

## Limitations of simulations in the microcanonical ensemble

In a classical mechanical system free from an external force the total energy  $E$  is conserved  $\Rightarrow$  simulations are performed at a constant  $(E, V, N)$  condition  $\Rightarrow$  this correspond to the **microcanonical ensemble** in statistical mechanics.

### Problems:

1. Experiments are usually performed at constant temperature and pressure. Simulation results for the microcanonical ensemble is difficult to relate to experiments.

2. It is difficult to perform simulation at specific  $T$  and  $P$ .

$$\left\langle \sum_i \frac{\vec{p}_i^2}{2m_i} \right\rangle = \frac{3}{2} N k_B T \quad P = \frac{1}{3V} \left\langle \sum_i \frac{\vec{p}_i^2}{m_i} + \sum_{i=1} \vec{r}_i \cdot \vec{F}_i^{\text{Int}} \right\rangle$$

We can try to control  $T$  and  $P$  at the first stage of the simulation by **scaling the velocity and the size of the unit cell**. But

**A.** It is difficult to predict them *a priori*, before the simulation;

**B.**  $P$  and  $T$  can keep changing during the simulation.

3. Difficult to relate to theory. Statistical mechanics for microcanonical ensemble is less studied.

## Early attempts of constant T simulations. 1. The constraint methods

**A. K.E. = const by velocity scaling** (not only during a preliminary simulation stage, but during the main part of the simulation).

Velocities of all particles are rescaled to keep kinetic energy constant. This approach breaks energy conservation, trajectories in the phase space becomes discontinuous... It is a very crude approach used in the early days (e.g. L. V. Woodcock, Chem. Phys. Lett. **10**, 257-261 (1971) – simulation of liquid salts; F. F. Abraham, S. W. Koch, R. C. Desai, Phys. Rev. Lett. **49**, 923-926 (1982) – scaling on every step in simulations of spinodal decomposition of 2D fluid).

This approach is also often used to equilibrate the system during the the first few hundred MD steps before the production run starts and data are collected (see Heating() subroutine of MSE627-MD code).

**B. Gaussian thermostat method** (a more elegant isokinetic formulation by Evans et al., Phys. Rev. A **28** 1016 (1983)):

$$\begin{cases} \frac{d\vec{r}_i}{dt} = \frac{\vec{p}_i}{m_i} \\ \frac{d\vec{p}_i}{dt} = \vec{F}_i - \zeta\vec{p}_i \end{cases} \quad \frac{d}{dt} \sum_i \frac{\vec{p}_i^2}{2m_i} = \sum_i \frac{\vec{p}_i \cdot d\vec{p}_i}{m_i} = 0$$

K.E. = const constraint

Equations of motion

$$\zeta = \frac{\sum_i \vec{F}_i \vec{p}_i}{\sum_i \vec{p}_i^2}$$

- friction coefficient

Potential energy of a system described by the above equations has the canonical distribution, kinetic energy is constant.

## Early attempts of constant T simulations. 2. The stochastic methods

**A. Andersen thermostat** (H. C. Andersen, J. Chem. Phys. 72, 2384 (1980)): Velocities of randomly selected molecules are occasionally changed so that Maxwell-Boltzmann distribution for desired T is reproduced. This is close to the MC that picks short spans of phase trajectories from the canonical distribution. One can also reset the velocities of all particles at the same time after a certain interval. The dynamics during the interval is truly microcanonical, and time correlation functions can be calculated inside this interval.

**B. Approach, based on the Langevin's equation** for Brownian dynamics (W. F. van Gunsteren, H. J. C. Berendsen, and J. A. C. Rullmann, Molecular Physics **44**, 69-95 (1981)):

$$m \frac{dv_i}{dt} = -m\beta v_i + R_i - \frac{\partial U}{\partial r_i}$$

- thermal motion of particles is driven by random force
- a friction force and a random force  $R_i$  are added to the equation of motion
- the temperature is kept at a constant value by the balance between the thermal agitation due to the random force and the slowing down due to the friction

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In some cases a deterministic methods (microcanonical MD, constraint methods, extended system methods that will be considered next) exhibit a nonergodic behavior and it takes a very long time to reach an equilibrium state. We can avoid this by using a stochastic method.

## Early attempts of constant P simulations

Any isobaric simulations should involve volume changes. The most straightforward way to adjust pressure is to scale the size of the unit cell and all the interparticle distances during the simulation.

One practical scheme is called Berendsen barostat [J. Chem. Phys. **81**, 3684, 1984]. It rescales the volume of the system at every step by the scaling factor

$$\zeta = 1 - \beta_T \frac{\Delta t}{\tau} (P_0 - P)$$

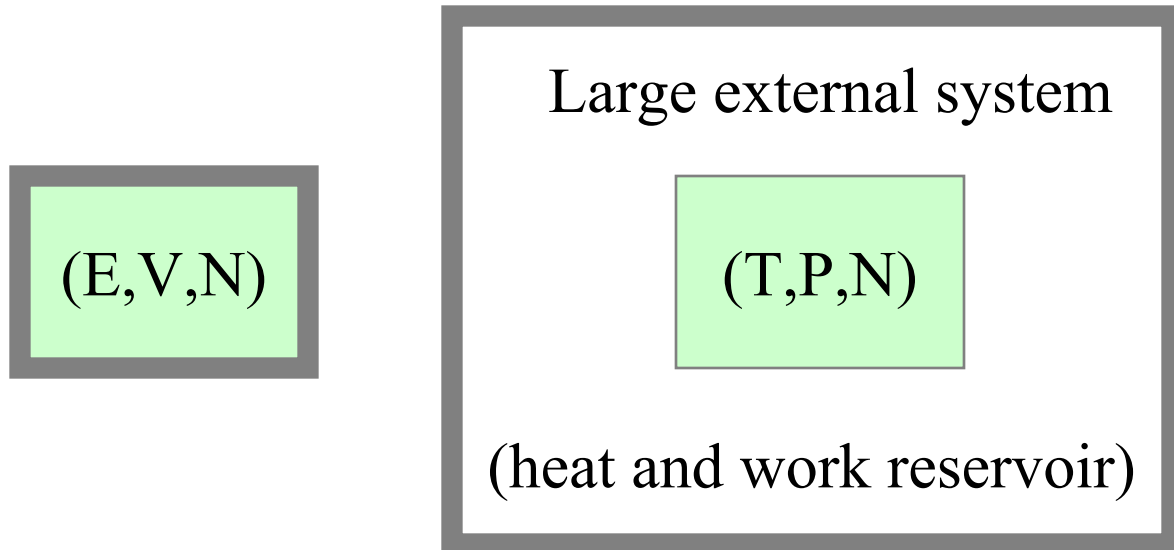
where  $P_0$  is the desired pressure,  $P$  is the current instantaneous internal pressure,  $\Delta t$  is the timestep of integration,  $\beta_T$  is the isothermal compressibility, and  $\tau$  is the characteristic time of volume relaxation. This corresponds to the rescaling of the particle coordinates:

$$\vec{r}' = \zeta^{1/3} \vec{r}$$

This method is widely used in simulations because of its simplicity. More rigorous approach for constant pressure simulation is based on the extended system method that is considered next.

