模拟物理导论

凝聚态物质的数值模拟方法(IV)

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分子模型

Molecular systems:

$$H(X) = \sum_{i=1}^{N} \frac{p_i^2}{2m} + V_N$$

In most cases the interaction part can be approximated by pair interactions:

$$V_N = \frac{1}{2} \sum_{i,j;i \neq j} v(\mathrm{r}_i - \mathrm{r}_j)$$

One famous example is the Lennard-Jones potential

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

正则分布：

$$P(E(r,p)) = \frac{e^{-\beta H}}{Q}$$

$$Q = \frac{1}{N!h^{3N}} \int dr dp e^{-\beta H(r,p)}$$

对动量的积分可以算出来

$$Q = \frac{1}{N!\lambda^{3N}} Z_N, \quad \lambda = \frac{h}{\sqrt{2\pi m k T}}$$

A very important quantity in statistical mechanics is the pair correlation function $g(\mathrm{r},\mathrm{r}')$, defined as

$$g\left(\mathrm{r},\mathrm{r}'\right)=\frac{V^2}{Z_N}\int_V d^3r_3d^3r_4\cdots d^3r_N\exp\left[-\beta V_N\left(\mathrm{r},\mathrm{r}',\mathrm{r}_3,\cdots,\mathrm{r}_N\right)\right],$$

where

$$Z_N=\int_V d^3r_1d^3r_2\cdots d^3r_N\exp\left[-\beta V_N\left(\mathrm{r}_1,\mathrm{r}_2,\mathrm{r}_3,\cdots,\mathrm{r}_N\right)\right].$$

It may also be written as

$$g\left(\mathrm{r},\mathrm{r}'\right)=\frac{V^2}{N\left(N-1\right)}\left\langle\sum_{i,j;i\neq j}\delta\left(\mathrm{r}-\mathrm{r}_i\right)\delta\left(\mathrm{r}'-\mathrm{r}_j\right)\right\rangle.$$

分子模型

For a homogeneous system the pair correlation function depends only on the distance between r and r′. In this case we denote it as $g(r)$.

The $g(\mathrm{r},\mathrm{r}')$ is proportional to the probability that given a particle at point r and find another particle at point r′. At large distances $g(r)$ tends to 1, we may define the total correlation function

$$h(\mathrm{r}) = g(\mathrm{r}) - 1.$$

The Fourier transform of the above function gives the static structure function (or structure factor)

$$S(\mathrm{k}) = 1 + n\int h(\mathrm{r})\, e^{i\mathrm{k}\cdot\mathrm{r}} d^3r.$$

分子模型

The structure function is defined as the correlation function of Fourier component of density fluctuations

$$S(\mathrm{k}) = \frac{1}{N}\langle \Delta n_{-\mathrm{k}} \Delta n_{\mathrm{k}} \rangle$$

The density is defined as $n(\mathrm{r}) = \sum_i^N \delta(\mathrm{r} - \mathrm{r}_i)$ and the density fluctuation is $\Delta n(\mathrm{r}) = \sum_i^N \delta(\mathrm{r} - \mathrm{r}_i) - \frac{N}{V}$ and its Fourier component is: $\Delta n_{\mathrm{k}} = \int d\mathrm{r}\, \Delta n(\mathrm{r}) e^{-i\mathrm{k}\cdot\mathrm{r}} = \sum_i^N e^{-i\mathrm{k}\cdot\mathrm{r}_i} - N\delta_{\mathrm{k},0}$

$$S(\mathrm{k}) = \frac{1}{N}\langle \Delta n_{-\mathrm{k}} \Delta n_{\mathrm{k}} \rangle = \frac{1}{N} \sum_{ij;i\neq j} \left\langle e^{i\mathrm{k}\cdot(\mathrm{r}_i - \mathrm{r}_j)} \right\rangle + 1 - N\delta_{\mathrm{k},0}$$

