Molecular Dynamics of a Coulomb System with Deformable Periodic Boundary Conditions

Hiroo Totsuji*, Hideki Shirokoshi*, and Shigetoshi Nara*

SYNOPSIS

Variable shape molecular dynamics is formulated for the one-component plasma and the structural transition from the *fcc* lattice to the *bcc* lattice has been observed. It is emphasized that the condition of constant volume should be imposed when deformations of periodic boundary conditions are taken into account.

1. Introduction

Spatial structures of systems composed of charged particles are one of fundamental data for the analyses on electronic properties of materials. The simplest example of this kind of information may be the structural phase transition of the classical one-component plasma (OCP), the system of classical charged particles of one species in the uniform background. It is known that the OCP undergoes the transition from the liquid state to the solid phase of the body centered cubic (*bcc*) lattice at some value of the coupling parameter [1]. The critical value of the transition has been determined by a comparison of the free energies in both phases based on the results from numerical experiments mostly of the Monte Carlo method. Molecular dynamics

---

*Department of Electrical and Electronic Engineering

simulations have also been used to investigate various properties including dynamical ones in the liquid phase or in the supercooled liquid state [2].

In these numerical experiments, the periodic boundary conditions are usually adopted in order to avoid the effect of surfaces and the well known Ewald method is employed. As the periodicity, the simple cubic lattice is used in almost all cases: The number of independent particles in the cubic cell is determined so as to be consistent with the low temperature phase, the *bcc* lattice, and the deformation of the cell is not allowed during the numerical experiment.

Recently it has been pointed out [3, 4] that one can perform the molecular dynamics simulation with variable shape as well as variable volume of the boundary conditions and the shape of boundaries has a strong effect on the properties of the system under investigation, especially when those related to the structural transition are concerned [5]. The purpose of this paper is to formulate such a molecular dynamics simulation for the OCP and analyze the effect of the boundary conditions on their properties.

2. Formulation

We denote three fundamental vectors of periodicity by $e^{(\alpha)}$ where $\alpha = 1$, 2, and 3. Following Parinello and Rahman [4], we take into account the degrees of freedom related to the shape of the boundary conditions by adding, to the usual Lagrangian, a term

$$(W/2)\mathsf{Tr}(^t\dot{\mathsf{h}} \cdot \dot{\mathsf{h}}). \tag{1}$$

Here h is the tensor composed of fundamental vectors as

$$\mathsf{h}_{\alpha\beta} = e_\alpha^{(\beta)} = \left\{\mathsf{e}^{(\beta)}\right\}_\alpha, \tag{2}$$

W is the mass assigned to these extra degrees of freedom which is to be determined empirically, and we denote time derivatives by dots.

We thus write the Lagrangian L_0 for our system with N independent particles in the form

$$L_0 = \frac{1}{2} \sum_i m_i \, {}^t\dot{\mathbf{s}}_i \cdot \mathsf{G} \cdot \dot{\mathbf{s}}_i - \sum_{i>j} \phi(\mathbf{r}_{ij}) - \frac{N}{2} \phi_0 + (W/2) \mathsf{Tr}({}^t\dot{\mathsf{h}} \cdot \dot{\mathsf{h}}) \tag{3}$$

where

$$\mathsf{G} = {}^t\mathsf{h} \cdot \mathsf{h}. \tag{4}$$

The position vector $\mathbf{r}_i$ of the particle i is expressed by $\mathbf{s}_i$ as

$$\mathbf{r}_i = \mathsf{h} \cdot \mathbf{s}_i = \sum_\alpha \mathbf{e}^{(\alpha)} (\mathbf{s}_i)_\alpha, \tag{5}$$

summations over Greek indices running from 1 to 3 or over x, y, and z. The potential $\phi(\mathbf{r}_{ij})$, $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$, between particles i and j are given by

$$\phi(\mathbf{r}_{ij}) = \left[\sum_{\mathbf{p}} v(|\mathbf{r}_{ij} - \mathbf{p}|) \right]_{u.b.} \tag{6}$$

and ϕ_0 is the interaction energy with each particle's own images. Here the periodicity is denoted by $\mathbf{p}$ as $\mathbf{p} = \sum_\alpha \mathbf{e}^{(\alpha)} n_\alpha = \mathsf{h} \cdot \mathbf{n}$, n_1, n_2, n_3 being integers, $v(r) = e^2/r$, and $[\ ]_{u.b.}$ denotes that the existence of the uniform background is taken into account.

