

Statistical mechanics for unstable states in Gel'fand triplets and investigations of parabolic potential barriers

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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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I. 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 the so-called "principle of equal *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. A Gel'fand triplet consists of the following triplet:

$$\Phi \subset \mathcal{H} \subset \Phi^\times,$$

where Φ , \mathcal{H} , and Φ^\times , respectively, stand for a nuclear space, Hilbert space and the conjugate space of Φ . From this relation we see that the conjugate space Φ^\times of the Gel'fand triplet contains the original Hilbert space \mathcal{H} and in general it can include eigenstates with complex energy eigenvalues that are not included in the original Hilbert space \mathcal{H} . It should also be noticeable that the complex energy eigenvalues are represented by pairs of complex conjugates such as $a \mp ib$ for $a, b \in \mathbb{R}$, that is, since Hamiltonians \hat{H} are real on Φ , for any solutions $\psi \in \Phi^\times$ satisfying the equation

$$\hat{H}\psi = (a - ib)\psi \quad \text{for } a, b \in \mathbb{R},$$

we always find solutions having complex conjugate eigenvalues such that

$$\hat{H}\psi^* = (a + ib)\psi^*.$$

An explicit example has been presented in a parabolic potential barrier (PPB) $V(x) = -m\gamma^2 x^2/2$, where the energy eigenvalues are obtained by $\mp i(n + 1/2)\hbar\gamma$, n being positive integers including zero [2-7]. We can see that there is a possibility that the imaginary parts of energy eigenvalues cancel each other in many body states consisting of the states with complex energy eigenvalues in Gel'fand triplets and then the total imaginary part of the many body states can be very small including exact zero value. Furthermore we can expect stationary states with zero imaginary energy eigenvalues in more than two-dimensional space. Such an example has been presented in the two-dimensional PPB $V(x, y) = -m\gamma^2(x^2 + y^2)/2$, where the eigenvalues including zero energy eigenvalue are obtained as $\mp i(n_x - n_y)\hbar\gamma$, where n_x and n_y are positive integers including zero. From the eigenvalues we see that the stationary states with the zero energy eigenvalue appear for $n_x = n_y$ and the states with an equal energy are infinitely degenerate [8]. It has been shown that the degeneracy plays an interesting role to investigate vortex structures that are determined by nodes of wave functions described in terms of the superposition of the infinitely degenerate states [8]. It is natural that we expect that some kind

of statistical mechanics will be applicable to the systems involving the states with complex energy eigenvalues in the conjugate spaces of Gel'fand triplets.

It is known that states with complex energies have been investigated in terms of the method of complex scaling [9,10] and the analytical continuation of semiclassical solutions [11–13]. They have been successfully applied to some chemical processes [9,10] and helium negative ion resonances [11–13]. In these methods the complex scaling of solutions of Hilbert spaces and the analytical continuation of semiclassical solutions solved by the WKB approximations are used. In such cases, however, the states with negative imaginary energies are chosen, while those with positive imaginary energies are eliminated. This choice is quite natural, because the decay processes that are described by the states with the negative imaginary energies are experimentally observed whereas the states with the positive imaginary energies that represent the processes forming resonances cannot directly be observed in experiments. In the PPB case the situation is same, that is, the states with negative imaginary energies represent the resonance decays which are expressed by well-known Breit-Wigner resonance formulas, whereas those with positive imaginary energies represent the resonance formations. (For details, see Ref. [6].) It is, however, noted that both processes, the decay processes and the formation processes, generally coexist in many body systems. A similar situation occurs in the two-dimensional PPB, that is, the analytical continuation from the solutions of the two-dimensional harmonic oscillator (HO) derives the states having the energy eigenvalues $\mp i(n_x + n_y + 1)\hbar\gamma$, which do not contain any stationary states and represent diverging and converging flows. The abovementioned states with the energy eigenvalues $\mp i(n_x - n_y)\hbar\gamma$ including the stationary states, which satisfy the different boundary condition from those taken in the original HO and represent corner flows, cannot be obtained by the analytical continuation. (For details, see Ref. [8].) In statistical mechanics the complete knowledge of the states in the physical space are required in the count of the number of different states describing complex systems (thermodynamical weight). For the purpose of the exact evaluation of thermodynamical weight we have to construct statistical mechanics on Gel'fand triplets.