## The extended system method. The “right way” to do it.

The total energy of the system is allowed to fluctuate due to the exchange of work or/and heat between the MD simulation cell and an extended system.



### Constant P:

The idea of the extended system method was first proposed by Andersen [ J. Chem. Phys. **72**, 2384 (1980)] for constant pressure simulations. The method provides the exchange of work between the computational cell and an external system.

### Constant T:

The extended system method for constant temperature simulation is originally proposed by Nosé [J. Chem. Phys. **81**, 511 (1984)] and reformulated by Hoover [Phys. Rev. A 31, 1695 (1985)]. The total energy of the computational cell is allowed to fluctuate due to the thermal contact with a heat bath.

## Review of classical mechanics used in following pages

**Lagrangian:**  $L = K(q_i, \dot{q}_i, t) - U(q_i, t), \quad i = 1, 2, \dots, g$

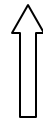
$K$  – kinetic energy,  $U$  – potential energy,  $q_i$  – coordinates,

$\dot{q}_i$  – velocities,  $g$  - number of degrees of freedom

**Equations of motion:** 
$$\frac{d}{dt} \frac{\partial L}{\partial \dot{q}_i} - \frac{\partial L}{\partial q_i} = 0$$

**Integral of motion:** 
$$\sum_i \dot{q}_i \frac{\partial L}{\partial \dot{q}_i} - L = \text{const}$$

$$\frac{\partial L}{\partial t} = 0$$



$$\frac{dL}{dt} = \sum_i \frac{\partial L}{\partial q_i} \dot{q}_i + \sum_i \frac{\partial L}{\partial \dot{q}_i} \ddot{q}_i = \sum_i \dot{q}_i \frac{d}{dt} \frac{\partial L}{\partial \dot{q}_i} + \sum_i \frac{\partial L}{\partial \dot{q}_i} \ddot{q}_i = \sum_i \frac{d}{dt} \left( \frac{\partial L}{\partial \dot{q}_i} \dot{q}_i \right)$$

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Lagrangian of a classical N-body system: 
$$L = \sum_i \frac{m \dot{x}_i^2}{2} - U(x_1, \dots, x_{3N})$$

Equations of motion: 
$$m \ddot{x}_i = - \frac{\partial}{\partial x_i} U(x_1, \dots, x_{3N})$$

Integral of motion: 
$$\sum_i \frac{m \dot{x}_i^2}{2} + U(x_1, \dots, x_{3N}) = E$$

## The extended system method for constant pressure I

proposed by Andersen in [ J. Chem. Phys. **72**, 2384 (1980)]

Constant pressure is maintained by changing the volume to balance an internal pressure and an external pressure.

The volume of the computational cell  $V$  is considered as an additional degree of freedom.

Scaled variables  $\mathbf{d}_i = \mathbf{x}_i/L$  are introduced to derive the method ( $L = V^{1/3}$  is length of the edge of the cubic computational cell). Scaled coordinates are independent from the volume.

Then potential and kinetic energies expressed in scaled coordinates are

$$\text{P.E.} = U(V^{1/3} \mathbf{d}_1, \dots, V^{1/3} \mathbf{d}_{3N}) + PV$$

$$\text{K.E.} = \sum_i \frac{mV^{2/3} \dot{\mathbf{d}}_i^2}{2} + \frac{M\dot{V}^2}{2}$$



Hans C. Andersen

The second term in the potential energy,  $PV$ , is a potential energy for the volume change. The second term in the kinetic energy accounts for the inertia in the volume change.  $M$  is the “piston mass”.

Lagrangian for this system is

$$L = \sum_i \frac{mV^{2/3} \dot{\mathbf{d}}_i^2}{2} - U(V^{1/3} \mathbf{d}_1, \dots, V^{1/3} \mathbf{d}_{3N}) + \frac{M\dot{V}^2}{2} - PV$$

## The extended system method for constant pressure II

Lagrangian for the system proposed by Andersen is

$$L = \sum_i \frac{m_i V^{2/3} \dot{d}_i^2}{2} - U(V^{1/3} d_1, \dots, V^{1/3} d_{3N}) + \frac{M \dot{V}^2}{2} - PV$$

$$\text{Equations of motion: } \frac{d}{dt} \frac{\partial L}{\partial \dot{q}_i} - \frac{\partial L}{\partial q_i} = 0 \quad q_i = \{d_i, i = 1, \dots, 3N, V\}$$

Let us first calculate all elements of this equation:

$$\frac{d}{dt} \frac{\partial L}{\partial \dot{d}_i} = \frac{d}{dt} (m_i V^{2/3} \dot{d}_i) = m_i V^{2/3} \ddot{d}_i + \frac{2}{3} m_i V^{-1/3} \dot{V} \dot{d}_i$$

$$\frac{d}{dt} \frac{\partial L}{\partial \dot{V}} = M \ddot{V}$$

$$\frac{\partial L}{\partial d_i} = - \frac{\partial U(V^{1/3} d_1, \dots, V^{1/3} d_{3N})}{\partial d_i} = V^{1/3} F_i$$

$$\frac{\partial L}{\partial V} = \frac{V^{-1/3}}{3} \sum_i m_i \dot{d}_i^2 - P - \sum_i \frac{d_i V^{-2/3}}{3} \frac{\partial U(V^{1/3} d_1, \dots, V^{1/3} d_{3N})}{\partial x_i}$$

$$= -P + \frac{V^{-1/3}}{3} \sum_i m_i \dot{d}_i^2 + \frac{V^{-2/3}}{3} \sum_i F_i d_i$$

## The extended system method for constant pressure III

### Equations of motion:

$$\begin{cases}
 M\ddot{V} = -P + \frac{1}{3V} \left\{ \overbrace{V^{2/3} \sum_i m_i \dot{d}_i^2 + V^{1/3} \sum_i F_i d_i}^{\text{Internal pressure in the system, } P^{\text{int}}} \right\} = P^{\text{int}} - P \\
 m_i \ddot{d}_i = V^{-1/3} F_i - \frac{2}{3V} m_i \dot{V} \dot{d}_i
 \end{cases}$$

If  $V = \text{const}$  then the first equation is just the equation of state of the system and the second equation is Newton's equations of motion.