分子模型

$$
\begin{aligned}
& S\left(\mathrm{k}\right)+N\delta_{\mathrm{k},0} \\
&= \frac{1}{N}\left\langle \Delta n_{-\mathrm{k}}\Delta n_{\mathrm{k}}\right\rangle = \frac{1}{N}\sum_{ij;i\neq j}\left\langle e^{i\mathrm{k}\cdot\left(\mathrm{r}_i-\mathrm{r}_j\right)}\right\rangle + 1 \\
&= \int d\mathrm{r}d\mathrm{r}' e^{i\mathrm{k}\cdot\left(\mathrm{r}-\mathrm{r}'\right)}\frac{1}{N}\sum_{ij;i\neq j}\left\langle \delta\left(\mathrm{r}-\mathrm{r}_i\right)\delta\left(\mathrm{r}'-\mathrm{r}_j\right)\right\rangle + 1 \\
&= \frac{N-1}{V^2}\int d\mathrm{r}d\mathrm{r}' e^{i\mathrm{k}\cdot\left(\mathrm{r}-\mathrm{r}'\right)}g(\mathrm{r}-\mathrm{r}') + 1 \\
&= 1+\left(n-\frac{1}{V}\right)\int d\mathrm{r}g(\mathrm{r})e^{i\mathrm{k}\cdot\mathrm{r}} \\
&= 1+\left(n-\frac{1}{V}\right)\int d\mathrm{r}h(\mathrm{r})e^{i\mathrm{k}\cdot\mathrm{r}} + (N-1)\delta_{\mathrm{k},0}
\end{aligned}
$$

当体积趋于无限时，红颜色的部分可以略去.

The structure factor can be measured directly by scattering experiments and can also be calculated by simulations.

Many physical quantities can be expressed in terms of the pair correlation function, for example the energy in NVT ensemble is

$$E = \frac{3}{2} N k_B T + \frac{N}{2} n \int d^3 r \, v(\mathrm{r}) \, g(\mathrm{r}) .$$

The pressure is

$$\begin{aligned} \frac{\beta P}{n} &= 1 - \frac{\beta}{3N} \left\langle \sum_{i=1}^{N} \hat{\mathrm{r}}_i \cdot \nabla_i V_N \right\rangle \\ &= 1 - \frac{\beta}{6} n \int d^3 r \, \hat{\mathrm{r}} \cdot \nabla v(\mathrm{r}) \, g(\mathrm{r}) . \end{aligned}$$

The compressibility

$$k_B T \left(\frac{\partial n}{\partial p}\right)_T = 1 + n \int d^3 r \left(g\left(\mathrm{r}\right) - 1\right).$$

This expression can be derived from the fluctuations of particle numbers

$$\left\langle N^2 \right\rangle - \left\langle N \right\rangle^2 = k_B T \left(\frac{\partial \left\langle N \right\rangle}{\partial \mu}\right)_{T,V} = -k_B T \frac{\left\langle N \right\rangle^2}{V^2} \left(\frac{\partial V}{\partial P}\right)_{T,\langle N \rangle}.$$

Since $n = \frac{\langle N \rangle}{V}$,, $dV = -\frac{V^2}{\langle N \rangle} dn$, so

$$\left\langle N^2 \right\rangle - \left\langle N \right\rangle^2 = \left\langle N \right\rangle k_B T \left(\frac{\partial n}{\partial P}\right)_T.$$

On the other hand, it can be proved that

$$\left\langle N^2\right\rangle - \left\langle N\right\rangle^2 = \left\langle N\right\rangle \left(1 + n\int d^3r\,(g\,(\mathrm{r}) - 1)\right).$$

We have the final result.

The time correlation function is the correlations of two physical quantities at different times,

$$C_{AB}(t,t') = \left\langle A(t)B(t')\right\rangle.$$

For systems at equilibrium the time correlation function is a function of the time difference only and can be written as

$$C_{AB}(t) = \left\langle A(t)B(0)\right\rangle.$$

分子模型

The velocity auto correlation function of the ith particle is

$$C_{\mathrm{vv}}(t) = \langle \mathrm{v}_i(t) \cdot \mathrm{v}_i(0) \rangle .$$

Which is related to the diffusion constant of the particle.

$$D = \frac{1}{3} \int_0^\infty dt \, \langle \mathrm{v}(t) \cdot \mathrm{v}(0) \rangle$$

This can be derived from the definition (we will back to this point)

$$\left\langle (\mathrm{r}_i(t) - \mathrm{r}(0))^2 \right\rangle = 6Dt$$

which holds for large t.

