Statistical Mechanics for Unstable States in Gel’fand Triples and Investigations of Parabolic Potential Barriers

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Abstract

Free energies and other thermodynamical quantities are investigated in canonical and grand canonical ensembles of statistical mechanics involving unstable states which are described by the generalized eigenstates with complex energy eigenvalues in the conjugate space of Gel’fand triplet. The theory is applied to the systems containing parabolic potential barriers (PPB’s). The entropy and energy productions from PPB systems are studied. An equilibrium for a chemical process described by reactions $A + CB \rightleftharpoons AC + B$ is also discussed.

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1. Introduction

Many experimental and theoretical investigations show that thermodynamics is a fundamental dynamics for describing realistic phenomena governed by temperatures. We also know that quantum mechanics is a fundamental one to describe microscopic processes. And we believe that statistical mechanics is a theory connecting quantum mechanics to thermodynamics. In statistical mechanics we know that so-called “principle of equal \textit{a priori} probability” is taken as the guiding principle in the construction of the theory and the Boltzmann entropy is the key word connecting the two fundamental dynamics. Rigorously speaking, thermodynamics is applicable only to true equilibriums described by the maximums of entropies. We, however, know the fact that thermodynamics is applicable to phenomena which are slowly varying with time, such as phenomena in chemical processes, cosmological processes and so on. This fact indicates that the principle of thermodynamics can also be applicable to those phenomena varying very slowly as compared with time-scales needed for making thermal equilibriums locally. In statistical mechanics states included in the count of thermodynamical weights are the eigenstates of quantum mechanics which can have only real energy eigenvalues on Hilbert spaces. All eigenstates in Hilbert spaces are stable and then there is no possibility for introducing the changes with respect to time in statistical mechanics based on quantum mechanics on Hilbert spaces. At present, therefore, we have no reliable theory to investigate paths which connect an initial equilibrium to a final equilibrium. Taking account of the fact that thermodynamics can be applicable to some phenomena slowly varying with time, it seems to be very interesting that we examine statistical mechanics on some extended spaces including unstable states. For this purpose we find out an interesting possibility of the extension of Hilbert spaces to the conjugate spaces in Gel’fand triplets [1], where complex energy eigenvalues describing unstable states are involved.

In the previous paper [2] we have shown the fundamental idea of the extension of statistical mechanics on Hilbert spaces to that on the conjugate spaces of Gel’fand triplets on the basis of principle of equal \textit{a priori} probability and derived canonical distributions with a common time-scale. The fundamental difference between statistical mechanics on Hilbert spaces (SMHS) and that on Gel’fand triplets (SMGT) appears in the count of the states for the evaluation of thermodynamical weight, that is, the new freedom arising from the states with imaginary eigenvalues appears in SMGT, while there is no such freedom in SMHS. This fact changes the entropy $S$ which is defined by

$$S(\mathcal{E}) = k_B \log W(\mathcal{E}),$$

where $W(\mathcal{E})$ is the thermodynamical weight at the total complex energy $\mathcal{E} = E - i\Gamma$ and $k_B$ is the Boltzmann constant. In the evaluation of $W(\mathcal{E})$ two freedoms that arise from the variety of the combinations for composing the real part of the total energy $E = \sum_i \epsilon_i$ and that for composing the imaginary one $\Gamma = \sum_i \gamma_i$ must be taken into account, where $\epsilon_i$ and $\gamma_i$, respectively, denote the real and imaginary parts of the complex
energy eigenvalue \( \varepsilon_i = \epsilon_i - i\gamma_i \) for the \( i \)th constituent. Provided that there is no correlation between the real energy eigenvalues and the imaginary ones, \( W \) is given by the product of the thermodynamical weight for the real part \( W^R(E) \) and that for the imaginary part \( W^3(\Gamma) \)

\[
W(\mathcal{E}) = W^R(E)W^3(\Gamma).
\] (2)

Thus the entropy in SMGT is represented by the sum of the Boltzmann entropy \( S^R(E) \) and the new one \( S^3(\Gamma) \) induced from the freedom of the imaginary energy eigenvalues such that

\[
S(\mathcal{E}) = S^R(E) + S^3(\Gamma),
\] (3)

where \( S^R(E) = k_B \log W^R(E) \) and \( S^3(\Gamma) = k_B \log W^3(\Gamma) \). An explicit example for eqs. (2) and (3) was presented in ref. 3 by using parabolic potentials. The canonical distribution has also been derived as

\[
P(\mathcal{E}_{lm}) = Z^{-1} \exp(-\beta^R E_l - \beta^3 \Gamma_m),
\] (4)

where the canonical partition function is given by

\[
Z = \sum_l \sum_m \exp(-\beta^R E_l - \beta^3 \Gamma_m).
\]