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### What is the integral of motion (conserved quantity) for this system?

$$\begin{aligned}
 \sum_i \dot{q}_i \frac{\partial L}{\partial \dot{q}_i} - L &= \dot{V} M \dot{V} + \sum_i \dot{d}_i (m_i V^{2/3} \dot{d}_i) - \sum_i (m_i V^{2/3} \dot{d}_i^2) / 2 + \\
 &+ PV + U - M \dot{V}^2 / 2 = M \dot{V}^2 / 2 + \underbrace{\sum_i (m_i V^{2/3} \dot{d}_i^2) / 2}_{\text{Total internal energy of the system, } E} + U + PV = \\
 &= E + PV = H
 \end{aligned}$$

Thus, in addition to number of particles  $N$  and pressure  $P$ , the enthalpy is conserved. We have, therefore, an isobaric - isoenthalpic (NPH) ensemble.

## The extended system method for constant pressure IV

### Notes on the inertia parameter M

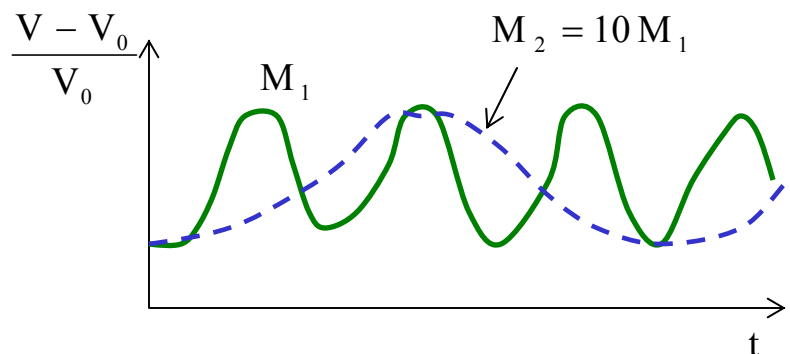
1. It can be interpreted as the mass of a piston whose motion expands or compresses the material.
2. Although dynamics of the system depends on the value of M, the trajectory averages are independent of the value of M.
3. The time-scale for fluctuation of a small micro-volume of material embedded in a bulk of material is approximately equal to the length of the micro-volume divided by the speed of sound in the sample. Thus, it is desirable to choose the mass M so that the time-scale of the fluctuations of volume V in the scaled system is approximately equal to L divided by the speed of sound.

For small volume fluctuations: 
$$M \ddot{V} = \frac{B}{V_0} (V - V_0)$$

where B is the bulk modulus

Period of fluctuations of volume V is 
$$\tau_v = 2\pi \sqrt{\frac{MV_0}{B}}$$

Therefore 
$$M = \frac{B\tau_v^2}{4\pi^2 V_0}$$



## The extended system method for constant pressure V. Summary

Equations of motion:

$$\left\{ \begin{array}{l} M\ddot{V} = P^{\text{int}} - P^{\text{ext}} \\ m_i \ddot{\mathbf{d}}_i = V^{-1/3} \mathbf{F}_i - \frac{2}{3V} m_i \dot{V} \dot{\mathbf{d}}_i \end{array} \right.$$

The equation of motion for the volume is defined so that deviation of the internal pressure from its average works as a negative feedback and keeps the pressure around a constant.

The simulation is performed in a constant-enthalpy – constant-pressure ensemble.

Two systems of variables are used:

1. Real variables should be used to calculate forces, energy, structural parameters of the system.
2. Scaled variables to simulate evolution of the system (perform MD simulation).

**Relation between the equations of motion expressed in real coordinates  $\mathbf{r}_i$  (Andersen paper in J. Chem. Phys. 72, 2384, 1980) and scaled coordinates  $\mathbf{d}_i$  (this handout):**

$$\mathbf{r}_i = V^{1/3} \mathbf{d}_i$$

$$\dot{\mathbf{r}}_i = V^{1/3} \dot{\mathbf{d}}_i \quad \text{- not Eq. 3.3 in Andersen's paper!}$$

$$\ddot{\mathbf{r}}_i = \frac{1}{3} V^{-2/3} \dot{\mathbf{d}}_i \dot{V} + V^{1/3} \ddot{\mathbf{d}}_i \quad \text{And, using } \dot{\mathbf{d}}_i = V^{-1/3} \dot{\mathbf{r}}_i$$

$$\ddot{\mathbf{d}}_i = V^{-1/3} \ddot{\mathbf{r}}_i - \frac{1}{3} V^{-4/3} \dot{\mathbf{r}}_i \dot{V}$$

Now we can translate the equation in scaled coordinates to real coordinates:

$$m_i \ddot{\mathbf{d}}_i = V^{-1/3} \mathbf{F}_i - \frac{2}{3V} m_i \dot{V} \dot{\mathbf{d}}_i \quad \text{- equation given in my handout}$$

$$m_i \left( V^{-1/3} \ddot{\mathbf{r}}_i - \frac{1}{3} V^{-4/3} \dot{\mathbf{r}}_i \dot{V} \right) = V^{-1/3} \mathbf{F}_i - \frac{2}{3V} m_i \dot{V} (V^{-1/3} \dot{\mathbf{r}}_i)$$

$$m_i \ddot{\mathbf{r}}_i = \mathbf{F}_i - \frac{1}{3V} m_i \dot{V} \dot{\mathbf{r}}_i = \mathbf{F}_i - \frac{1}{3} m_i \dot{\mathbf{r}}_i \frac{d \ln(V)}{dt}$$

equation in Andersen's paper

## The extended system method for constant temperature I

proposed by Nosé in [ J. Chem. Phys. **81**, 511 (1984)]

An additional degree of freedom  $s$  corresponding to a heat bath is introduced. The total energy of the computational cell is allowed to fluctuate due to a thermal contact with a heat bath.

The thermal interactions between a system and a heat bath are expressed as a scaling of particle's velocity by a variable  $s$ . Two sets of variables, real and virtual, can be considered:

$$\begin{array}{ccc} & \mathbf{x}_i' = \mathbf{x}_i & \\ & \dot{\mathbf{x}}_i' = \dot{\mathbf{x}}_i s & \\ \mathbf{Real} & dt' = dt / s & \mathbf{Virtual} \\ & t' = \int dt / s(t) & \end{array}$$

Virtual variables are independent from  $s$

Potential and kinetic energies are:

$$P.E. = U(\mathbf{x}_1, \dots, \mathbf{x}_{3N}) + gkT \ln s$$

$$K.E. = \sum_i \frac{ms^2 \dot{\mathbf{x}}_i^2}{2} + \frac{Q\dot{s}^2}{2}$$



Shūichi Nosé

The second term in the potential energy is chosen so that integration of the equations of motion leads to the average values of physical quantities characteristic for canonical ensemble.  $Q$  is the inertia parameter associated with the change of variable  $s$  (similar to  $M$  in Andersen method).  $g$  is the number of degrees of freedom.