分子模型

In general, a transport coefficient is defined in terms of the response of a system to a perturbation.

$$\gamma = \int_0^\infty dt \left\langle \dot{A}(t)\, \dot{A}(0) \right\rangle$$

where γ is the transport coefficient, and A is a physical variable appearing in the perturbation Hamiltonian. There is also an Einstein relation associated with this kind of expression

$$\left\langle (A(t) - A(0))^2 \right\rangle = 2\gamma t$$

which holds for large t , $(t \gg \tau$, where τ is the relaxation time of $\dot{A})$.

The shear viscosity η is given by

$$\eta = \frac{V}{k_B T} \int_0^\infty dt \ \langle P_{\alpha\beta}(t) P_{\alpha\beta}(0) \rangle$$

or

$$\frac{V}{k_B T} \langle Q_{\alpha\beta}(t) Q_{\alpha\beta}(0) \rangle = 2\eta t.$$

Here

$$P_{\alpha\beta} = \frac{1}{V} \sum_i \left(\frac{p_{i\alpha} p_{i\beta}}{m_i} + r_{i\alpha} f_{i\beta} \right)$$

$$Q_{\alpha\beta} = \frac{1}{V} \sum_i r_{i\alpha} p_{i\beta}.$$

The negative of $P_{\alpha\beta}$ is often called stress tensor.

Monte Carlo simulation of Particle Systems

粒子系统的Monte Carlo 模拟和自旋系统原则上是一样的。Metropolis 算法为：

1，随机或顺序选取一个粒子，其位置矢量为 r_i，对此粒子做移动

$$x_i \Rightarrow x_i + d_x\,(\mathrm{ran}() - 0.5)$$

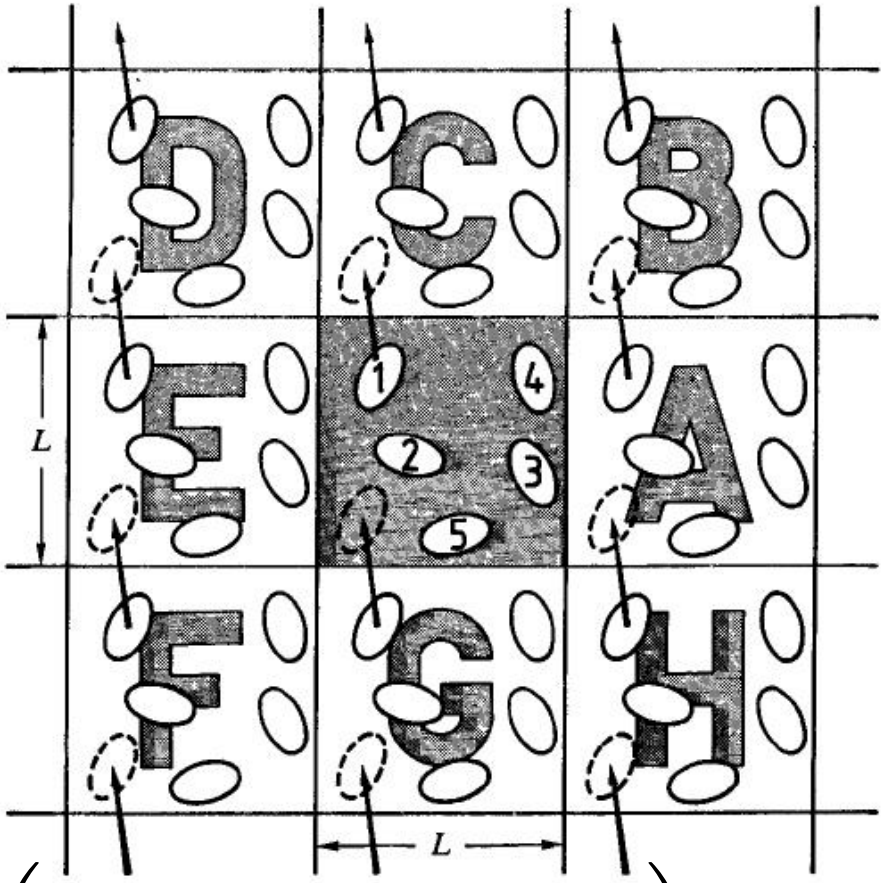
$$y_i \Rightarrow y_i + d_y\,(\mathrm{ran}() - 0.5)$$