In the partition function the two \( \beta \) factors are related to the two temperatures as

\[
\beta^R \equiv \beta = (k_B T)^{-1}, \quad \beta^3 = (k_B T^3)^{-1},
\] (5)

where \( T \) is the usual temperature of canonical distributions and \( T^3 \) is newly introduced in SMGT [2]. Comparing the time-dependence of the probability distributions for the quantum states on Gel’fand triplets having the total imaginary energy \( \Gamma \), which is given by \( e^{-2\Omega t/\hbar} \), with that of the canonical distribution, we have derived the relation \( \beta^3 = 2t/\hbar \) with the common time-scale \( t \) [2], that is, \( T^3 = \hbar/2k_B t \). (In details, see ref. 2.) We should understand that the canonical distribution is meaningful when \( |\Gamma| \) is small enough to make a thermal equilibrium before the change of the physical properties of the total system. In fact we see that such situations can happen, that is, \( |\Gamma| \) can be as small as possible, including exact zero value, because in Gel’fand triplet formalism [1] all eigenvalues appear in the pair of complex conjugates such as \( \epsilon \mp i\gamma \) and then the total imaginary part \( \Gamma \) can be zero. It is a striking fact that there exist stable systems which are composed of unstable states. An example for the stable systems was presented in ref. 2 in terms of 2-dimensional parabolic potential barriers (PPB’s). It should also be noted that in the 2-dimensional PPB we can show the existence of stationary states with zero imaginary eigenvalue which are understood as stationary flows round the center of PPB [4]. By using the stationary states the energy and entropy productions from PPB were studied and the entropy transfer from \( S^3 \) to \( S^R \) was suggested [3]. This new idea for statistical
mechanics seems to have many interesting applications such as chemical processes, energy production processes without nuclear fusions, the birth of the Universe and so forth.

In the previous paper [2] we presented the fundamental idea for the extension of SMHS to SMGT and derived the canonical distribution with the common time-scale. The presentation is, however, not enough to understand SMGT well, for instance, thermodynamical functions except the entropy are not discussed. In this paper we would like to investigate the new statistical mechanics i.e. SMGT involving unstable states on Gel’fand triplets more precisely. Namely, thermodynamical quantities such as free energies and chemical potentials will be investigated in SMGT in §§ 2 and 3. Consistency of the theory will be examined in terms of simple PPB models in § 4. The entropy transfer from $S^\mathbb{I}$ to $S^\mathbb{R}$ and the energy production are studied through a decay of a resonance system in PPB in § 5. An equilibrium for a simple process described by reactions $A + CB \rightleftharpoons AC + B$ will be discussed in this scheme in § 6. Throughout this paper we deal with the processes in which the real and the imaginary parts of the total energy of the system can be independently determined such as the case of parabolic potentials presented in refs. 2 and 3.

2. Free energies in canonical ensemble

Let us start from the canonical distribution of (4). In the present case where the real and the imaginary energies of the system can be independently determined, the canonical partition function for the system composed of $N$ constituents can be obtained as the product of the partition function for the real part and that for the imaginary one such that

$$Z_N(T,t) = Z_N^\mathbb{R}(T)Z_N^\mathbb{I}(t),$$  \hspace{1cm} (6)

where

$$Z_N^\mathbb{R}(T) = \sum_i \exp(-\beta E_i), \quad Z_N^\mathbb{I}(t) = \sum_m \exp(-\beta^3 \Gamma_m).$$

Following the same argument carried out in SMHS, we have two (Helmholtz) free energies corresponding to the usual free energy for the real part $F^\mathbb{R}$ and that for the imaginary part $F^\mathbb{I}$ as

$$F^\mathbb{R}(T) = -\beta^{-1} \log Z_N^\mathbb{R}, \quad F^\mathbb{I}(t) = -\beta^{-3} \log Z_N^\mathbb{I}.$$  \hspace{1cm} (7)

The mean energies are obtained as usual

$$\overline{E} = \frac{\partial}{\partial \beta} \left[ \beta F^\mathbb{R}(T) \right], \quad \overline{\Gamma} = \frac{\partial}{\partial \beta^3} \left[ \beta^3 F^\mathbb{I}(T) \right].$$  \hspace{1cm} (8)

The relations with respect to other quantities derived from $F^\mathbb{R}$ such as the total volume $V$, the pressure $p$ and so forth are same as SMHS. At present, however, it is not an easy
problem to clarify whether new quantities derived from $F^3$ are physically meaningful or not. The entropies $S^R$ and $S^3$ are derived from the free energies as

$$S^R = -\frac{\partial}{\partial T} F^R(T), \quad S^3 = -\frac{\partial}{\partial T^3} F^3(t).$$  \hspace{1cm} (9)