## The extended system method for constant temperature II

Lagrangian for the system proposed by Nose is

$$L = \sum_i \frac{m_i s^2 \dot{x}_i^2}{2} - U(x_1, \dots, x_{3N}) + \frac{Q \dot{s}^2}{2} - gkT \ln s$$

$$\text{Equations of motion: } \frac{d}{dt} \frac{\partial L}{\partial \dot{q}_i} - \frac{\partial L}{\partial q_i} = 0 \quad q_i = \{d_i, i = 1, \dots, 3N, s\}$$

Let us first calculate all elements of this equation:

$$\frac{d}{dt} \frac{\partial L}{\partial \dot{x}_i} = \frac{d}{dt} (m_i s^2 \dot{x}_i) = m_i s^2 \ddot{x}_i + 2m_i s \dot{s} \dot{x}_i$$

$$\frac{d}{dt} \frac{\partial L}{\partial \dot{s}} = Q \ddot{s}$$

$$\frac{\partial L}{\partial x_i} = - \frac{\partial U(x_1, \dots, x_{3N})}{\partial x_i} = F_i$$

$$\frac{\partial L}{\partial s} = s \sum_i m_i \dot{x}_i^2 - \frac{gkT}{s}$$

All derivatives here are derivatives by scaled time

## The extended system method for constant temperature III

**Equations of motion:**

$$\left\{ \begin{array}{l} Q\ddot{s} = s \sum_i m_i \dot{x}_i^2 - \frac{gkT}{s} \\ m_i \ddot{x}_i = s^{-2} F_i - 2s^{-1} m_i \dot{s} \dot{x}_i \end{array} \right.$$

All derivatives here are derivatives by scaled time.

It is not convenient to work with fluctuating time intervals. One can rewrite the equations of motion in terms of real time and real variables:

$$m_i \frac{d}{dt} \frac{dx_i}{dt} = \frac{m_i}{s} \frac{d}{dt'} \left( \frac{1}{s} \frac{dx_i}{dt'} \right) = \frac{m_i}{s^2} \ddot{x}_i - \frac{m_i}{s^3} \dot{s} \dot{x}_i$$

$$Q \frac{d}{dt} \frac{ds}{dt} = \frac{Q}{s} \frac{d}{dt'} \left( \frac{1}{s} \frac{ds}{dt'} \right) = \frac{Q}{s^2} \ddot{s} - \frac{Q}{s^3} \dot{s}^2$$

$$\left\{ \begin{array}{l} Q\ddot{s} = s \sum_i m_i \dot{x}_i^2 - sgkT + \frac{Q\dot{s}^2}{s} \\ m_i \ddot{x}_i = F_i - s^{-1} m_i \dot{s} \dot{x}_i \end{array} \right.$$

All derivatives here are derivatives by real time.

## The extended system method for constant temperature IV

$$\left\{ \begin{array}{l} Q\ddot{s} = s \sum_i m_i \dot{x}_i^2 - s g k T + \frac{Q \dot{s}^2}{s} \\ m_i \ddot{x}_i = F_i - s^{-1} m_i \dot{s} \dot{x}_i \end{array} \right. \quad \text{All derivatives here are derivatives by real time.}$$

Hoover [Phys. Rev. A **31**, 1695 (1985)] proposed to use a new variable  $\zeta = d(\ln s)/dt$  which gives  $\dot{s} = \zeta s$  and leads to an alternative formulation for the equations of motion (Nosé-Hoover thermostat):

$$\left\{ \begin{array}{l} Q\dot{\zeta} = \sum_i m_i \dot{x}_i^2 - g k T \\ m_i \ddot{x}_i = F_i - m_i \zeta \dot{x}_i \end{array} \right.$$

A negative feedback is apparent in this formulation: Equations for  $x_i$  describe the motion of a body with frictional force. The time development of the friction coefficient  $\zeta$  is driven by the imbalance between the kinetic energy and its average value  $(g/2)kT$ .

If the kinetic energy is larger than  $(g/2)kT$ , then  $d\zeta/dt' > 0$ ,  $\zeta$  increases and becomes positive. The equation for  $x_i$  with positive  $\zeta$  describes a system with frictional force. The velocities and kinetic energy decrease.

If the kinetic energy is lower than  $(g/2)kT$ , then  $d\zeta/dt' < 0$ ,  $\zeta$  decreases and becomes negative. The system is heated up.

The time average of a time derivative of a variable vanishes. This guarantees that the average of the kinetic energy coincides with the result of the equipartition theorem  $(g/2)kT$ .