$$z_i \Rightarrow z_i + d_z\,(\mathrm{ran}() - 0.5)$$

2，计算前后的能量差，决定是否接受移动。

3，在达到平衡后，收集数据，计算物理量。

周期性边界条件



设想把模拟的盒子在所有方周期性排列，实际上计算的一个无穷大的系统。

相互作用能

$$u_{\mathrm{PBC}}\left(\mathrm{r}_i-\mathrm{r}_j\right)=\sum_{\mathrm{n}} u\left(\mathrm{r}_i-\mathrm{r}_j+\sum_{\mu}\mathrm{L}_\mu n_\mu\right)$$

$$U=\frac{1}{2}{\sum_{i,j}}' u_{\mathrm{PBC}}(\mathrm{r}_i-\mathrm{r}_j)$$

约化单位，...

能量的的单位 ϵ

长度的单位： σ

温度的单位： ϵ/k_B

对于LJ势，

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

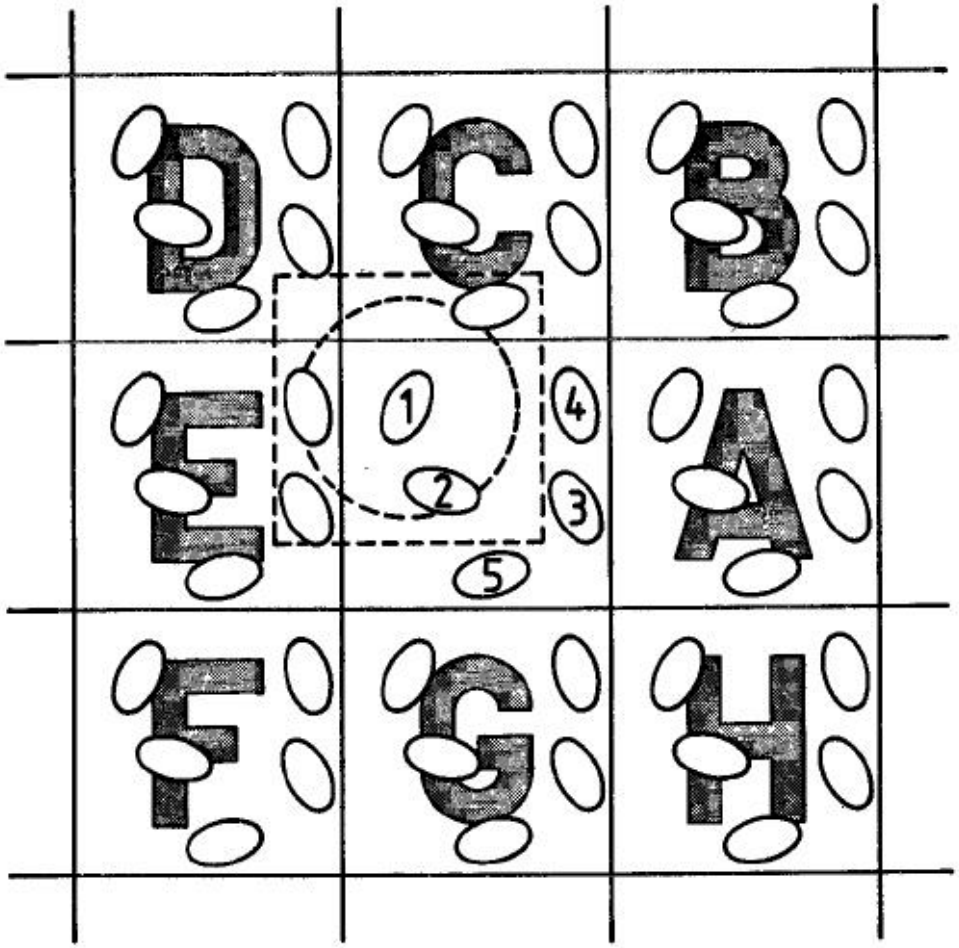
$$u = 4\left[\left(\frac{1}{r}\right)^{12} - \left(\frac{1}{r}\right)^{6}\right]$$