In a previous paper [14] 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 *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

$$S(\mathcal{E}) = k_B \ln W(\mathcal{E}), \quad (1)$$

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 ϵ_i and γ_i , respectively, denote the real and imaginary parts of the complex energy eigenvalue $\epsilon_i = \epsilon_i - i\gamma_i$ 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 $W^{\text{Re}}(E)$ and that for the imaginary part $W^{\text{Im}}(\Gamma)$

$$W(\mathcal{E}) = W^{\text{Re}}(E) W^{\text{Im}}(\Gamma). \quad (2)$$

Thus the entropy in SMGT is represented by the sum of the Boltzmann entropy $S^{\text{Re}}(E)$ and the new one $S^{\text{Im}}(\Gamma)$ induced from the freedom of the imaginary energy eigenvalues such that

$$S(\mathcal{E}) = S^{\text{Re}}(E) + S^{\text{Im}}(\Gamma), \quad (3)$$

where $S^{\text{Re}}(E) = k_B \ln W^{\text{Re}}(E)$ and $S^{\text{Im}}(\Gamma) = k_B \ln W^{\text{Im}}(\Gamma)$. An explicit example for Eqs. (2) and (3) was presented in Ref. [15] by using parabolic potentials. The canonical distribution has also been derived as

$$P(\mathcal{E}_{lm}) = Z^{-1} \exp(-\beta^{\text{Re}} E_l - \beta^{\text{Im}} \Gamma_m), \quad (4)$$

where the canonical partition function is given by

$$Z = \sum_l \sum_m \exp(-\beta^{\text{Re}} E_l - \beta^{\text{Im}} \Gamma_m).$$

In the partition function the two β factors are related to the two temperatures as

$$\beta^{\text{Re}} \equiv \beta = (k_B T)^{-1}, \quad \beta^{\text{Im}} = (k_B T^{\text{Im}})^{-1}, \quad (5)$$

where T is the usual temperature of canonical distributions and T^{Im} is newly introduced in SMGT [14]. Comparing the time-dependence of the probability distributions for the quantum states on Gel'fand triplets having the total imaginary energy Γ , which is given by $e^{-2\Gamma t/\hbar}$, with that of the canonical distribution, we have derived the relation $\beta^{\text{Im}} = 2t/\hbar$ with the common time-scale t [14], that is, $T^{\text{Im}} = \hbar/2k_B t$. (For details, see Ref. [14].) 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 Γ 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. [14] in terms of the two-dimensional parabolic potential barriers (PPB's). It should also be noted that in the two-dimensional PPB we can show the existence of stationary states with zero imaginary eigenvalue which are understood as stationary flows round the center of the PPB [8]. By using the station-

ary states the energy and entropy productions from the PPB were studied and the entropy transfer from S^{Im} to S^{Re} was suggested [15]. 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 a previous paper [14] 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 Secs. II and III. Consistency of the theory will be examined in terms of simple PPB models in Sec. IV. We can expect that the PPB is a good approximation to potentials standing for repulsive forces being very weak at the center, as the HO is well known to be a good approximation to potentials standing for attractive forces being very weak at the center. The entropy transfer from S^{Im} to S^{Re} and the energy production are studied through a decay of a resonance system in the PPB in Sec. V. An equilibrium for a simple process described by reactions $A + CB \rightleftharpoons AC + B$ will be discussed in this scheme in Sec. VI. 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 as discussed in Sec. IV.