The consistency of $S^3$ given in (9) with that of (3) given in microcanonical ensemble [2] will be studied in a PPB model in § 4. In general the entropy $S^3$ and the mean value $\bar{\Gamma}$ have time-dependence, which will also be investigated in the PPB model. The free energies satisfy the usual relation of SMHS such that

$$F^R = E - T S^R, \quad F^3 = \bar{\Gamma} - T^3 S^3.$$  \hspace{1cm} (10)

Since we do not know what are good observables in unstable systems and still have only one example of PPB to adopt SMGT [3], we have to examine SMGT more in other realistic examples in order to understand the meanings of SMGT in details.

3. Grand canonical ensemble

The most prominent aim of SMGT is the introduction of time-dependence through the decay of the constituents of systems. This means that the total number of constituents composing the systems also varies with time. This situation will be well described in grand canonical ensemble. In the construction of grand canonical ensemble the number of the constituents should be represented by natural numbers $N \ (N = 0, 1, 2, \cdots)$. Then we construct the grand partition function as

$$\Xi = \sum_{N=0}^{\infty} e^{\beta \mu N} Z_N,$$  \hspace{1cm} (11)

where $Z_N$ is the partition function for the total number $N$ and given by the product $Z^R_N Z^3_N$. In the definition of $\Xi$ the usual factor $\beta$ is taken so as to coincide with the partition function of SMHS when the freedom of the imaginary part disappears. The chemical potential $\mu$, of course, differs from that of SMHS and generally has the time-dependence. The specific difference of $\Xi$ from $Z_N$ is seen in the forms of (6) and (11), that is, the contributions from the real and the imaginary parts cannot be separated in $\Xi$, whereas they are separated as the product in $Z_N$. We, therefore, have only one thermodynamical function in the grand canonical ensemble given by

$$J(T, t, \mu) = -\beta^{-1} \log \Xi.$$  \hspace{1cm} (12)

The mean number is obtained by

$$\bar{N} = \beta^{-1} \frac{\partial}{\partial \mu} \log \Xi.$$  \hspace{1cm} (13)
which have the time-dependence in general. An example of the time-dependence will be seen in a PPB model.

Taking into account that the contributions of the real and imaginary parts are not separable in $\Xi$, the maximum of the probability in the grand canonical ensemble appears at

$$J/T = E/T - S^R + \Gamma/T^3 - S^\Im - \bar{N} (\partial S/\partial N),$$

where the relations $\partial S^R/\partial E = 1/T$ and $\partial S^\Im/\partial \Gamma = 1/T^3$ are used [2]. Now we can see that the definition of the chemical potential $\mu$ is given by the relation

$$\frac{\mu}{T} = -\frac{\partial S}{\partial N},$$

where $S = S^R + S^\Im$. The Gibbs free energy $G$ is given as usual

$$G = \mu \bar{N}.$$  

Note that the relation between the thermodynamical functions $J = F - G$ in SMHS should not be adopted. In SMGT the relation should be read as

$$J/T = F^R/T + F^\Im/T^3 - G/T.$$  

In simple cases where all constituents can be treated as independent each other, the canonical partition function is written by the

$$Z_N = (Z_1)^N,$$  

where $Z_1 = Z_1^R Z_1^\Im$ is the partition function for one constituent. We then obtain

$$\Xi = (1 - e^{\beta \mu} Z_1)^{-1}$$

with the constraint for the chemical potential

$$e^{\beta \mu} Z_1 < 1.$$  

When the constituents cannot be identified each other such as free particles, we should have

$$\Xi = \sum_{N=0}^{\infty} e^{\beta \mu N} (Z_1)^N/N!$$

and then we get

$$\Xi = \exp(e^{\beta \mu} Z_1).$$
4. Simple examples

4.1 HO+PPB case

We shall here examine SMGT in a simple example that is represented by 1-dimensional harmonic oscillator (HO) + 1-dimensional parabolic potential barrier (PPB)

\[ V(x, y) = \frac{1}{2} m \omega^2 x^2 - \frac{1}{2} m \gamma^2 y^2, \]

where \( m \) is a constant with the mass dimension. The eigenvalues of HO is well-known as

\[ \varepsilon_{nx} = \left( n_x + \frac{1}{2} \right) \hbar \omega \]

(21)

and the eigenvalues of PPB on the Gel’fand triplet are known to be pure imaginary values as [5–10]

\[ \varepsilon_{ny} = \mp i \left( n_y + \frac{1}{2} \right) \hbar \gamma, \]