We here note that, in the case of OCP, the volume Ω of the unit cell is kept constant by the uniform background: The change of the volume means the appearance of the average space charge which is repeated infinitely by the periodic boundary conditions. We thus have the freedom related to the metric h only under the condition of the fixed volume as

$$\det \mathsf{h} = \Omega = const. \tag{7}$$

The most convenient way of taking this constraint into our equations of motion may be to use the method of undetermined multiplier of Lagrange [6]. We add the term

$$\lambda(t)\Omega \tag{8}$$

to the Lagrangian and determine the time dependent value of the multiplier $\lambda(t)$ so as to satisfy the above constraint. Our final form of the Lagrangian is

$$L = L_0 + \lambda(t)\Omega. \tag{9}$$

Physically, the multiplier $\lambda(t)$ is the external pressure (with negative sign) which is necessary to keep the volume of our system constant.

The equations of motion are thus written as

$$m_i \ddot{\mathbf{s}}_i = -\sum_{j(\neq i)} \sum_{\mathbf{P}} \frac{1}{|\mathbf{r}_{ij} - \mathbf{p}|} \frac{\partial v(|\mathbf{r}_{ij} - \mathbf{p}|)}{\partial|\mathbf{r}_{ij} - \mathbf{p}|}(\mathbf{s}_i - \mathbf{s}_j - \mathbf{n}) - m_i \mathsf{G}^{-1} \cdot \dot{\mathsf{G}} \cdot \dot{\mathbf{s}}_i \tag{10}$$

for particles and

$$W\ddot{\mathsf{h}} = (\Pi + \lambda(t)\mathsf{I}) \cdot \sigma, \tag{11}$$

$$\Omega\Pi = \sum_i m_i \mathbf{v}_i \mathbf{v}_i - \frac{1}{2}\sum_{i\neq j}\sum_{\mathbf{P}} \frac{1}{|\mathbf{r}_{ij} - \mathbf{p}|} \frac{\partial v(|\mathbf{r}_{ij} - \mathbf{p}|)}{\partial|\mathbf{r}_{ij} - \mathbf{p}|}(\mathbf{r}_{ij} - \mathbf{p})(\mathbf{r}_{ij} - \mathbf{p}) + \Omega\Pi_0, \tag{12}$$

$$\sigma = \Omega^t \mathsf{h}^{-1}, \tag{13}$$

for h, where I is the unit tensor, $\mathbf{v}_i = \mathsf{h} \cdot \mathbf{s}_i$, and Π_0 is the contribution from ϕ_0 which is given in Appendix.

The value of $\lambda(t)$ is determined by the condition (7) or

$$\sum_{\alpha\beta} \frac{\partial\Omega}{\partial\mathsf{h}_{\alpha\beta}}\dot{\mathsf{h}}_{\alpha\beta} = \mathsf{Tr}(^t\sigma \cdot \dot{\mathsf{h}}) = 0. \tag{14}$$

Taking the time derivative of (14) and using (11), we have

$$\lambda(t) = \frac{\left\{(W/\Omega)\mathsf{Tr}(^t\sigma \cdot \dot{\mathsf{h}} \cdot^t \sigma \cdot \dot{\mathsf{h}}) - \mathsf{Tr}(^t\sigma \cdot \Pi \cdot \sigma)\right\}}{\mathsf{Tr}(^t\sigma \cdot \sigma)}. \tag{15}$$

The Hamiltonian of our system is given by

$$H = H_0 + \lambda(t)\Omega, \tag{16}$$

$$H_0 = (1/2)\sum_i m_i \dot{\mathbf{s}}_i \cdot \mathsf{G} \cdot \dot{\mathbf{s}}_i + \sum_{i>j} \phi(\mathbf{r}_{ij}) + \frac{N}{2}\phi_0 + (W/2)\mathrm{Tr}(^t\dot{\mathsf{h}} \cdot \dot{\mathsf{h}}). \tag{17}$$