II. FREE ENERGIES IN CANONICAL ENSEMBLE

Let us start from the canonical distribution of Eq. 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

$$Z_N(T, t) = Z_N^{\text{Re}}(T) Z_N^{\text{Im}}(t), \quad (6)$$

where

$$Z_N^{\text{Re}}(T) = \sum_l \exp(-\beta E_l), \quad Z_N^{\text{Im}}(t) = \sum_m \exp(-\beta^{\text{Im}} \Gamma_m).$$

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^{Re} and that for the imaginary part F^{Im} as

$$F^{\text{Re}}(T) = -\beta^{-1} \ln Z_N^{\text{Re}}, \quad F^{\text{Im}}(t) = -(\beta^{\text{Im}})^{-1} \ln Z_N^{\text{Im}}. \quad (7)$$

The mean energies are obtained as usual

$$\bar{E} = \frac{\partial}{\partial \beta} [\beta F^{\text{Re}}(T)], \quad \bar{\Gamma} = \frac{\partial}{\partial \beta^{\text{Im}}} [\beta^{\text{Im}} F^{\text{Im}}(T)]. \quad (8)$$

The relations with respect to other quantities derived from F^{Re} 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^{Im} are physically meaningful or not. The entropies S^{Re} and S^{Im} are derived from the free energies as

$$S^{\text{Re}} = -\frac{\partial}{\partial T} F^{\text{Re}}(T), \quad S^{\text{Im}} = -\frac{\partial}{\partial T^{\text{Im}}} F^{\text{Im}}(t). \quad (9)$$

The consistency of S^{Im} given in Eq. (9) with that of Eq. (3) given in microcanonical ensemble [14] will be studied in a PPB model in Sec. IV. In general the entropy S^{Im} 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

$$F^{\text{Re}} = \bar{E} - TS^{\text{Re}}, \quad F^{\text{Im}} = \bar{\Gamma} - T^{\text{Im}} S^{\text{Im}}. \quad (10)$$

Since we do not know what are good observables in unstable systems and still have only one example of PPB to adopt SMGT [15], we have to examine SMGT more in other realistic examples in order to understand the meanings of SMGT in details.

III. 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 ($N=0,1,2,\dots$). Then we construct the grand partition function as

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

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

$$J(T, t, \mu) = -\beta^{-1} \ln \Xi. \quad (12)$$

The mean number is obtained by

$$\bar{N} = \beta^{-1} \frac{\partial}{\partial \mu} \ln \Xi \quad (13)$$

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 Ξ , the maximum of the probability in the grand canonical ensemble appears at

$$J/T = \bar{E}/T - S^{\text{Re}} + \bar{\Gamma}/T^{\text{Im}} - S^{\text{Im}} - \bar{N}(\partial S/\partial N), \quad (14)$$

where the relations $\partial S^{\text{Re}}/\partial E = 1/T$ and $\partial S^{\text{Im}}/\partial \Gamma = 1/T^{\text{Im}}$ are used [14]. Now we can see that the definition of the chemical potential μ is given by the relation

$$\frac{\mu}{T} = -\frac{\partial S}{\partial N}, \quad (15)$$

where $S = S^{\text{Re}} + S^{\text{Im}}$. The Gibbs free energy G is given as usual

$$G = \mu \bar{N}. \quad (16)$$

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

$$J/T = F^{\text{Re}}/T + F^{\text{Im}}/T^{\text{Im}} - G/T. \quad (17)$$

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

$$Z_N = (Z_1)^N, \quad (18)$$

where $Z_1 = Z_1^{\text{Re}} Z_1^{\text{Im}}$ is the partition function for one constituent. We then obtain

$$\Xi = (1 - e^{\beta\mu} Z_1)^{-1} \quad (19)$$

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

$$\Xi = \sum_{N=0}^{\infty} e^{\beta\mu N} \frac{(Z_1)^N}{N!} \quad (20)$$

and then we get

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

IV. SIMPLE EXAMPLES

A. HO+PPB case

We shall here examine SMGT in a simple example that is represented by one-dimensional harmonic oscillator (HO) + one-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