(22)

where \( n_x \) and \( n_y \) are natural numbers \( n_x, n_y = 0, 1, 2, \ldots \). It is known that the \( \mp \) of the eigenvalues in PPB, respectively, stand for the decaying and growing resonance states. In this section we shall deal only with the states having the negative imaginary eigenvalues of PPB, which represent the decays of resonances for the time-scale \( t \geq 0 \) [1, 5–9]. Then the energy of a constituent is written by

\[ \varepsilon_{nxny} = \left( n_x + \frac{1}{2} \right) \hbar \omega - i \left( n_y + \frac{1}{2} \right) \hbar \gamma. \]

(23)

(1) Microcanonical ensemble

Let us start from microcanonical ensemble for the system composed of \( N \) independent particles being in the above potential \( V(x, y) \). The total complex energy of the system \( \mathcal{E} \) is represented by

\[ \mathcal{E}_{M^R M^3} = \left( M^R + \frac{1}{2} N \right) \hbar \omega - i \left( M^3 + \frac{1}{2} N \right) \hbar \gamma, \]

(24)

where \( M^R = \sum_{i=1}^{N} n_{xi} \) and \( M^3 = \sum_{i=1}^{N} n_{yi} \). Hereafter we shall use the notations \( E = (M^R + N/2)\hbar \omega \) for the total real energy and \( \Gamma = (M^3 + N/2)\hbar \gamma \) for the total imaginary energy. The thermodynamical weight is evaluated as

\[ W_N(M^R, M^3) = W_N^R(M^R)W_N^3(M^3), \]

(25)
where
\[{W^R_N(M^R)} = \frac{(M^R + N - 1)!}{M!^{R!}(N - 1)!},
\]
\[{W^\Im_N(M^\Im)} = \frac{(M^\Im + N - 1)!}{M!^{\Im!}(N - 1)!}.\]
The entropy is obtained by
\[S(E) = S^R(E) + S^\Im(\Gamma),\]
where the contributions from the real and imaginary parts are expressed in the same form as
\[S^\bullet = k_B [(M^\bullet + N) \log(M^\bullet + N) - M^\bullet \log M^\bullet - N \log N],\] (26)
where \(\bullet\) denotes \(R\) or \(\Im\) and \(M^\bullet, N \gg 1\) are postulated as usual. The complete symmetry between the contributions of HO and PPB in the entropy originates from the completely same structure of the total real and imaginary parts of the energy. We can introduce two temperatures corresponding to two constraints for giving the maximum of the entropy \(S\) as [2]
\[\frac{1}{T} = \frac{\partial S^R}{\partial E}, \quad \frac{1}{T^\Im} = \frac{\partial S^\Im}{\partial \Gamma}.\] (27)
The explicit forms are obtained as
\[\frac{1}{T} = \frac{k_B}{\hbar \omega} \log \frac{E/N + \hbar \omega/2}{E/N - \hbar \omega/2}, \quad \frac{1}{T^\Im} = \frac{k_B}{\hbar \gamma} \log \frac{\Gamma/N + \hbar \gamma/2}{\Gamma/N - \hbar \gamma/2}.\] (28)
Everything can be derived from the entropies, following the argument carried out in SMHS, e.g.
\[E = N \left(\frac{1}{2} \hbar \omega + \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1}\right), \quad \Gamma = N \left(\frac{1}{2} \hbar \gamma + \frac{\hbar \gamma}{e^{\beta \hbar \gamma} - 1}\right).\] (29)
Since \(\beta^\Im = 2t/\hbar\), we see the time-dependence of the total imaginary energy \(\Gamma\) in the second equation of (29), which will be examined afterwards.

(2) Canonical ensemble
Following the argument given in § 2, the partition functions for the real and imaginary parts are obtained as
\[Z^\bullet_N = \left(\frac{e^{-\beta^\bullet \hbar \Omega/2}}{1 - e^{-\beta^\bullet \hbar \Omega}}\right)^N,\] (30)
where $\Omega = \omega$ in the real part for $\bullet = \mathbb{R}$ and $\Omega = \gamma$ in the imaginary part for $\bullet = \mathbb{I}$ should be taken. The derivations of the free energies $F^\mathbb{R}$ and $F^\mathbb{I}$ given in (7) are trivial. It is easy to examine that the mean values of $E$ and $\Gamma$ are same as those derived in (29) of microcanonical ensemble. The entropies of (9) are evaluated as

$$S^\bullet = N k_B \left[ \beta^\bullet \hbar \Omega e^{\beta^\bullet \hbar \Omega} - 1 - \log(e^{\beta^\bullet \hbar \Omega} - 1) \right]. \quad (31)$$

We also easily see that they coincide with those given in (26) of microcanonical ensemble.