The term $\lambda(t)\Omega$ corresponds to the (minus) external pressure necessary to conserve the volume of the system. Due to this term, the Hamiltonian is not conserved,

$$\frac{dH}{dt} = \Omega\frac{d\lambda(t)}{dt}, \tag{18}$$

whereas H_0 is conserved,

$$\frac{dH_0}{dt} = 0. \tag{19}$$

This relation is useful to confirm accuracy of numerical processes.

The calculation of the summation with respect to lattice vector p in (10) and (12) have been performed by the Ewald method. We here give one of such expressions:

$$
\begin{aligned}
\left[\sum_{\mathbf{p}}\frac{(\mathbf{r}-\mathbf{p})(\mathbf{r}-\mathbf{p})}{|\mathbf{r}-\mathbf{p}|^3}\right]_{u.b.} = & \left[-\frac{\pi}{\Omega G^2} + \frac{1}{\Omega}\sum_{\mathbf{g}\neq 0}\frac{4\pi}{g^2}\exp\left(-\frac{g^2}{4G^2} + i\mathbf{g}\cdot\mathbf{r}\right)\right]\mathsf{I} \\
& - \frac{8\pi}{\Omega}\sum_{\mathbf{g}\neq 0}\frac{\mathbf{g}\mathbf{g}}{g^4}\left(\frac{g^2}{4G^2} + 1\right)\exp(-\frac{g^2}{4G^2} + i\mathbf{g}\cdot\mathbf{r}) \\
& + \sum_{\mathbf{p}}\left\{\frac{(\mathbf{r}-\mathbf{p})(\mathbf{r}-\mathbf{p})}{|\mathbf{r}-\mathbf{p}|^3}\mathrm{erfc}(G|\mathbf{r}-\mathbf{p}|)\right. \\
& + \left.\frac{2G}{\sqrt{\pi}}\frac{(\mathbf{r}-\mathbf{p})(\mathbf{r}-\mathbf{p})}{|\mathbf{r}-\mathbf{p}|^2}\exp(-G^2|\mathbf{r}-\mathbf{p}|^2)\right\},
\end{aligned}
\tag{20}
$$

where g is the reciprocal lattice vector,

$$\mathrm{erfc}(x) = \frac{2}{\sqrt{\pi}}\int_x^\infty dt\,\exp(-t^2), \tag{21}$$

and G is an auxiliary parameter.

3. Example

Numerical procedures to solve equations of motion (10) and (12) are similar to those of usual molecular dynamics. We have employed the Runge-Kutta method of 6th order and confirmed that the volume Ω and H_0 are conserved with sufficient accuracy.

As one of our results, we show an example of structural change from the *fcc* lattice to the *bcc* lattice; the latter has a little smaller Madelung energy than the former [7].

The behaviors of the elements of h are plotted in Figs.1 and 2. In the initial state, we have $108 = 4 \cdot 3^3$ particles with the *fcc* structure described by h = I. We observe our system relaxes to the *bcc* structure given by

$$
h = \left(\frac{1}{2}\right) \begin{pmatrix} \sqrt{2} & 0 & 0 \\ 0 & \sqrt{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}.
\tag{22}
$$

The value of the coupling constant of OCP, Γ, is estimated to be around 350.

When the deformation of periodic boundary conditions is forbidden, this kind of transition is impossible: The *bcc* lattice requires $2 \cdot (integer)^3$ as the number of independent particles.

In conclusion, we have formulated the molecular dynamics with deformable periodic boundary conditions for the classical one-component plasma and observed, as a preliminary result, a transition from the *fcc* lattice to the *bcc* lattice.