$$\varepsilon_{n_x} = \left(n_x + \frac{1}{2} \right) \hbar \omega \quad (21)$$

and the eigenvalues of PPB on the Gel'fand triplet are known to be pure imaginary values as [2–7]

$$\varepsilon_{n_y} = \mp i \left(n_y + \frac{1}{2} \right) \hbar \gamma, \quad (22)$$

where n_x and n_y are natural numbers $n_x, n_y = 0, 1, 2, \dots$. 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 $t \geq 0$ [1–7]. Then the energy of a constituent is written by

$$\varepsilon_{n_x n_y} = \left(n_x + \frac{1}{2} \right) \hbar \omega - i \left(n_y + \frac{1}{2} \right) \hbar \gamma. \quad (23)$$

(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

$$\mathcal{E}_{M^{\text{Re}} M^{\text{Im}}} = \left(M^{\text{Re}} + \frac{1}{2} N \right) \hbar \omega - i \left(M^{\text{Im}} + \frac{1}{2} N \right) \hbar \gamma, \quad (24)$$

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

$$W_N(M^{\text{Re}}, M^{\text{Im}}) = W_N^{\text{Re}}(M^{\text{Re}}) W_N^{\text{Im}}(M^{\text{Im}}), \quad (25)$$

where

$$W_N^{\text{Re}}(M^{\text{Re}}) = \frac{(M^{\text{Re}} + N - 1)!}{M^{\text{Re}}! (N - 1)!},$$

$$W_N^{\text{Im}}(M^{\text{Im}}) = \frac{(M^{\text{Im}} + N - 1)!}{M^{\text{Im}}! (N - 1)!}.$$

The entropy is obtained by

$$S(\mathcal{E}) = S^{\text{Re}}(E) + S^{\text{Im}}(\Gamma),$$

where the contributions from the real and imaginary parts are expressed in the same form as

$$S = k_B [(M + N) \ln(M + N) - M \ln M - N \ln N], \quad (26)$$

where \cdot denotes Re or Im and $M, N \geq 1$ 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 [14]

$$\frac{1}{T} = \frac{\partial S^{\text{Re}}}{\partial E}, \quad \frac{1}{T^{\text{Im}}} = \frac{\partial S^{\text{Im}}}{\partial \Gamma}. \quad (27)$$

The explicit forms are obtained as

$$\frac{1}{T} = \frac{k_B}{\hbar \omega} \ln \frac{E/N + \hbar \omega/2}{E/N - \hbar \omega/2}, \quad \frac{1}{T^{\text{Im}}} = \frac{k_B}{\hbar \gamma} \ln \frac{\Gamma/N + \hbar \gamma/2}{\Gamma/N - \hbar \gamma/2}. \quad (28)$$

Everything can be derived from the entropies, following the argument carried out in SMHS, e.g.,

$$E = N \left(\frac{1}{2} \hbar \omega + \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1} \right), \quad \Gamma = N \left(\frac{1}{2} \hbar \gamma + \frac{\hbar \gamma}{e^{\beta^{\text{Im}} \hbar \gamma} - 1} \right). \quad (29)$$

Since $\beta^{\text{Im}} = 2t/\hbar$, we see the time dependence of the total imaginary energy Γ in the second equation of Eq. (29), which will be examined afterwards.

