THEORETICAL INVESTIGATION OF THE THERMODYNAMIC
STABILITY OF NANO-SCALE SYSTEMS—II: RELAXATION
OF A JUNCTION PROFILE

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Abstract—Nonlinear relaxation of a sharp density profile typical of layered semiconductor
junctions is studied using an irreversible statistical mechanical technique, the Path Probability
Method, taking into account nearest neighbor correlations. The vacancy mechanism and the pair
approximation are used. It is found that atoms near a sharp density profile diffuse up against the
density gradient. Our numerical examples demonstrate that in this range there is a possibility that
the atom flux can go either down along or up against the local chemical potential (μ) gradient.
However, the calculations do not deny the possibility of modifying the definition of μ in such a way
that the atoms always flow toward the direction of decreasing μ.

INTRODUCTION

In the first of this series (1) we studied equilibrium properties of nanoscale layer structures.
We showed how the layer profile varies with temperature and the layer thickness, and how the
phase separating temperature decreases as the layer thickness decreases. The present paper is the
sequel of the previous study into the time dependent behavior.

Due to recent advances in epitaxial growth technology, very sharp and defect free
heterojunctions can be fabricated. These junctions are not in equilibrium, although they look
stable. The junction profile can change under disturbances, for example by thermal means or by
elastic stresses. When the temperature of a junction is raised by whatever means to the range which
is high enough, the junction profile relaxes. Since a layer structure is made of many steep junctions,
the basic process involved in the relaxation of a layer structure is the atomic interdiffusion. In the
present paper we study the isothermal relaxation of a junction profile.

We work with a pseudobinary alloy semiconductor of the composition AₓB₁₋ₓC. One of the
fcc sublattices of the zinc-blende structure is fully occupied by the C component, and the other fcc
sublattice is shared by A and B components. Assuming that the C component is practically immobile, we work on the composition relaxation of the A and B components in an fcc lattice. We assume the vacancy mechanism for the substitutional diffusion. We also assume that the pair interaction is of the phase-separating kind, so that no ordered structure comes into consideration.

In the previous paper (1), we used an analytical statistical mechanical technique, the Cluster Variation Method (CVM) (2). The present paper employs the Path Probability Method (PPM) (3) which is the time-dependent version of the CVM. This analytical technique is suited to the present purpose for several reasons. Compared with numerical simulation methods, analytical methods lead to the accuracy which would be easily obscured by fluctuations in simulations. The present paper is concerned about validity of the linear theories in cases when the composition gradient is steep and a system is far from equilibrium, as is encountered at the early stages of relaxation from an initial sharp profile.

THEORETICAL BACKGROUND

Conventional Treatment of Interdiffusion

The classical theory for atomic interdiffusion is Fick's laws. The first law states that the atom flux is linearly proportional to the concentration gradient when the gradient is small. When the gradient is large, we need to include the square gradient term as in the Cahn-Hilliard equation (4). Tsujimoto (5) showed that this equation leads to overshooting of the concentration profile near the sharp junction in early stages of interdiffusion. In a previous paper (6), we examined the same equation and showed that the square gradient term is essential in producing the overshooting. Since the need arises later, we briefly summarize Ref. 6.

The free energy of the system with a one-dimensional variation of the concentration \( c(x) \) is written as

\[
F = A \int \left( f_0(c(x)) + \kappa \left( \frac{\partial c}{\partial x} \right)^2 \right) dx
\]

where \( A \) is the cross-sectional area normal to the \( x \) direction, \( f_0(c) \) is the local free energy density and \( \kappa \) is a constant. The continuity equation is

\[
\frac{\partial c(x; t)}{\partial t} = -\frac{\partial J(x; t)}{\partial x}
\]

where \( J(x; t) \) is the atomic flux toward the \( x \) direction. The next step is an important approximation for \( J(x; t) \) written as

\[
J(x; t) = -M \frac{\partial}{\partial x} \left( \frac{\delta F}{\delta c(x)} \right)
\]

where the mobility coefficient \( M \) is assumed constant. From these equations we obtain the Cahn-Hilliard equation (4) for \( c(x; t) \):
We call attention to two points. One is the approximation for writing \( J(x,t) \) as in [3]. The other is the use of a single function, the concentration density \( c(x,t) \), in describing the state of the system. To examine these two points is the theoretical interest of the present paper.