计算能量时的切断

对于短程相互作用，实际计算时，需要对能量的表达式做切断近似，然后考虑尾修正。

切断后，计算对第i个粒子的相互作用时，只考虑离开第i粒子距离小于切断半径的粒子。

注意包含周期性边界条件后像中的粒子。



切断势定义为：

$$u(r) := \begin{cases} u(r), & r \le r_c \\ 0, & r > r_c \end{cases}$$

能量的尾修正（平均每个粒子）：

$$u^{\mathrm{tail}} = \frac{1}{2}\int_{r_c}^{\infty} 4\pi r^2 dr \rho u(r)$$

压强的尾修正：

$$P^{\mathrm{tail}} = \frac{1}{6}\rho^2 \int_{r_c}^{\infty} 4\pi r^3 dr \frac{\partial u}{\partial r}$$

对于LJ势， 能量的尾修正（平均每个粒子）：

$$u^{\mathrm{tail}} = \frac{8}{3}\pi\rho\left[\frac{1}{3}\left(\frac{1}{r_c}\right)^9 - \left(\frac{1}{r_c}\right)^3\right]$$

压强的尾修正：

$$P^{\mathrm{tail}} = \frac{16}{3}\pi\rho\left[\frac{2}{3}\left(\frac{1}{r_c}\right)^9 - \left(\frac{1}{r_c}\right)^3\right]$$

切断导致的冲击力对于压强的修正：

$$\Delta P^{\mathrm{imp}} = \frac{8\pi}{3}\rho^2 g(r_c)\left[\left(\frac{1}{r_c}\right)^9 - \left(\frac{1}{r_c}\right)^3\right]$$

切断势定义为：

$$u(r) := \begin{cases} u(r) - u(r_c), & r \le r_c \\ 0, & r > r_c \end{cases}$$

分子动力学模拟

Molecular dynamics simulations

MD method is essentially the integration of the equation of motion of the classical many-particle system in a period of time. The trajectories of the system in the phase space are thus obtained and averages of the trajectories give various physical properties. Since we work on real dynamics in MD simulations we can also study the dynamic properties of the system such as relaxation to equilibrium, transport etc.

Consider a rectangular volume of $L_1 \times L_2 \times L_3$, with N classical particles put in. The particles are interact with each other. In principle, the interaction includes pair interactions, three body interactions as well as many body interactions. For simplicity we will consider here only pair interactions. In this case each particle feel a force by all other particles and we further assume the force depends only on distances from other particles and for each pair the force directed along the line join the pair of particles. So the force on the ith particle is

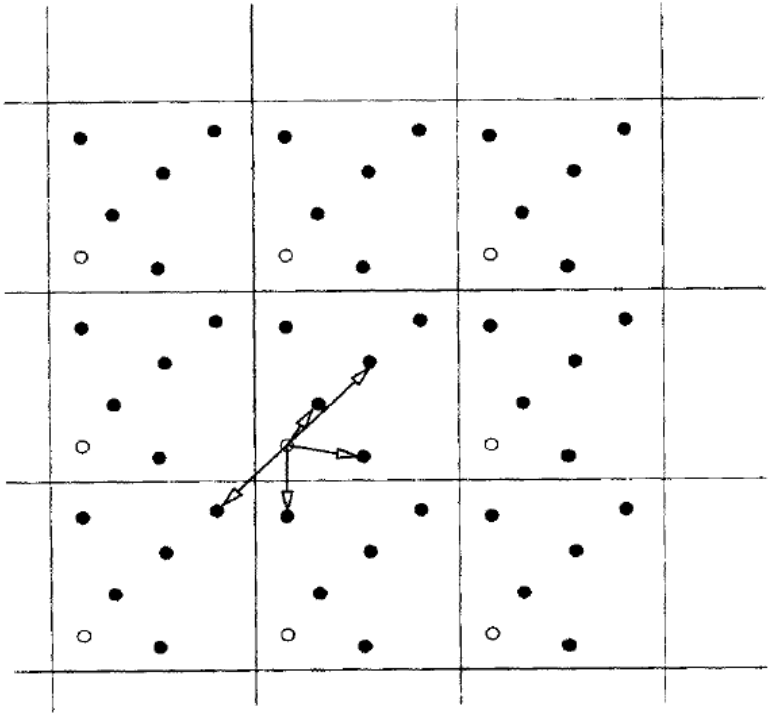
$$\mathrm{F}_i = \sum_{j=1,N;j\neq i} F(|\mathrm{r}_i - \mathrm{r}_j|)\hat{\mathrm{r}}_{ij},$$

where $\hat{\mathrm{r}}_{ij}$ is an unit vector along $\mathrm{r}_i - \mathrm{r}_j$.