(2) *Canonical ensemble*. Following the argument given in Sec. II, the partition functions for the real and imaginary parts are obtained as

$$Z_N = \left(\frac{e^{-\beta \cdot \hbar \Omega/2}}{1 - e^{-\beta \cdot \hbar \Omega}} \right)^N, \quad (30)$$

where $\Omega = \omega$ in the real part for $\cdot = \text{Re}$ and $\Omega = \gamma$ in the imaginary part for $\cdot = \text{Im}$ should be taken. The derivations of the free energies F^{Re} and F^{Im} given in Eq. (7) are trivial. It is easy to examine that the mean values of E and Γ are same as those derived in Eq. (29) of microcanonical ensemble. The entropies of Eq. (9) are evaluated as

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

We also easily see that they coincide with those given in Eq. (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 Eq. (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

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

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

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

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 μ for small t as follows:

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

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

B. d -dimensional free motion + PPB case

Let us briefly discuss one more example described by the 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

$$Y = \int_0^\infty e^{-\beta p V} Z_N dV, \quad (36)$$

where the canonical partion function $Z_N = Z_N^{\text{Re}} Z_N^{\text{Im}}$. The real part Z_N^{Re} for the free motions is given by

$$Z_N^{\text{Re}} = \frac{1}{N!} \frac{1}{(2\pi\hbar)^{dN}} V^N (2\pi m k_B T)^{dN/2} \quad (37)$$

and the imaginary part Z_N^{Im} for the one-dimensional PPB is the same as that of the previous model. After the integration we have

$$Y = \frac{1}{(2\pi\hbar)^{dN}} (2\pi m k_B T)^{dN/2} \left(\frac{k_B T}{p} \right)^{N+1} Z_N^{\text{Im}}. \quad (38)$$

From the thermodynamical relation $G = -\beta^{-1} \ln Y$ for $N \gg 1$ we obtain

$$G = -N\beta^{-1} \left[\frac{d+2}{2} \ln T - \ln p + \ln \frac{m^{d/2} k_B^{(d+2)/2}}{(2\pi\hbar^2)^{d/2}} - \frac{1}{2} \beta^{lm} \hbar \gamma - \ln(1 - e^{-\beta^{lm} \hbar \gamma}) \right]. \quad (39)$$

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

$$pV = Nk_B T.$$

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

$$\mu = k_B T \left[\ln \frac{p}{k_B T} \left(\frac{2\pi\hbar^2}{mk_B T} \right)^{d/2} + \frac{1}{2} \beta^{lm} \hbar \gamma + \ln(1 - e^{-\beta^{lm} \hbar \gamma}) \right]. \quad (40)$$

It has the t dependence of the $\ln t$ type at small t , which is same as the previous case given by Eq. (34). The same result for μ 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.

V. ENTROPY TRANSFER FROM S^{lm} TO S^{Re}

Let us consider the entropy transfer from S^{lm} to S^{Re} in an adiabatic process described by a decay of a system that is composed of N resonances in a one-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 equilibriums of SMHS. We can, therefore, consider that S^{lm} and S^{Re} , 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 Eq. (31) as

$$S^{lm} = Nk_B \left[2\gamma t \frac{e^{2\gamma t}}{e^{2\gamma t} - 1} - \ln(e^{2\gamma t} - 1) \right]. \quad (41)$$

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

$$S^{lm} \approx -Nk_B \ln \tau \quad (42)$$

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

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

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

$$dS = dS^{Re} + dS^{lm} = 0 \quad (44)$$

holds, we have the relation

$$dS^{Re} = -dS^{lm}. \quad (45)$$

Note here that dS^{Re} is always positive because $dS^{lm} < 0$ 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

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

where K_0 and δ should be positive constants. Since the direct observable in this process is the real energy E^{Re} 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

$$dE^{Re} = T(t) dS^{Re} = Nk_B K_0 \tau^{\delta-1} d\tau \quad \text{for } \tau \ll \frac{1}{2}. \quad (47)$$

Then we can estimate the real energy produced in the process during the short period from 0 to t ($\ll 1/2\gamma$) as

$$E^{Re} = \int_0^{\gamma t} \frac{dE^{Re}}{d\tau} d\tau = Nk_B \frac{K_0}{\delta} (\gamma t)^\delta. \quad (48)$$

Since $\delta > 0$, this process produces a real positive energy. Even if S^{lm} diverges at $t=0$, we obtain a finite energy production. The unknown constants K_0 and δ 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^{lm} in the system. This means that the total produced energy which is evaluated by the integration from $t=0$ to ∞ must coincide with the energy consumed in the process for making the initial system. This integration will derive a relation between K_0 and δ .