## The extended system method for constant temperature V

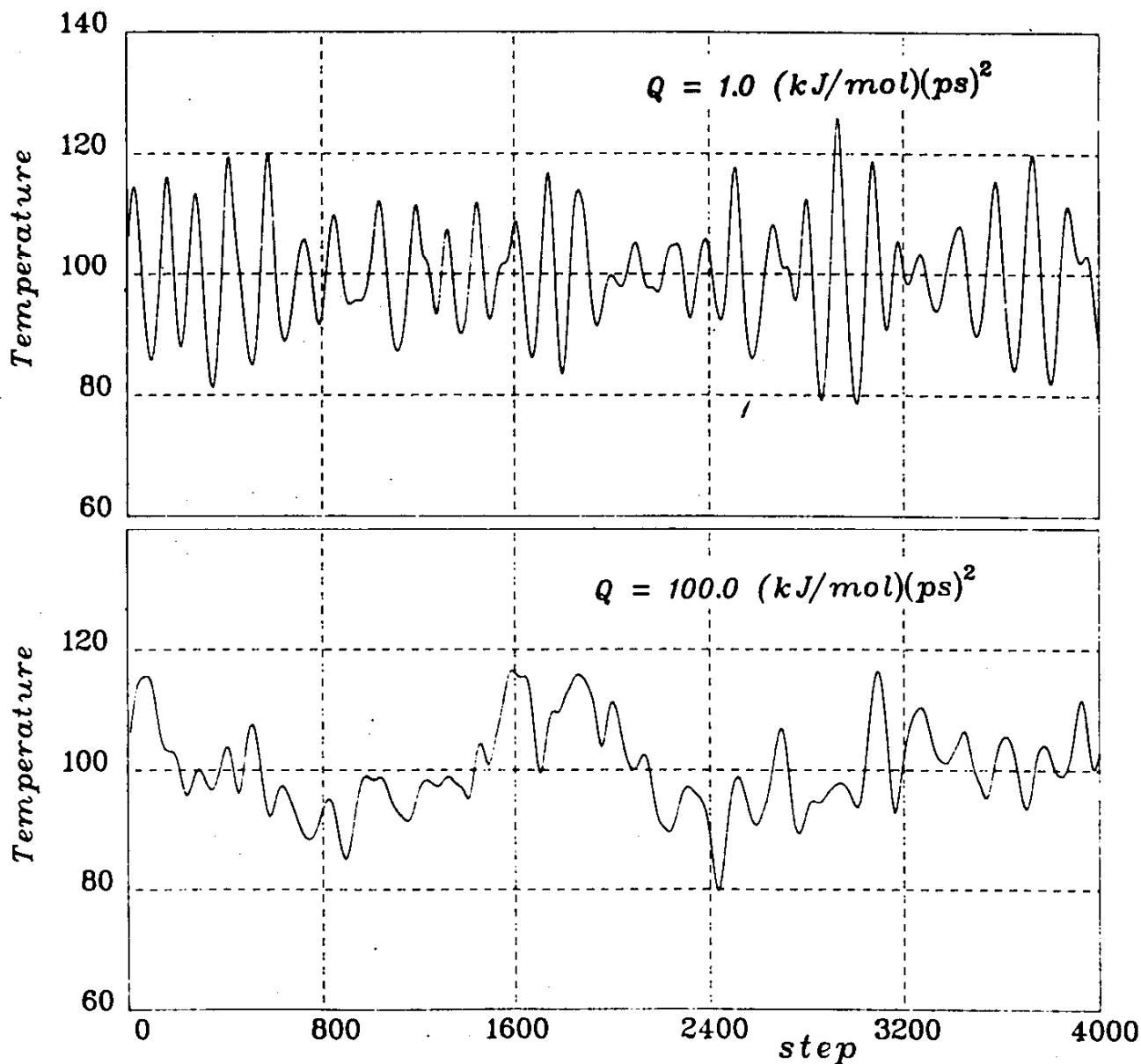
### The dynamic properties I

- The relaxation from a non-equilibrium state to equilibrium in constant-temperature simulations does not correspond to any realistic process in the experiment. The relaxation process is introduced artificially to control the temperature.
- The speed of the relaxation is determined by the value of mass  $Q$ . The response is quick with a small  $Q$ , slow with a large  $Q$ .
- The parameter  $Q$  determines the time scale of the temperature fluctuations. The period of temperature oscillations  $\sim (Q/T)^{1/2}$ .
- In equilibrium, the fluctuation of  $s$  is of the order of  $N^{-1/2}$ . Nosé equations of motion are approaching Newtonian ones as size of the system is increasing.
- A sudden change of input temperature can lead to a large amplitude of temperature oscillations. A natural damping of this large oscillations can take a long time. It could be a good idea to apply a damping approach realized in `Quench()` subroutine of MSE627-MD to  $s$  variable as well.
- All behaviors mentioned above are artifacts introduced by the extended system method. The correct dynamical behavior in non-equilibrium state can not be obtained using this method.

## The extended system method for constant temperature V

### The dynamic properties II

By Shūichi Nosé, A molecular dynamics method for simulations in the canonical ensemble, *Molecular Physics* **52**, 255-268 (1984)

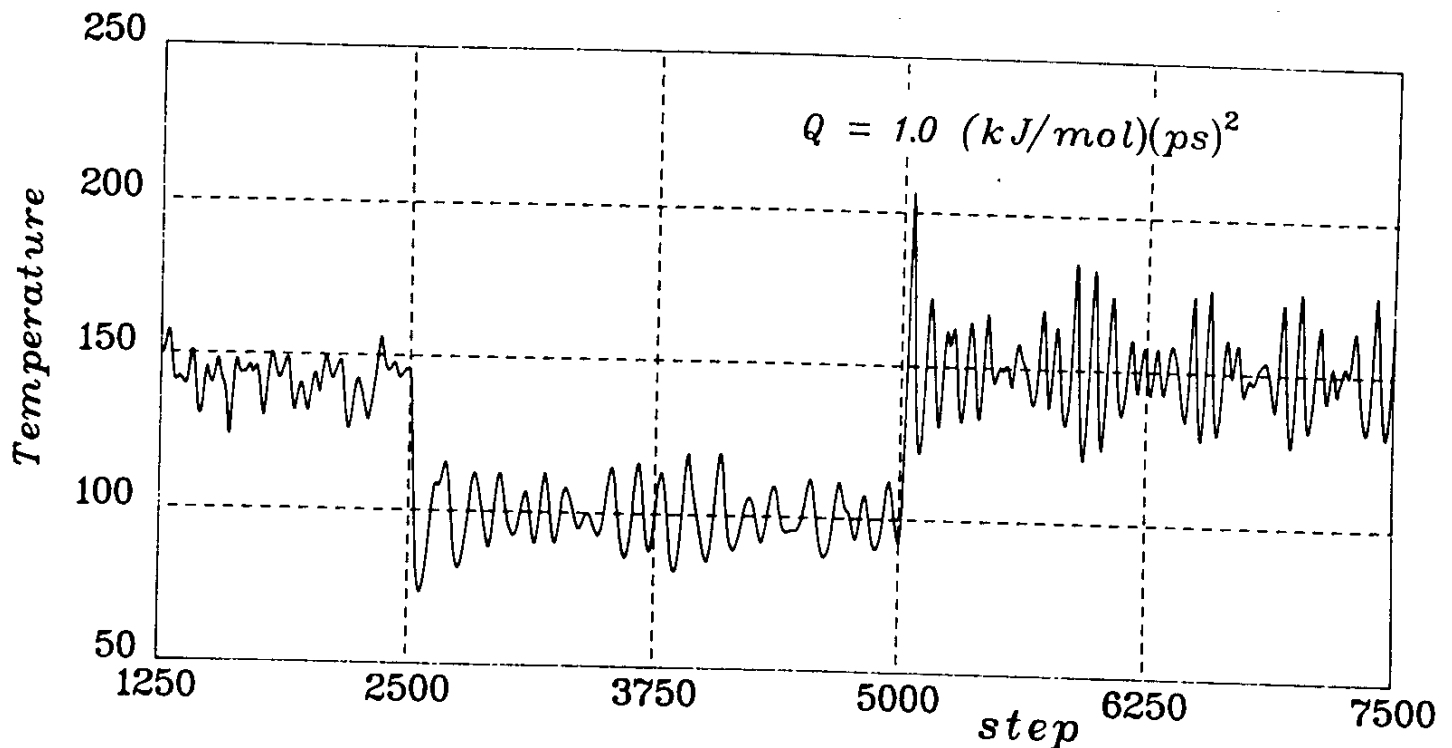


Comparison of the temperature fluctuations in runs with different  $Q$  values at 100 K. Above:  $Q = 1 \text{ (kJ mol}^{-1}\text{)(ps}^2\text{)}$ , Below:  $Q = 100 \text{ (kJ mol}^{-1}\text{)(ps}^2\text{)}$ . The total real time is about 7 ps.