Periodic boundary condition(PBC)

$$\mathrm{F}_{PBC}\left(\mathrm{r}_i-\mathrm{r}_j\right)=\sum_{\mathrm{n}}\mathrm{F}\left(\mathrm{r}_i-\mathrm{r}_j+\sum_{\mu}\mathrm{L}_\mu n_\mu\right)$$

where L_μ are vectors along the edges of the rectangular system volume and the sum over n is with all integers n_μ. Usually this sum is the most time consuming part in a simulation.



General procedure of MD (NVE ensemble)

1. Initialize;

2. Start simulation and let the system reach equilibrium;

3. Continue simulation and store results.

Initialize:

1, Specify the number of particles and interaction;

2, Setup the simulation box;

3, Specify the total energy of the system;

4, Assign position and momenta of each particle.

a, In many cases we assign particles in a FCC lattice,

If we use cubic unit cell and cube BOX then the number of particles per unit cell is 4, and the total numbers of particles are $4M^3$, M=1,2,3,⋯ . That is we may simulate systems with total number of particles N=108, 256, 500, 864, ⋯.

b, The velocities of particles are draw from a Maxwell distribution with the specified temperature.

This is accomplished by drawing the three components of the velocity from the Gaussian distribution.

The distribution of the x-component of velocity is

$$P(v_x) \propto \exp\left[-\frac{mv_x^2}{2k_BT}\right].$$

Draw numbers from a Gaussian:

Consider:

$$P(v_x, v_y) \propto \exp\left[-\frac{mv_x^2}{2k_BT}\right] \exp\left[-\frac{mv_y^2}{2k_BT}\right] = \exp\left[-\frac{m\left(v_x^2+v_y^2\right)}{2k_BT}\right].$$

Then

$$P(v_x, v_y)dv_xdv_y = \tilde{P}(v)vdvd\phi,$$

where $v^2 = v_x^2 + v_y^2$ and

$$\tilde{P}(v) \propto \exp\left[-\frac{mv^2}{2k_BT}\right].$$

So the distribution of v_x and v_y may be obtained from v and ϕ.

The distribution of v:

$$P(v) \propto v \exp\left[-\frac{mv^2}{2k_BT}\right]$$

The distribution of ϕ is uniform in the interval $[0, 2\pi]$.

Generate random numbers for a given distribution

For a given distribution $P(y)$ we consider how to get a random number y draw from $P(y)$ from a random number x draw from uniform $[0,1]$, i.e., we are going to find a function $f(x)$, from which for a series of random numbers x distributed uniformly in the interval $[0,1]$, $y = f(x)$ will distributed according to $P(y)$.

Since

$$\int_{-\infty}^{y} P(y')\,dy' \equiv F(y) = \int_{0}^{x} dx = x,$$

then

$$y = F^{-1}(x)$$

Exponential distribution

$$P(y) = \begin{cases} 0, & y < 0 \\ \lambda e^{-\lambda y}, & y > 0 \end{cases}.$$

$$F(y) = \int_{-\infty}^{y} P(y')\,dy' = \begin{cases} 0, & y < 0 \\ 1 - e^{-\lambda y}, & y > 0 \end{cases},$$

$$y = f(x) \equiv F^{-1}(x) = -\frac{1}{\lambda}\ln(1-x).$$

The distribution of v:

$$P(v) = \frac{m}{k_B T} v \exp\left[-\frac{mv^2}{2k_B T}\right]$$

$$\frac{m}{k_B T}\int_0^v v \exp\left[-\frac{mv^2}{2k_B T}\right] dv = -\exp\left[-\frac{mv^2}{2k_B T}\right] + 1.$$

$$v = \sqrt{-\frac{k_B T}{m}\ln(1-x)}$$

Draw random numbers uniformly distributed in the interval $[0, 2\pi]$.

$$v_x = v\cos\phi$$

$$v_y = v\sin\phi$$

Another method of draw random numbers in the Gaussian distribution is through the following empirical methods.

