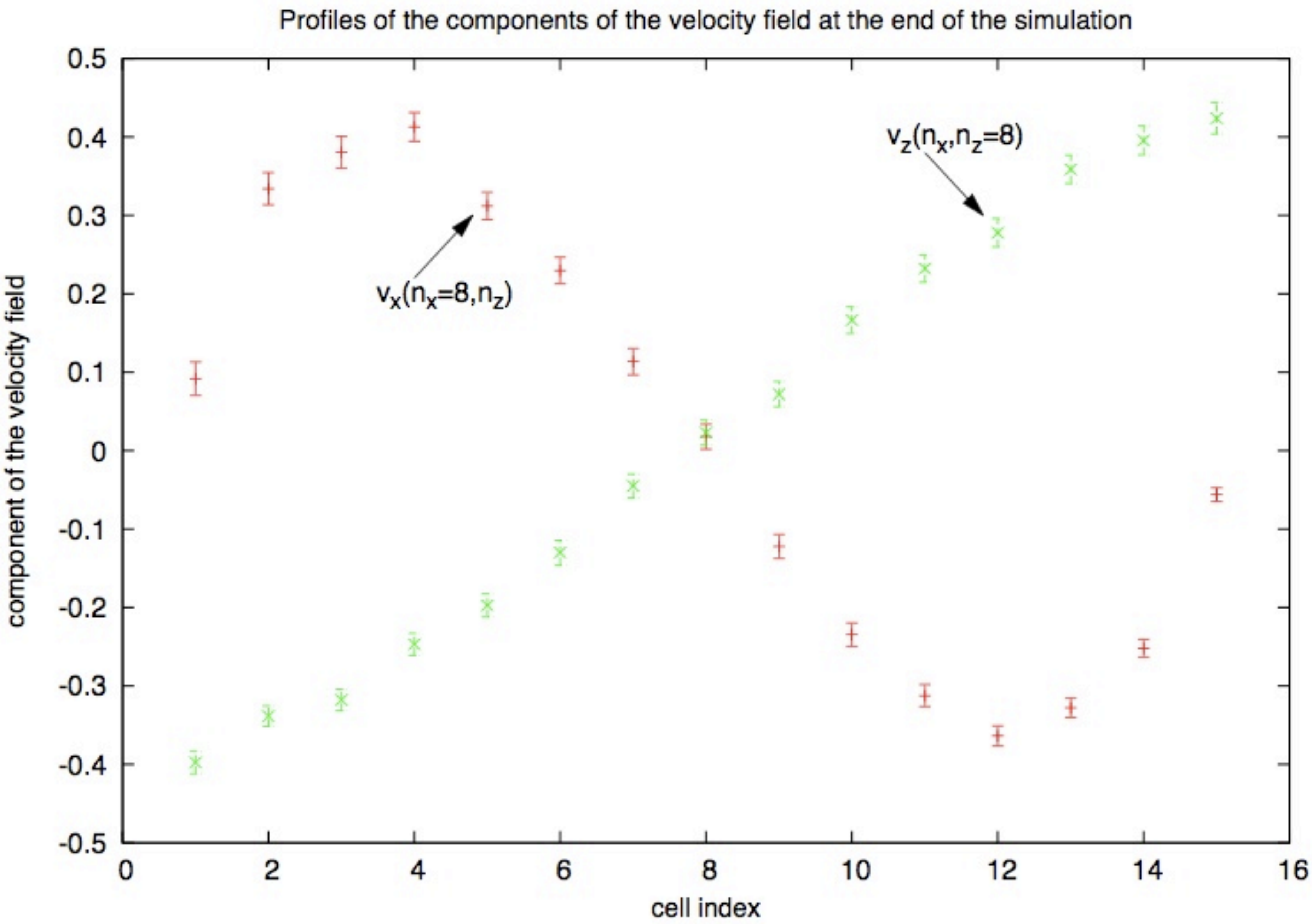
velocity field at about t=9T/4 (T=temperature oscillation period)



velocity field at about t=10T/4 (T=temperature oscillation period)

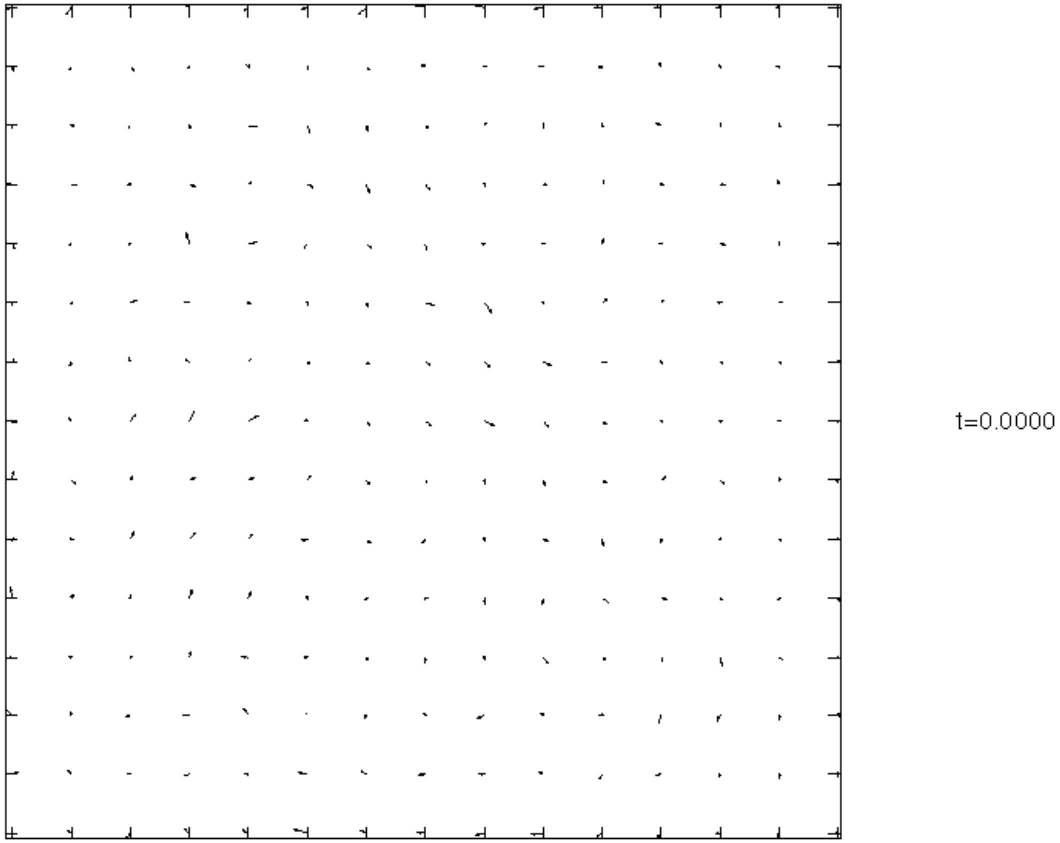



velocity field at about t=250 (LJ units)
z
x



Profiles of the components of the velocity field at the end of the simulation
component of the velocity field
cell index
$v_x(n_x=8,n_z)$
$v_z(n_x,n_z=8)$
0.5
0.4
0.3
0.2
0.1
0
-0.1
-0.2
-0.3
-0.4
-0.5
0
2
4
6
8
10
12
14
16

Establishing Benard Convection



Conclusions

1. It is possible to study, numerically, **time dependent non-equilibrium responses** beyond the linear regime (where LRT gives the answer)

2. **Coupling non-equilibrium non-stationary systems** is fundamental in multi-scale approaches

3. The method proposed is just waiting for **challenging applications**