## The extended system method for constant temperature V

### The dynamic properties III

By Shūichi Nosé, A molecular dynamics method for simulations in the canonical ensemble, *Molecular Physics* **52**, 255-268 (1984)



Evolution of the temperature. The first 1250 steps shown (1250-2500 steps) are carried out with the standard MD method. At step 2500, the simulation is changed to the constant temperature method with  $T_{\text{eq}} = 100 \text{ K}$ . At step 5000,  $T_{\text{eq}}$  is changed to 150 K.

## Formulation for constant temperature and pressure I

By S. Nosé, Molecular Physics **52**, 255 (1984)

$$L = \sum_i \frac{m s^2 V^{2/3} \dot{d}_i^2}{2} - U(V^{1/3} d_i) + \frac{M \dot{V}^2}{2} - PV + \frac{Q \dot{s}^2}{2} - gkT \ln s$$

Equations of motion:

$$\left\{ \begin{array}{l} M\ddot{V} = -P + \frac{s^2}{3V^{1/3}} \sum_i m_i \dot{d}_i^2 + \frac{1}{3V^{2/3}} \sum_i F_i d_i \\ Q\ddot{s} = sV^{2/3} \sum_i m_i \dot{d}_i^2 - \frac{gkT}{s} \\ m_i \ddot{d}_i = \frac{1}{s^2 V^{1/3}} F_i - \frac{2}{3V} m_i \dot{V} \dot{d}_i - \frac{2}{s} m_i \dot{s} \dot{d}_i \end{array} \right.$$

Real coordinates are  $x_i = V^{1/3} d_i$ ,

Real velocities are  $\dot{x}_i = sV^{1/3} \dot{d}_i$

All derivatives here are derivatives by scaled time

The averages of static quantities which are functions of real coordinates and velocities corresponds to the averages in the (N,P,T) ensemble.

Microcanonical (N,V,E) ensemble:  $s = 1$ ,  $\dot{s} = 0$ ,  $V = N/\rho$ ,  $\dot{V} = 0$

Isoenthalpic-isobaric (N,P,H) ensemble:  $s = 1$ ,  $\dot{s} = 0$

## Formulation for constant temperature and pressure II

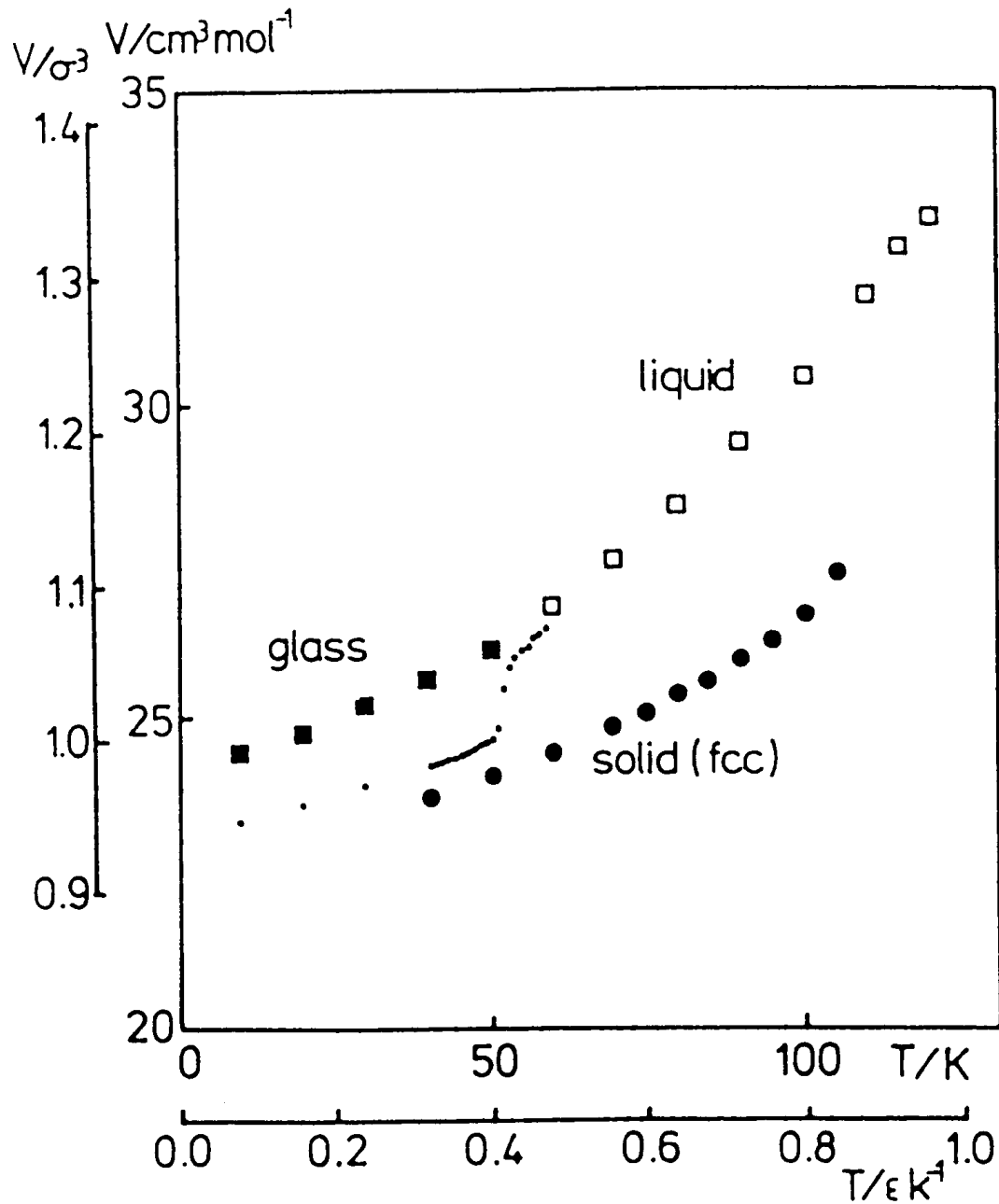
It could be a good idea to rewrite the equations of motion in real time:

$$\left\{ \begin{array}{l} M\ddot{V} = -s^2 P + \frac{s^2}{3V^{1/3}} \sum_i m_i \dot{d}_i^2 + \frac{s^2}{3V^{2/3}} \sum_i F_i d_i + \frac{M}{s} \dot{V} \dot{s} \\ Q\ddot{s} = sV^{2/3} \sum_i m_i \dot{d}_i^2 - s g k T + \frac{Q \dot{s}^2}{s} \\ m_i \ddot{d}_i = \frac{1}{V^{1/3}} F_i - \frac{2}{3V} m_i \dot{V} \dot{d}_i - \frac{1}{s} m_i \dot{s} \dot{d}_i \end{array} \right.$$