Consider the distribution

$$\exp\left[-\frac{x^2}{2}\right]$$

According to the central limit theorem, if we draw uniform random numbers r_i in interval $[0,1]$, and define a variable

$$\xi = \frac{\frac{1}{n}\sum_{i=1}^{n} r_i - \frac{1}{2}}{\sqrt{\frac{1}{12n}}}$$

when $n \gg 1$ the distribution of ξ is the Gaussian distribution

$$\exp\left[-\frac{\xi^2}{2}\right]$$

If we take $n = 12$, we get

$$\xi = \sum_{i=1}^{12} r_i - 6.$$

After the generation of the velocity of each particle, we may shift the velocity so that the total momentum is zero.

The standard Verlet algorithm is the first successful method in history and still wide used today in different forms. It is

$$\mathrm{r}(t+h) = 2\mathrm{r}(t) - \mathrm{r}(t-h) + h^2\mathrm{F}(\mathrm{r}(t))/m$$

$$\mathrm{v}(t) = \frac{\mathrm{r}(t+h) - \mathrm{r}(t-h)}{2h}.$$

To start the integration we need $r(h)$, given by

$$\mathrm{r}(h) = \mathrm{r}(0) + h\mathrm{v}(0) + h^2\mathrm{F}(\mathrm{r}(0))/m.$$

Variations of this method are

$$\mathrm{v}\left(t+h/2\right)=\mathrm{v}\left(t-h/2\right)+h\mathrm{F}\left(\mathrm{r}\left(t\right)\right)$$
$$\mathrm{r}\left(t+h\right)=\mathrm{r}\left(t\right)+h\mathrm{v}\left(t+h/2\right).$$

and

$$\mathrm{r}\left(t+h\right)=\mathrm{r}\left(t\right)+h\mathrm{v}\left(t\right)+h^{2}\mathrm{F}\left(\mathrm{r}\left(t\right)\right)$$
$$\mathrm{v}\left(t+h\right)=\mathrm{v}\left(t\right)+h\frac{\mathrm{F}\left(\mathrm{r}\left(t+h\right)\right)+\mathrm{F}\left(\mathrm{r}\left(t\right)\right)}{2}.$$

Both of these variations are mathematically equivalent to the original one but more stable under finite precision arithmetic.

The temperature of the system is given by the equal partition theorem, that is the average of kinetic energy of each degree of freedom is half k_BT,

$$\frac{3}{2}k_BT_D = \frac{1}{N-1}\sum_{i=1}^{N}\left\langle \frac{1}{2}mv_i^2 \right\rangle .$$

The $N-1$ is due to the conservation of the total momentum which reduce the degree of freedom by 3.

To reach the desired temperature we may scale the velocity at every few steps of integration

$$\mathrm{v}_i(t) \to \lambda \mathrm{v}_i(t)$$

$$\lambda = \sqrt{\frac{(N-1)\,3k_BT}{\sum_{i=1}^{N} mv_i^2}}$$

After the system reach to equilibrium the integration continue in the same method as above without scaling of velocity. The data are stored or accumulated for the calculating of physical properties. The static properties of physical quantity A is given by time average

$$\bar{A} = \frac{1}{n - n_0} \sum_{\nu > n_0}^{n} A_\nu$$

here A_ν is the value of A at νth time step. Usually the data stored in each step include:

1, the kinetic energy $$\sum_{i=1}^{N} \frac{1}{2} m v_i^2$$

2, the potential energy $$U = \sum_{\langle i,j \rangle} v\left(r_{ij}\right)$$

3, the virial $$\sum_{\langle i,j \rangle} r_{ij} \frac{\partial v\left(r_{ij}\right)}{\partial r_{ij}}.$$

We also need data to calculate the pair correlation function, this is done by divide the interval $[0, r]$ into sub intervals $[ir, (i+1)r]$, at each stage of updating, add the number of pairs with separation in the interval $[ir, (i+1)r]$, to an array $n(i)$ and find the average value after simulation, the pair correlation function is given by

$$g(r) = \frac{2V}{N(N-1)} \frac{\langle n(r) \rangle}{4\pi r^2 \Delta r}$$

一些成熟的MD程序库：

Lammps： http://lammps.sandia.gov/

Gromacs： http://www.gromacs.org/

Ccp5: http://www.ccp5.ac.uk/

常用计算程序： http://netlib.org/