We comment on a related important relation which holds when \( c(x,t) \) is the sole function, even for non-linear cases, as was described by Cahn (7). The integrand of \( F \) can be of any function of \( c \): \( f(c(x,t)) \). The time derivative of \( F \) leads, using the continuity equation [2] and after a partial integration, to

\[
\frac{dF}{dt} = A \int \frac{d\mu(x)}{dx} J(x) \, dx \leq 0 \quad \text{where} \quad \mu(x) \equiv \frac{df(c)}{dc}.
\]  

\( \mu(x) \) is the chemical potential. The inequality in [5] represents the second law of thermodynamics. Since this inequality is to hold for any functional form of \( c(x,t) \), [5] requires at any location \( x \)

\[
\frac{d\mu}{dx} J(x) \leq 0.
\]  

It is significant to point out that even when \( f(x) \) depends not only on \( c(x) \) but also on the pair correlation \( y(ij) \)'s at \( x \), as will be discussed below, if the local equilibrium holds and \( y(ij) \)'s become functions of \( c(x) \), i.e. when \( y(ij) \)'s are slaved by \( c(x) \) using Cahn's terminology, then the inequality [6] holds, as the necessary consequence of the second law (7). We will show in a later section an example in which [6] breaks down.

**Correlations in Irreversible Statistical Mechanics**

In equilibrium theories of cooperative systems, correlations of atomic configurations in local clusters play the essential role. In time-dependent theories, nearest neighbor pair correlations were taken into account in the diffusion theory in many papers (8) by one of the authors and Sato. The main interest of these papers was, different from the present one, on the diffusion coefficient, and thus the treatments were limited to the small driving forces, although the basic formulation was applicable to large deviations from equilibrium. In these treatments, the independent variables to describe the state of an alloy system include the pair probabilities \( y_{\nu}(ij;t) \) for nearest neighbor \( i-j \) pairs at a \( \nu \) position, in addition to the concentration \( x_{i,n}(t;t) \) for the \( i \) species at an \( n \) lattice point. We use the discrete lattice description in the rest of the paper, and replace the continuous distance variable \( x \) by the lattice position \( n \) and the bond position \( \nu \), both discrete; \( x \) is used as the composition variable, replacing the previous \( c \).

The particular feature to be noted in our diffusion papers (8), in which the state is not far from equilibrium, is that it is not necessary to assume, but rather the theory derives, that the gradients of local chemical potentials \( \mu_{\nu}(j) \)'s are the driving forces for the fluxes \( J_{\nu}(i) \), including \( j \neq i \). This result supports Onsager's irreversible thermodynamics (9) that [3] holds when the system is not far from equilibrium. On the other hand, when the state is far from equilibrium, our previous
diffusion theory (8) says that the driving force for $J_v(i)$ cannot be simply written as $V\mu_n(j)$'s. In this paper we use the word "linear" diffusion when the diffusion process is near equilibrium.

In studying diffusion in the non-linear regime near a junction with steep gradient, we propose to go a step beyond the prevailing treatments based on the sole variable $c(x;t)$, which is based on a point cluster, and examine the significance of correlations. As the first step in this direction, we report the effect of the pair correlations $y(ij;t)$ in this paper. To work with a cluster larger than the point is particularly meaningful because the atomic migration in fcc ordered structures requires a still larger tetrahedron cluster as the basis of CVM and PPM.

**MODEL AND THEORY**

We study isothermal relaxation of a layer structure of a binary atomic system A-B on a fcc lattice as is described in the Introduction. Atoms relax from the initial density profile of sharp step-functions. The theoretical method we use is the Path Probability Method (PPM) (3) in the pair approximation, which is known to lead to the same kinetic differential equations as those derived by the Master Equation Method (MEM) (10) based on the pair variables. The PPM is most suited for our purposes because it is closely tied to the CVM (2) for equilibrium, and also it can avoid possible human errors which may occur when the kinetic difference-differential equations are written intuitively in MEM.

We place the density gradient of the fcc lattice along the [100] direction as in Figure 1. Around a lattice point in an n plane, there are four nearest neighbor bonds in the n plane, four v-l bonds and four v bonds. In order to make the calculation easier to handle, we assume the vacancy density is statistically the same for every lattice point and is $x_n(0; t) = x(0) = 10^{-5}$. This assumption excludes the phenomenon of vacancy accumulation near the boundary, but it is decided that this exclusion is not harmful for the present purposes of studying the behavior of relaxation of sharp junctions. This condition makes the fluxes of A and B components satisfy a constraint relation $J_A + J_B = 0$.