One of authors (H. T.) would like to thank Professor P. Vashishta for useful discussions. The authors also thank K. Yamasaki for his help in the early stage of this work. Numerical computations have been done at the Okayama University Computer Center.
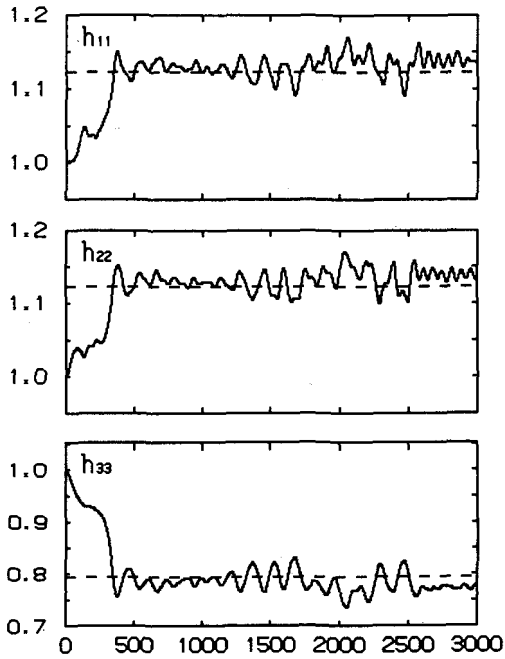
FIG. 1. Behavior of diagonal elements of h. Time is measured in units of $1/\omega_p$. Broken lines correspond to the *bcc* structure.
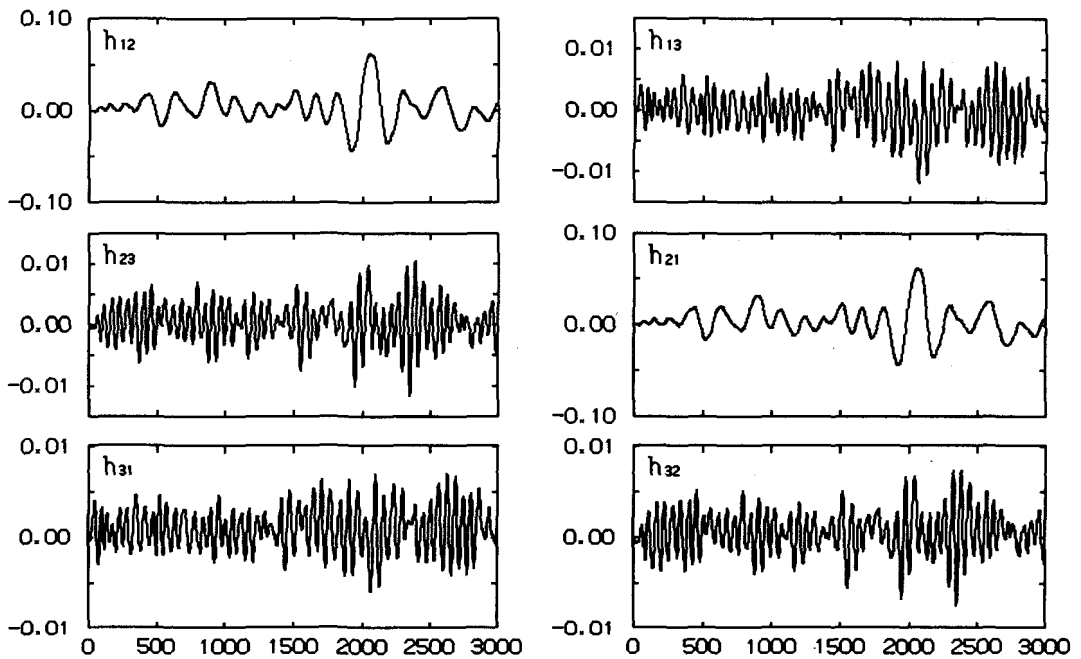
FIG. 2. Nondiagonal elements of h. The matrix h is almost symmetric.

References

[1] For example, W. L. Slattery, G. D. Doolen, and H. E. DeWitt, Phys. Rev. **A26**, 2255(1982).

[2] H. Totsuji, *Strongly Coupled Plasma Physics*, ed. by F. J. Rogers and H. E. DeWitt, Plenum, 1987, p.19.

[3] H. C. Andersen, J. Chem. Phys. **72**, 2384(1980).