(3) Grand canonical ensemble

The present case is the independent particle model discussed in the last of the previous section. Then we can immediately get the partition function from (19);

$$\Xi = \frac{1}{1 - e^{\beta \mu} Z_1}, \quad (32)$$

where the canonical partition function $Z_1$ for a particle is given by

$$Z_1 = \left( \frac{e^{-\beta \hbar \omega/2}}{1 - e^{-\beta \hbar \omega}} \right) \left( \frac{e^{-\beta^3 \hbar \gamma/2}}{1 - e^{-\beta^3 \hbar \gamma}} \right).$$

The mean number is obtained as

$$\bar{N} = \frac{e^{\beta \mu} Z_1}{1 - e^{\beta \mu} Z_1}. \quad (33)$$

From this equation the chemical potential is expressed by

$$\mu = \beta^{-1} \left[ \frac{1}{2} \beta \hbar \omega + \log(1 - e^{-\beta \hbar \omega}) + \frac{1}{2} \beta^3 \hbar \gamma + \log(1 - e^{-\beta^3 \hbar \gamma}) - \log(1 + \frac{1}{\bar{N}}) \right]. \quad (34)$$

For $\bar{N} \gg 1$ the contribution of the last term in the right-hand side of the above equation vanishes. Then we see the behavior of $\mu$ for small $t$ as follows;

$$\mu \sim \log \gamma t \quad \text{for} \quad t \to 0. \quad (35)$$

The divergence at $t = 0$ appears so as to cancel the divergence of $Z_1^3$ at $t = 0$, because in the canonical distribution (4) the dumping factor $e^{-\beta^3 \Gamma}$ disappears at $t = 0$ and then $Z_1^3$ becomes infinity, of which divergence is easily obtained as the $t^{-1}$ type. Note here that the divergences also appear in $S^3$ and $\bar{\Gamma}$ as $\log t$ and $t^{-1}$ types, respectively.

Thus we obtain the $t$-dependence of all thermodynamical quantities for the systems involving unstable states for small $t$-values.
4.2 \textit{d-dimensional free motion + PPB case}

Let us briefly discuss one more example described by the \textit{d-dimensional free motion + PPB}, where the equation of states with respect to the temperature \( T \), volume \( V \) and pressure \( p \) are treatable. Here we study the problem in terms of \( T-p \) distribution of which partition function is defined by

\[
Y = \int_0^\infty e^{-\beta pV} Z_N dV,
\]

(36)

where the canonical partition function \( Z_N = Z_N^R Z_N^\Im \). The real part \( Z_N^R \) for the free motions is given by

\[
Z_N^R = \frac{1}{N! (2\pi \hbar)^d N} (2\pi m k_B T)^{dN/2}
\]

(37)

and the imaginary part \( Z_N^\Im \) for the 1-dimensional PPB is the same as that of the previous model. After the integration we have

\[
Y = \frac{1}{(2\pi \hbar)^d N} (2\pi m k_B T)^{dN/2} \left( \frac{k_B T}{p} \right)^N Z_N^\Im.
\]

(38)

From the thermodynamical relation \( G = -\beta^{-1} \log Y \) for \( N \gg 1 \) we obtain

\[
G = -N \beta^{-1} \left[ \frac{d + 2}{2} \log T - \log p + \log \frac{(d+2)/k_B}{(2\pi \hbar^2)^{d/2}} - \frac{1}{2} \beta^3 \hbar \gamma - \log(1 - e^{-\beta \hbar \gamma}) \right].
\]

(39)

The equation of states is immediately derived from the relation \( V = \partial G/\partial p \) as usual

\[ pV = N k_B T. \]

Note here that this equation describes the relation between \( V \) and \( p \) for the free motions. In order to answer the question whether physical quantities for the imaginary freedom corresponding to the volume and the pressure are meaningful or not, we have to study the meanings of continuous imaginary spectra on Gel’fand triplet, which do not represent usual resonances described by the Breit-Wigner resonance formula in cross-sections.

The chemical potential is gotten from the relation \( G = \mu N \) as

\[
\mu = k_B T \left[ \log \frac{p}{k_B T} \left( \frac{2\pi \hbar^2}{m k_B T} \right)^{d/2} + \frac{1}{2} \beta^3 \hbar \gamma + \log \left( 1 - e^{-\beta \hbar \gamma} \right) \right].
\]

(40)

It has the \( t \)-dependence of the log \( t \) type at small \( t \), which is same as the previous case given by (34). The same result for \( \mu \) can be obtained in grand canonical ensemble, where the number \( N \) should be replaced by the mean number \( \bar{N} \).
From the above examples we see that SMGT is applicable to realistic processes.