All derivatives here are derivatives by real time

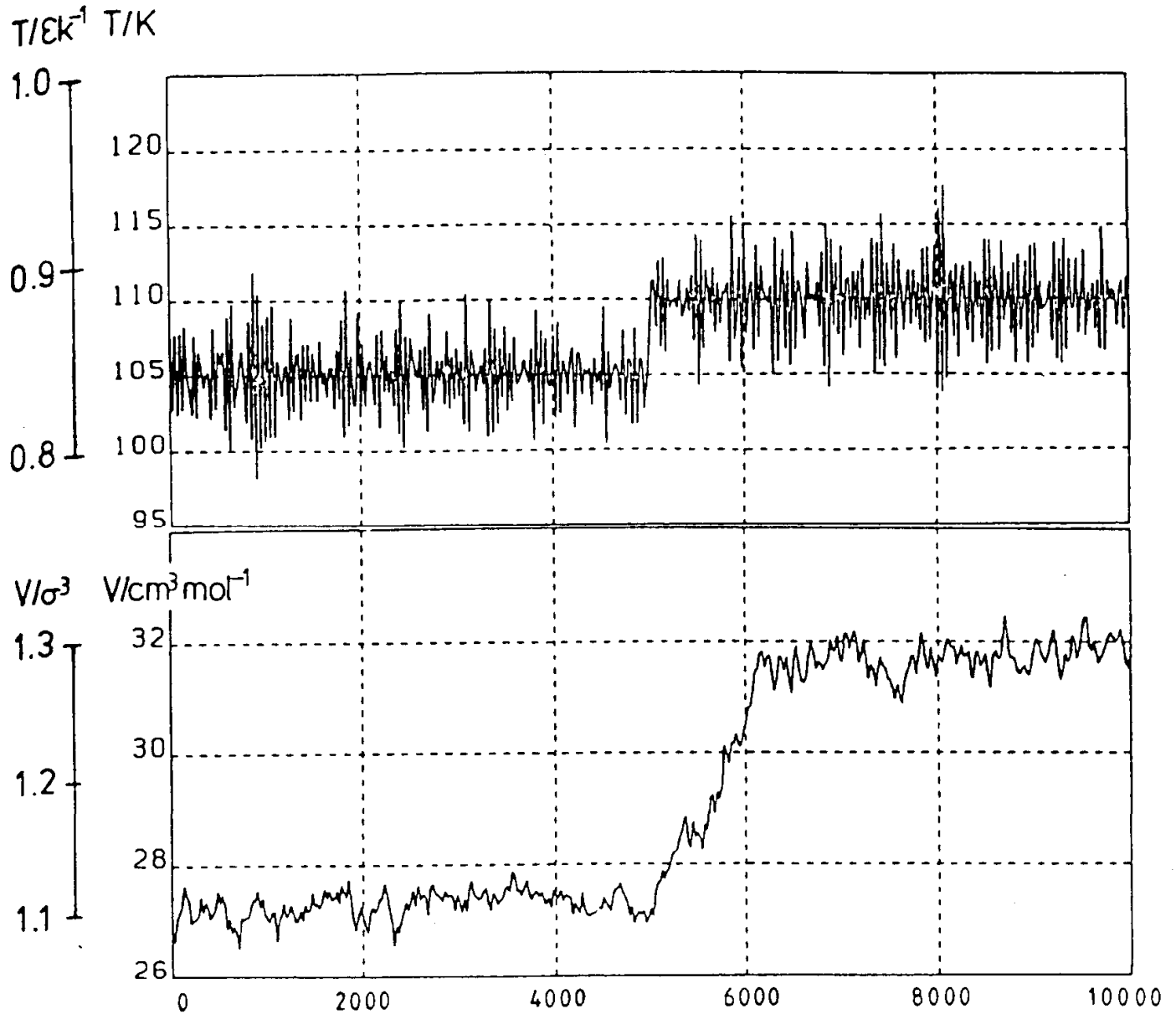
For more discussion of (N,P,T) MD simulation technique you can read B. L. Holian, A. F. Voter, and R. Ravelo, Thermostatted molecular dynamics: how to avoid the Toda demon hidden in Nosé-Hoover dynamics, Phys. Rev.E **52**, 2338 (1995).

Shūichi Nosé and Fumiko Yonezawa, Isothermal-isobaric computer simulations of melting and crystallization of a Lennard-Jones system, *J. Chem. Phys.* **84**, 1803 (1986)



Volume (V) vs temperature (T) for crystals (filled circles) and liquids (open squares). Small dots represent the cooling-crystallization process. The corresponding results are also shown for LJ glasses obtained by rapid quenching.