In using PPM (3) we define two sets of variables. One is the "state" variables to describe the state of the system at time $t$, and the other is the "path" variables to describe the change of state in a short time interval $\Delta t$. Using these variables we construct the path probability function which describes the probability that a change defined by the path variables occurs in $\Delta t$. A maximum of the path probability function leads to the most probable direction the system changes into. Since the procedures for deriving these equations are standard (3), the details are omitted. After the difference-differential equations for the state variables are derived, integration was done using the Euler technique. The computer round-off errors are negligibly small.

**RESULTS**

In order not to obscure the main points of concern, we made the jump probabilities of 1 and 2 atoms the same, and made $\epsilon_{11} = \epsilon_{22}$, but chose $4\epsilon = \epsilon_{11} + \epsilon_{22} - 2\epsilon_{12} > 0$, where $\epsilon_{ij} > 0$ is defined as the energy needed to break the i-j bond. Since $\epsilon > 0$, A-rich and B-rich phases separate at low temperatures. Taking account of the critical temperature of the phase separation at $2\epsilon/(kT_c) = 0.182$ for fcc, we choose $2\epsilon/(kT) = 0.15$ for our calculations so that $T > T_c$ and the equilibrium profile is uniform throughout the system.
Figure 1. The gradient direction, the lattice plane number $n$ and the bond number $v$.

Figure 2. Relaxation of the composition profile obtained by integration. The initial composition is $x_n(0) = 0.15$ at the flat bottom, and 0.85 at the flat top. Other curves are at the time steps 450, 1000, 10000, 30000, 100000, 150000, 200000 and 300000 in an arbitrary time interval.
Figure 2 is an example of how the composition changes. The initial profile is a square-shape layer structure in which \( x_n(i=1) = 0.15 \) and \( x_{n+1}(i=1) = 0.85 \) alternate with the layer thickness \( h \), which we choose \( h = 10 \). The initial profile and the jump probabilities are designed for examining the symmetric case. We notice overshooting above 0.85 and below 0.15 in early time steps. Only one peak and one dip are observed around each junction. The peak gradually moves away from the junction toward the center of the hill. These properties are the same as what Tsujimoto (5) and the present authors (6) obtained previously using Cahn-Hilliard equation [4]. As time elapses, the profile smooths out toward the final uniform profile: \( x_n(i; t \to \infty) = 0.5 \).

In order to examine whether \( x_n(1) \) overshoots into unphysical negative region or not, the case when the initial profile is \( x_n(1) = 0.001 \) and \( x_{n+1}(1) = 0.4 \) was studied as shown in Figure 3. We see satisfactorily that near the bottom of \( x_n(1) \) there is no overshooting into the negative values, although we verified numerically that the curve does dip slightly within the positive range. This result is different from Tsujimoto’s (5), the reason being that our free energy curve behaves correctly near \( x_n = 0 \).

**Flux and the Chemical Potential Gradient**

The overshooting in Figure 2 indicates that the net flux \( J_{v=1.5}(1)_R \) of the species #1 from \( n=1 \) to \( n=2 \) is positive. If Onsager’s irreversible thermodynamics for the “linear” diffusion is to hold for this bond, we expect the discrete version of [3]:

\[
J_v(1)_R = - M \frac{\Delta \mu_n}{\Delta n}
\]

Figure 3. Relaxation of the composition profile obtained by integration. The initial composition is \( x_n(1)=0.001 \) at the flat bottom, and 0.4 at the flat top. Other curves are for the time steps 500, 1000, and 2000 in the same time interval as Figure 2.
between \( n = 1 \) and \( 2 \), where the local chemical potential \( \mu_n \) is defined as \( 2\mu_n = \mu_n(1) - \mu_n(2) \). We now examine if [7] holds or not in detail. Since the pair approximations of PPM and of CVM are mutually consistent, we can use the formula of the local chemical potential \( \mu_n \) derived in CVM in interpreting the output of PPM. In the pair approximation of CVM for a one-dimensionally inhomogeneous system, the free energy \( F \) is a function of \( \chi_n(i) \), \( y_n(ij) \) and \( y_v(ij) \). We expand the definition of the chemical potential in the equilibrium state into cases including systems away from equilibrium, and we define the local chemical potential \( \mu_n(i) \) as the change of \( F \) when a species \( i \) is added at \( n \), without destroying the distribution of correlations around the point. Mathematically then \( \mu_n(i) \) is the partial derivative \( \partial F/\partial \chi_n(i) \) keeping independent \( y_n(ij) \) and \( y_v(ij) \) fixed. We then obtain