5. Entropy transfer from $S^3$ to $S^R$

Let us consider the entropy transfer from $S^3$ to $S^R$ in an adiabatic process described by a decay of a system that is composed of $N$ resonances in a 1-dimensional PPB+some ordinary potentials, where the ordinary potentials mean potentials which are described by Hilbert spaces and the systems described the potentials can have thermal equilibrium of SMHS. We can, therefore, consider that $S^3$ and $S^R$, respectively, stand for the entropy of the PPB system and that of the ordinary system. Here we study the process where the decays of the resonance system are absorbed into the system described by the ordinary potentials. After the decay processes are opened at $t = 0$, the entropy of the system being in the PPB is obtained from (31) as

$$S^3 = Nk_B \left[ 2\gamma t \frac{e^{2\gamma t}}{e^{2\gamma t} - 1} - \log(e^{2\gamma t} - 1) \right].$$

For small $t$ such that $\gamma t \ll 1/2$ the entropy behaves

$$S^3 \simeq -Nk_B \log \tau$$

where $\tau = \gamma t$. As already noted, it diverges at $t = 0$. This relation gives us

$$dS^3 = -Nk_B \frac{d\tau}{\tau} \text{ for } \tau \ll \frac{1}{2}.$$  \hfill (43)

Since the total entropy conserves in the adiabatic process, that is, the relation

$$dS = dS^R + dS^3 = 0$$

holds, we have the relation

$$dS^R = -dS^3.$$  \hfill (45)

Note here that $dS^R$ is always positive because $dS^3 < 0$ is kept. In the system described only by PPB’s the temperature $T$ originated from the freedom of real energy eigenvalues is zero, i.e. $T = 0$, since the system has no real energy freedom. This means that the temperature must be zero at $t = 0$, i.e., just at the moment when the decay processes are opened. Let us write it as

$$T(t) = K_0 \tau^\delta \text{ for } \tau \ll \frac{1}{2}.$$  \hfill (46)

where $K_0$ and $\delta$ should be positive constants. Since the direct observable in this process is the real energy $E^R$ released into the ordinary potentials by the decay of resonances, we should evaluate the real energy produced in this process. For the small $t$ we have

$$dE^R = T(t)dS^R = Nk_B K_0 \tau^{\delta-1} d\tau \text{ for } \tau \ll \frac{1}{2}.$$  \hfill (47)
Then we can estimate the real energy produced in the process during the short period from 0 to \( t \) \((\ll 1/2\gamma)\) as

\[
E^R = \int_0^{\gamma t} \frac{dE^R}{d\tau} d\tau = Nk_B \frac{K_0}{\delta} (\gamma t)^{\delta}.
\]

Since \( \delta > 0 \), this process produces a real positive energy. Even if \( S^3 \) diverges at \( t = 0 \), we obtain a finite energy production. The unknown constants \( K_0 \) and \( \delta \) will depend on the property of the system where the produced energy is absorbed. We see that the system in PPB’s can be the source of the energy production. It, of course, does not mean the break down of the energy conservation law. In the process where the system is composed in the PPB the real energy produced in the decay process is stored as \( S^3 \) in the system. This means that the total produced energy which is evaluated by the integration from \( t = 0 \) to \( \infty \) must coincide with the energy consumed in the process for making the initial system. This integration will derive a relation between \( K_0 \) and \( \delta \).

6. Equilibrium of a process described by reactions \( A + CB \rightleftharpoons AC + B \)

As discussed by Child, the chemical reaction \( A + CB \rightarrow AC + B \) is well described by the potential having two bumps [11, 12]. Connor studied the reaction by representing the potential in terms of PPB’s [13]. They investigated the reaction cross-sections of the processes in the WKB method and showed that the cross-sections were given by the Breit-Wigner resonance formula. The Breit-Wigner formulas of the cross-sections for PPB scatterings have already been obtained in our scheme based on the Gel’fand triplet [9]. Here we shall study chemical equilbriums of the systems containing two reactions \( A + CB \rightarrow AC + B \) and \( AC + B \rightarrow A + CB \) \((A + CB \rightleftharpoons AC + B)\) simultaneously. We study the case where the potentials for the exchanged particle \( C \) is described by two 1-dimensional PPB’s having the centers at the positions of \( A \) and \( B \) which are spatially separated enough to treat them as two independent systems. The PPB constants of the systems \( A \) and \( B \) are denoted by \( \gamma_1 \) and \( \gamma_2 \), respectively. The total systems are described by an ensemble composed of \( N \)-number of independent reactions \( A + CB \rightleftharpoons AC + B \). In the present discussion we postulate that the systems \( A \) and \( B \) are heavy enough to neglect their movements in the interactions with \( C \). Note here that the reaction \( A + CB \rightarrow AC + B \) describing the process that the particle \( C \) is approaching to \( A \) is understood as the growing resonance state for the system \( A \), but the same process is, on the other hand, understood as the decaying resonance state for the system \( B \) because the particle \( C \) is leaving from \( B \). The reaction \( AC + B \rightarrow A + CB \) describing the process that \( C \) is approaching to \( B \) is understood vice versa. From this consideration on the growing and decaying resonance states, we see that there are the following relations between the number of the growing resonances \( N_1^- \) for the system \( AC \) and that of the decaying resonances \( N_2^+ \) for the system \( BC \) and also between the number of the decaying ones \( N_1^+ \) for \( AC \) and that of the growing
the relations \( E \) are written by