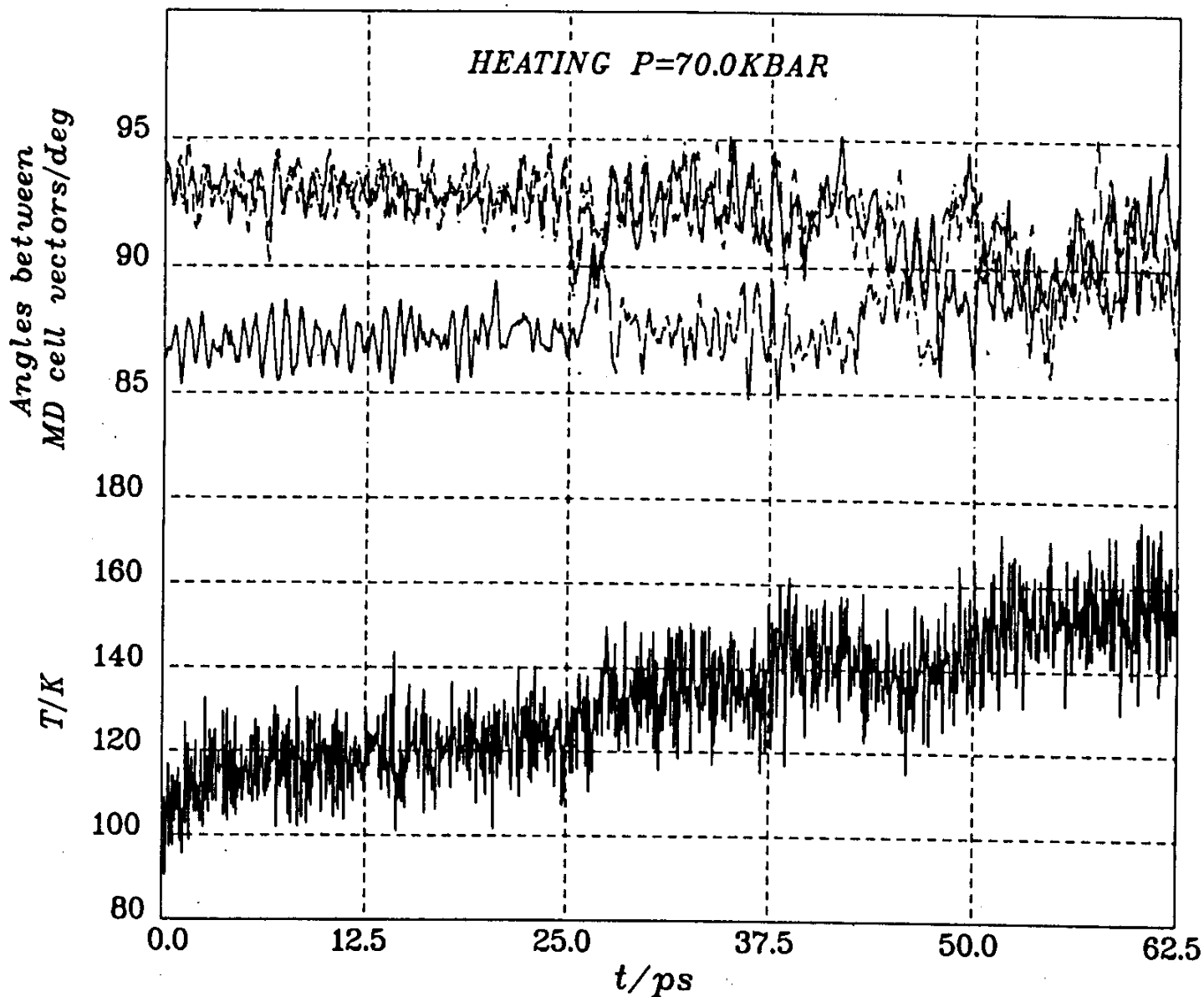
Shūichi Nosé and Fumiko Yonezawa, Isothermal-isobaric computer simulations of melting and crystallization of a Lennard-Jones system, J. Chem. Phys. **84**, 1803 (1986)



Temperature and volume vs time-steps after switching of temperature from 105 to 110 K.

Shūichi Nosé and M. L. Klein, Constant pressure molecular dynamics for molecular systems, *Molecular Physics* **50**, 1055-1076 (1983)

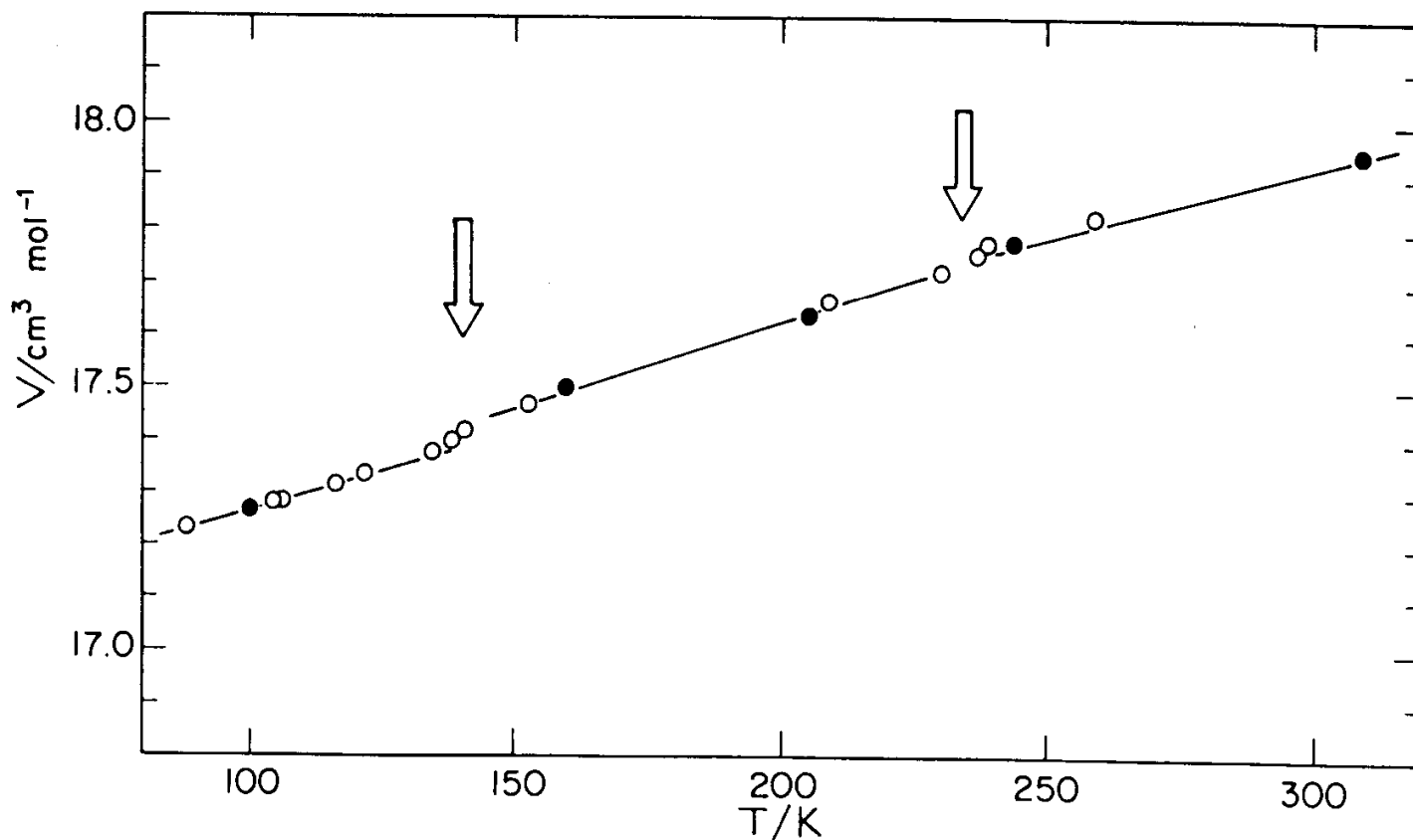
### Parrinello – Rahman method for constant stress tensor



The evolution of the angles between MD cell vectors in cooling and heating processes.

Shūichi Nosé and M. L. Klein, Constant pressure molecular dynamics for molecular systems, *Molecular Physics* **50**, 1055-1076 (1983)

### Parrinello – Rahman method for constant stress tensor



Molar volume of solid nitrogen as a function of temperature for  $P_{\text{ex}} = 70.0$  kbar. Solid circles indicate data reported in [S. Nosé and M. L. Klein, *Phys. Rev. Lett.* **50**, 1207 (1983)]. The line is a guide to the eye and arrows indicate the regions of the phase transitions.