\[
2/3 \mu_n = -6/7(\varepsilon_{11} - \varepsilon_{22}) - 11\ln \frac{x_n(1)}{x_n(2)} + \ln \left( \frac{y_{v-1}(21)y_{v-1}(11)y_{v}(11)y_{v}(12)}{y_{v-1}(12)y_{v-1}(22)y_{v}(22)y_{v}(21)} \right). \tag{8}
\]

Actually \( \mu_n \) in [8] is defined as the difference of two \( \mu_n(i) \)'s, so that \( F \) is differentiated with respect to \( (x_n(1) - x_n(2))/2 \) to obtain \( \mu_n \). If we assumed the local equilibrium, \( y_n(ij) \) and \( y_v(ij) \) would be determined as a minimum of \( F \) keeping \( x_n(i) \) fixed, and then would be slaved, i.e. would become a function of \( x(i)'s \), to be written as \( y^0_n(ij) \) and \( y^0_v(ij) \). In deriving [8], we do not assume the local equilibrium, and the \( y \) part in [8] contains the contribution not only from \( x_n(i) \) at \( n \) but also from the \( v-1 \) and \( v \) bonds, and hence takes into account the curvature of the density profile. Also it is to be noted that in the equilibrium state, \( \mu_n \) in [8] is constant throughout the one-dimensionally inhomogeneous system including the interphase boundary region.

In order to study the effect of correlations on the sign of \( \Delta \mu_n/\Delta n \), we work with two initial distributions. In both cases \( x_n(l;t=0)'s \) are the same, but we define \( y(ij;t=0) \) differently. In the “local equilibrium initial distribution” (LEID), atomic rearrangement has occurred within the \( n \) plane and the \( v \) bond so that the initial \( F \) has been minimized with respect to \( y_n(ij;t=0) \) and \( y_v(ij;t=0) \) keeping \( x_n(i;t=0) \) fixed, with the exception that at the discontinuous junction we assume no correlation and use the product: \( y_v(ij;t=0) = x_n(i;t=0) x_{n+1}(j;t=0) \). In the “no correlation initial distribution” (NCID), the distribution of species \( i \) and \( j \) within the \( n \) plane is random and the neighbors are not correlated so that we use the product form \( y_n(ij;t=0) = x_n(i;t=0) x_n(j;t=0) \) and \( y_v(ij;t=0) = x_n(i;t=0) x_{n+1}(j;t=0) \) for all \( n \)'s and \( v \)'s. Note that above conditions are only for the initial distribution, and that after \( t=0 \), \( y_n(i;j;t) \) and \( y_v(i;j;t) \) are integrated independently from \( x_n(i;t) \).

The results of integration for the relaxation of the density profile are shown in Figure 4. We watch the \( n = 1.5 \) bond and \( x_{n=2}(1;t) \). The latter builds up and takes its maximum value of about 0.859 at \( t^* \approx 400 \) for LEID and \( t^* \approx 500 \) for NCID, where \( t^* \) is the number of integration steps. In Figure 4, the decreasing curves are the flux \( J_{y_{v=1.5}(1)} \) and the increasing curves are \( (\Delta \mu_n/\Delta n)_{y_{v=1.5}} \) for the NCID and the LEID initial conditions. The flux curves are almost the same for the two cases. We note the following four significant features.

(i). The \( (\Delta \mu_n/\Delta n)'s \) for both NCID and LEID are calculated using the same \( \mu_n \) expression [8] and the same \( x_n(i;t=0) \), the only difference being their initial pair correlation \( y(ij;t=0)'s \). We note that the bond configurations from NCID are farther away from equilibrium than those from LEID. The large difference between NCID and LEID curves indicates the significance of interparticle correlations, \( y(ij)'s \), in the \( \mu \) expression.