\[
N_1^− = N_2^+, \quad N_1^+ = N_2^−, \quad \text{(49)}
\]

Thus the total number \( N \) is expressed by the sum \( N = N_1^− + N_1^+ \) provided that we pay attention to the system \( AC \), whereas it is written down by the sum \( N = N_2^+ + N_2^− \) from the side of the system \( BC \). In microcanonical ensemble the imaginary parts of the energies of the growing and decaying states for the reactions \( A + CB \rightleftharpoons AC + B \) are, respectively, given by

\[
\begin{align*}
\Gamma_1^- &= \left( M_1^- + \frac{1}{2} N_1^- \right) \hbar \gamma_1, & \Gamma_2^+ &= \left( M_2^+ + \frac{1}{2} N_1^- \right) \hbar \gamma_2, & \text{for } A + CB \rightarrow AC + B, \\
\Gamma_2^- &= \left( M_2^- + \frac{1}{2} N_1^+ \right) \hbar \gamma_2, & \Gamma_1^+ &= \left( M_1^+ + \frac{1}{2} N_1^+ \right) \hbar \gamma_1, & \text{for } AC + B \rightarrow A + CB,
\end{align*}
\]

\[
\text{(50)}
\]

where the imaginary parts are defined by \( \mathcal{E}_i^\pm = \mp i \Gamma_i^\pm \) (suffix \( i = 1, 2 \)), \( M_i^\pm = 0, 1, 2, \ldots \) and the relations of (49) are used. Note that the total imaginary energies of \( AC \) and \( BC \) are written by \( \mathcal{E}_1 = -i(\Gamma_1^+ - \Gamma_1^-) \) and \( \mathcal{E}_2 = -i(\Gamma_2^+ - \Gamma_2^-) \), respectively. In the equilibrium the relations

\[
\Gamma_1^- = \Gamma_2^+, \quad \Gamma_1^+ = \Gamma_2^-
\]

\[
\text{(51)}
\]

must be satisfied, since the \( t \)-dependence of the canonical ensemble for the reaction \( A + CB \rightarrow AC + B \), which is given by \( e^{-\beta(t^+_2 - t^-_1)} \), and that for \( AC + B \rightarrow A + CB \) given by \( e^{-\beta(t^+_1 - t^-_2)} \) must vanish in the equilibrium. Now we have the thermodynamical weight as

\[
W = W_1 W_2,
\]

\[
\text{(52)}
\]

where

\[
\begin{align*}
W_1 &= \left( \frac{(M_1^+ + N_1^+ - 1)! (M_1^- + N - N_1^+ - 1)!}{M_1^+!(N_1^+ - 1)! M_1^-(N - N_1^+ - 1)!} \right), \\
W_2 &= \left( \frac{(M_2^- + N_1^+ - 1)! (M_2^+ + N - N_1^+ - 1)!}{M_2^-!(N_1^+ - 1)! M_2^+(N - N_1^+ - 1)!} \right)
\end{align*}
\]

\[
\text{(53)}
\]

The maximum of the entropy is realized at the point, where the relation

\[
\frac{\partial}{\partial N_1^+} \log W = \log \frac{(M_1^+ + N_1^+)(M_2^- + N_1^+)(N - N_1^+)^2}{(M_1^- + N - N_1^+)(M_2^+ + N - N_1^+)(N_1^+)^2} = 0,
\]

\[
\text{(54)}
\]

is fulfilled, where \( M, N \gg 1 \) are used. We have the equation satisfied in the equilibrium

\[
(M_1^- + N_1^-)(M_2^- + N_1^-)(N_1^+)^2 = (M_1^+ + N_1^+)(M_2^+ + N_1^+)(N_1^-)^2,
\]

\[
\text{(55)}
\]
where $N_1^- = N - N_1^+$ is put. By using the relations of (50) and (51) we obtain the equation
\[
\left( \frac{\Gamma_1^-}{N_1^-} + \frac{1}{2} \hbar \gamma_1 \right) \left( \frac{\Gamma_1^-}{N_1^-} + \frac{1}{2} \hbar \gamma_2 \right) = \left( \frac{\Gamma_1^+}{N_1^+} + \frac{1}{2} \hbar \gamma_1 \right) \left( \frac{\Gamma_1^+}{N_1^+} + \frac{1}{2} \hbar \gamma_2 \right).
\] (56)