[4] M. Parrinello and A. Rahman, Phys. Rev. Lett. **45**, 1196(1980).

[5] For example, M. Parrinello, A. Rahman, and P. Vashishta, Phys. Rev. Lett. **50**, 1073(1983).

[6] For example, L. D. Landau and E. M. Lifshitz, *Mechanics*, third ed., Pergamon, 1976, Ch.6.

[7] S. G. Brush, H. L. Sahlin, and E. Teller, J. Chem. Phys. **45**, 2101(1966).

Appendix

Since the interaction of a charge with its own image depends on the periodicity, the equation of motion for h includes the term due to $-(N/2)\phi_0$ in L_0. From the explicit expression for ϕ_0

$$
\frac{\phi_0}{e^2} = \lim_{r \to 0} \left(\left[\sum_{\mathbf{p}} \frac{1}{|\mathbf{r} - \mathbf{p}|} \right]_{u.b.} - \frac{1}{r} \right)
$$

$$
= \frac{1}{\Omega} \sum_{\mathbf{g} \neq 0} \frac{4\pi}{g^2} \exp(-\frac{g^2}{4G^2}) + \sum_{\mathbf{p} \neq 0} \frac{1}{p} \text{erfc}(Gp)
$$

$$
- \frac{2G}{\sqrt{\pi}} - \frac{\pi}{\Omega G^2}, \tag{A1}
$$

we have for $\partial L / \partial h_{\alpha\beta}$

$$
- \frac{1}{\Omega} \frac{N}{2} \lim_{r \to 0} \left\{ \left[\sum_{\mathbf{p}} \frac{1}{|\mathbf{r} - \mathbf{p}|} \frac{\partial v(|\mathbf{r} - \mathbf{p}|)}{\partial |\mathbf{r} - \mathbf{p}|} (\mathbf{r} - \mathbf{p})_\alpha \left\{ {}^t (\mathbf{r} - \mathbf{p}) \cdot \sigma \right\}_\beta \right]_{u.b.} \right.
$$

$$
\left. - \frac{1}{r} \frac{\partial v(r)}{\partial r} \mathbf{r}_\alpha ({}^t \mathbf{r} \cdot \sigma)_\beta \right\}
$$

$$= \frac{e^2}{\Omega} \frac{N}{2} \lim_{r \to 0} \left(\left\{ \left[\sum_{\mathbf{P}} \frac{(\mathbf{r} - \mathbf{p})_\alpha {}^t(\mathbf{r} - \mathbf{p})}{|\mathbf{r} - \mathbf{p}|^3} \right]_{u.b.} - \frac{\mathbf{r}_\alpha {}^t\mathbf{r}}{r^3} \right\} \cdot \sigma \right)_\beta . \tag{A2}$$

By the Ewald-type formula (20) for the lattice sum, the expression in the braces is calculated as

$$\lim_{r \to 0} \left\{ \left[\sum_{\mathbf{P}} \frac{(\mathbf{r} - \mathbf{p})(\mathbf{r} - \mathbf{p})}{|\mathbf{r} - \mathbf{p}|^3} \right]_{u.b.} - \frac{\mathbf{r}\mathbf{r}}{r^3} \right\}$$

$$= \left[-\frac{\pi}{\Omega G^2} + \frac{1}{\Omega} \sum_{\mathbf{g} \neq 0} \frac{4\pi}{g^2} \exp(-\frac{g^2}{4G^2}) \right] \mathbf{1} - \frac{8\pi}{\Omega} \sum_{\mathbf{g} \neq 0} \frac{\mathbf{g}\mathbf{g}}{g^4} (\frac{g^2}{4G^2} + 1) \exp(-\frac{g^2}{4G^2})$$

$$+ \sum_{\mathbf{p} \neq 0} \left\{ \frac{\mathbf{p}\mathbf{p}}{p^3} \mathrm{erfc}(Gp) + \frac{2G}{\sqrt{\pi}} \frac{\mathbf{p}\mathbf{p}}{p^2} \exp(-G^2 p^2) \right\} . \tag{A3}$$