(ii). Although \( \Delta \mu_n/\Delta n \) starting with NCID always stays positive while \( \Delta \mu_n/\Delta n \) with LEID starts from negative, the corresponding flux curves are almost the same. This fact indicates that
we cannot interpret $(\Delta \mu_{ij}/\Delta n)_{v=1.5}$ as the driving force for the flux $J_{v=1.5}(1)_{R}$ in the initial region.

(iii). If (7) holds, $\Delta \mu_{ij}/\Delta n$ and the flux starting with LEID should become zero at the same $t^*$. Actually, the former becomes zero at $t^*=270$ and the latter at $t^*=600$. This difference indicates that (7) breaks down, and can be interpreted as the measure of the "non-linearity" of diffusion. Another way of interpreting this difference is to go back to (6). Between the two $t^*$'s, $J_v$ and $\Delta \mu_{ij}/\Delta n$ have the same sign, and violates the inequality (6). Therefore, the difference is the measure of deviation of $y_v(ij)$ from the slaved $y^{0}_{v}(ij)$. In the NCID case, in which the system is farther away from local equilibrium, the non-linearity is larger. The breaking down of (7) observed here is based on the pair approximation. How far we can generalize this is discussed at the end of the section.

(iv). The finite deviation of $y_v(ij)$ from $y^{0}_{v=1.5}(ij)$ signifies that the relaxation time for the pair correlation is sufficiently long compared with the rate of change of the local density $x_n(i)$ near the junction in this model.

Since the density peak at $n=2$ gradually moves inward to $n=3, 4$ and $5$, we examined the fluxes and $(\Delta \mu_{ij}/\Delta n)_v$ for the bonds at $v=2.5, 3.5$ and 4.5. For these cases (7) is not significantly violated, and hence the non-linearity is not very large away from the sharp junction.

It is important, however, to verify that the free energy $F$ for the entire system does decrease with $t^*$. We calculated the dimensionless quantity $BF/N$ per lattice point averaged over the entire system in the two cases and plotted them in Figure 5. The curves show that $F$ decreases monotonically in both LEID and NCID cases, in agreement with the general proof that the free energy always decreases along the natural path of the PPM (11).
Figure 5. Behavior of the free energy in the initial stage of relaxation for the two initial configurations, LEID (solid curve) and NCID (broken curve). The time steps are in the same interval as in Figure 2.

Cause of the Overshooting

Since we have found that $\Delta \mu_\alpha / \Delta n$ cannot be interpreted as the driving force for the atomic flux in the pair approximation of this work, we consider the kinetic explanation for the driving force. We can understand $J_v(1)_R > 0$ for the $v=1.5$ bond as follows. We write

$$J_v(1)_R = Y_v(1)_R - Y_v(1)_L$$

where $Y_v(1)_R$ is the probability of a species #1 to jump from an $n=1$ point to an adjacent $n=2$ point towards right through the $v=1.5$ bond, and $Y_v(1)_L$ is the reverse jump towards left. The most probable path in the pair approximation PPM leads to the following expressions

$$Y_v(1)_R = \Delta t \Theta_1 y_v(0; t) B\{v-1,n,v;t\} G\{n,n+1,v+1;t\}$$
$$Y_v(1)_L = \Delta t \Theta_1 y_v(0; t) G\{v-1,n,v;t\} B\{v,n+1,v+1;t\}$$