Taking account of the constraints $\Gamma_1^- / N_1^- > 0$ and $\Gamma_1^+ / N_1^+ > 0$, we get the solution
\[
\frac{\Gamma_1^-}{N_1^-} = \frac{\Gamma_1^+}{N_1^+}.
\] (57)

This result shows that the mean grow width for a growing resonance, $\Gamma_1^- / N_1^-$, is equal to the mean decay width for a decaying resonance, $\Gamma_1^+ / N_1^+$, for the system $AC$. From the relations of (49) and (51) we can, of course, derive the relation $\Gamma_2^- / N_2^- = \Gamma_2^+ / N_2^+$ for the system $BC$. Generally the relations
\[
\frac{\Gamma_1^-}{N_1^-} = \frac{\Gamma_1^+}{N_1^+} = \frac{\Gamma_2^-}{N_2^-} = \frac{\Gamma_2^+}{N_2^+}
\] (58)
are obtained. These relations indicate that a kind of balance like a detailed balance is held between the grow processes and the decay ones in the reaction $A + CB \rightleftharpoons AC + B$.

Though this model is too much simple to describe realistic chemical processes, we can at least say that this scheme (SMGT) is consistent with our primitive understandings.

7. Discussions

We have proposed a statistical mechanics which can contains unstable states on Gel’fand triplets (SMGT) and applied it to a few simple processes. The validity of this theoretical scheme will be examined by applying it to many realistic processes and by comparing with experiments. We should, however, remember that SMGT is applicable to the processes where the change of systems with respect to time are so slow that the systems can be dealt with as being in a thermal equilibrium at any moment.

Here we shall comment on a general formula for the equation of motion for the mean values in canonical ensembles. Provided that the real and imaginary parts are separable as the canonical distribution given by (4), the mean value of the quantity $A(\Gamma)$ is obtained by
\[
\bar{A} = \int A(\Gamma)e^{-\beta \mathcal{I}_\Gamma W_\mathcal{I}(\Gamma)}d\Gamma \bigg/ \int e^{-\beta \mathcal{I}_\Gamma W_\mathcal{I}(\Gamma)}d\Gamma.
\] (59)

In general we should consider that the average with respect to the real energy part has already been taken as for $A(\Gamma)$. The derivative of $\bar{A}$ with respect to $t$ is evaluated as
\[
\frac{d\bar{A}}{dt} = \frac{2}{\hbar} \left\{ -\int A(\Gamma)e^{-\beta \mathcal{I}_\Gamma W_\mathcal{I}(\Gamma)}d\Gamma \int e^{-\beta \mathcal{I}_\Gamma W_\mathcal{I}(\Gamma)}d\Gamma \mathcal{I}_\Gamma A(\Gamma) + \int A(\Gamma)e^{-\beta \mathcal{I}_\Gamma W_\mathcal{I}(\Gamma)}d\Gamma \int \mathcal{I}_\Gamma e^{-\beta \mathcal{I}_\Gamma W_\mathcal{I}(\Gamma)}d\Gamma \int e^{-\beta \mathcal{I}_\Gamma W_\mathcal{I}(\Gamma)}d\Gamma \right\} \right/ \left[ \int e^{-\beta \mathcal{I}_\Gamma W_\mathcal{I}(\Gamma)}d\Gamma \right]^2 \bigg/ \left[ \int e^{-\beta \mathcal{I}_\Gamma W_\mathcal{I}(\Gamma)}d\Gamma \right]^2
\] (60)
For $A = \Gamma$ we have the equation

$$\frac{d\tilde{\Gamma}}{dt} = -\frac{2}{\hbar}(\Delta \Gamma)^2 < 0,$$

(61)

where $(\Delta \Gamma)^2 = \tilde{\Gamma}^2 - (\tilde{\Gamma})^2$. This equation means that $\tilde{\Gamma}$ becomes small in the time evolution in all processes. Considering the fact that states with large imaginary eigenvalues decay rapidly, we can comply with this result.

Throughout this paper we have discussed the cases where the total real and imaginary parts $E$ and $\Gamma$ are independently determined. Gel’fand triplets, however, contain many other solutions such that the real and imaginary eigenvalues $\epsilon$ and $\gamma$ have some correlations. In such processes the thermodynamical weight cannot be obtained by the simple product of $W^\mathbb{R}$ and $W^\mathbb{I}$ as given in (2) [2]. Study of such processes is still an open question in the present SMGT.

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