where $\Theta_1$ is the attempt frequency factor including the activation energy contribution. The bond-breaking contribution $B\{n-1,n,v;t\}$ and the bond-forming contribution $G\{v-1,n,v;t\}$ depend on $y_v(1)(ij;t)$, $y_n(ij;t)$, $y_v(ij;t)$ and $x_n(i;t)$ as indicated by the arguments. The functional forms of $B$ and $G$ are written in previous papers on PPM (8) and on diffusion (6) and are intuitively understandable, but the details are not needed here.
Since \( y_v(t_0; t) \) and \( y_v(0; t) \) are approximately equal to the products \( x_n(t; t) \times (0) \) and \( x(0) x_{n+1}(t; t) \), respectively, the \( y_v \) factors in [10] make \( J_v(1)_R \) proportional to the negative gradient of \( x_n(1; t) \). When we expand \( y_{v-1}, y_v \) and \( y_{v+1} \) up to linear terms of the gradient and neglect higher order terms, the contributions from the B and G factors make \( J_v(1)_R \) proportional to \(- (\Delta \mu_n/\Delta n)_v \). When we cannot neglect the higher order terms of the gradient, as in the case of the bond connecting \( n=1 \) and \( 2 \) in Figures 2 and 3, we have to consider the gradient of \( x_n(1; t) \) and the bond-breaking and the bond-forming effects explicitly. For \( Y_{v=1.5}(1)_R \), a species 1 at \( n=1 \) is repelled by \( x_{n=0}(2) = 0.85 \), while in \( Y_{v=1.5}(1)_L \) a species 1 at \( n=2 \) is repelled by a weaker force due to \( x_{n=3}(2) = 0.15 \). This makes the contributions of the B and G factors supersede the density gradient contribution for the \( v=1.5 \) bond, and makes \( Y_{v=1.5}(1)_R \) larger than \( Y_{v=1.5}(1)_L \). This is the reason why \( J_v=1.5(1)_R \) in [9] is positive against the concentration gradient. It is, in agreement with the interpretation of the square gradient term in the Cahn-Hilliard equation [4], also that it is due to the repulsive interaction.

**Breaking-down of the Relation [7]**

We observed in (iii) above that the [7] breaks down in the non-linear regime in the pair approximation. It is based on the definition of \( \mu_n \) in [8]. On the other hand, some mathematicians are using the existence of a function \( \Psi(r,t) \) which makes the flux \( J \) to be written as \( J = - MV \Psi(r,t) \) as an axiom from which many theorems are derived. Although their \( \Psi(r,t) \) is always a function of position \( r \) only and does not take into account the correlations among atoms, and also there is no physical reason to accept this relation as an axiom, it is legitimate to ask whether it is possible to modify \( \mu_n \) in [8] in such a way that [7] is always valid, including higher order approximation cases. We cannot deny the possibility. However, we present here an argument that such a modification is extremely difficult.

Before we start, it may be worthwhile to remind us that Onsager's proof (9) of the chemical potential gradient as the driving force was only for the linear case. Now, we note that the breaking-down of [7] occurs near the initial period of integration. Nevertheless, \( \mu_n \) has to satisfy the following long-time requirement when the set of differential equations has asymptotically reached the stationary, i.e. equilibrium, state. This requirement is for all temperatures. When \( T < T_c \), the equilibrium state is phase-separated and there is at least one interphase boundary in the system. In such a structure including the IPB, \( \mu_n \) in [8] is constant independent of \( n \). The numerical results of our PPM satisfies this long-time requirement. Because of the long-time requirement, it seems unlikely to be able to find the \( \mu_n \) expression which satisfies [7] for the initial period of integration. For higher order approximations, and hence in the rigorous limit of statistical mechanics, it seems more unlikely. However, we are not completely denying the possibility of finding the modified expression of chemical potential which always makes [7] valid.

**CONCLUSION**

The irreversible statistical mechanics based on the pair variables is ideally suited in studying the qualitative nature of the junction profile relaxation that exhibits strongly "non-linear" diffusion. Such junctions are abundant in nanoscale layer structures and other components of advanced materials. The present paper concludes the following, which are novel findings except (i). However, we emphasize that the following results are based on the pair approximation.

(i) At the initial stage of relaxation of a sharp profile, overshooting of the profile occurs.
(ii) Near a sharp junction profile, the atom flux changes sign during relaxation, which gives a rare opportunity to examine the condition for validity of the “linear” diffusion theory.

(iii) Near the junction, the chemical potential gradient becomes zero at a different time $t^*$ from that of the atom flux. There is a time period in which atoms do not flow downhill along the chemical potential gradient. This is the indication that the “linear” diffusion theory does not hold here.

(iv) The local chemical potential gradient in non-equilibrium state depends not only on the density gradient but also on atomic pair correlation.

(v) While the overshooting is occurring, the free energy of the entire system monotonically decreases.

(vi) The overshooting can be understood by a kinetic reasoning as due to the repulsion of atoms.

We cannot deny the possibility of modifying the chemical potential $\mu_n$ expression in [8] in such a way that [7] holds in the initial non-linear period of integration, but the possibility is considered remote because of the condition, $\mu_n = \text{constant}$, to be satisfied when the system approaches the equilibrium state after a long-time integration.

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