VI. 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 [16,17]. Connor studied the reaction by representing the potential in terms of PPB's [18]. 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 [6]. Here we shall study chemical equilibriums 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 one-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 γ_1 and γ_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 ones N_2^- for BC ;

$$N_1^- = N_2^+, \quad N_1^+ = N_2^- . \quad (49)$$

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

$$\begin{aligned} \Gamma_1^- &= \left(M_1^- + \frac{1}{2} N_1^- \right) \hbar \gamma_1, & \Gamma_2^+ &= \left(M_2^+ + \frac{1}{2} N_1^- \right) \hbar \gamma_2, \\ &\text{for } A + CB \rightarrow AC + B, & & \\ \Gamma_2^- &= \left(M_2^- + \frac{1}{2} N_1^+ \right) \hbar \gamma_2, & \Gamma_1^+ &= \left(M_1^+ + \frac{1}{2} N_1^+ \right) \hbar \gamma_1, \\ &\text{for } AC + B \rightarrow A + CB & & \end{aligned} \quad (50)$$

where the imaginary parts are defined by $\mathcal{E}_i^\pm = \mp i \Gamma_i^\pm$ (suffix $i=1,2$), $M_i^\pm = 0,1,2,\dots$, and the relations of Eq. (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

$$\Gamma_1^- = \Gamma_2^+, \quad \Gamma_1^+ = \Gamma_2^- \quad (51)$$

must be satisfied, since the t dependence of the canonical ensemble for the reaction $A + CB \rightarrow AC + B$, which is given by $e^{-\beta \text{Im}(\Gamma_2^+ - \Gamma_1^-)}$, and that for $AC + B \rightarrow A + CB$ given by $e^{-\beta \text{Im}(\Gamma_1^+ - \Gamma_2^-)}$ must vanish in the equilibrium. Now we have the thermodynamical weight as

$$W = W_1 W_2, \quad (52)$$

where

$$\begin{aligned} W_1 &= \frac{(M_1^+ + N_1^+ - 1)! (M_1^- + N - N_1^+ - 1)!}{M_1^+! (N_1^+ - 1)! M_1^-! (N - N_1^+ - 1)!}, \\ W_2 &= \frac{(M_2^- + N_1^+ - 1)! (M_2^+ + N - N_1^+ - 1)!}{M_2^-! (N_1^+ - 1)! M_2^+! (N - N_1^+ - 1)!} \end{aligned} \quad (53)$$

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

$$\frac{\partial}{\partial N_1^+} \ln W = \ln \frac{(M_1^+ + N_1^+)(M_2^- + N_1^+)(N - N_1^+)^2}{(M_1^- + N - N_1^+)(M_2^+ + N - N_1^+)(N_1^+)^2} = 0, \quad (54)$$

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

$$\begin{aligned} (M_1^- + N_1^-)(M_2^+ + N_1^-)(N_1^+)^2 \\ = (M_1^+ + N_1^+)(M_2^- + N_1^+)(N_1^-)^2, \end{aligned} \quad (55)$$

where $N_1^- = N - N_1^+$ is put. By using the relations of Eqs. (50) and (51) we obtain the equation

$$\begin{aligned} \left(\frac{\Gamma_1^-}{N_1^-} + \frac{1}{2} \hbar \gamma_1 \right) \left(\frac{\Gamma_1^-}{N_1^-} + \frac{1}{2} \hbar \gamma_2 \right) \\ = \left(\frac{\Gamma_1^+}{N_1^+} + \frac{1}{2} \hbar \gamma_1 \right) \left(\frac{\Gamma_1^+}{N_1^+} + \frac{1}{2} \hbar \gamma_2 \right). \end{aligned} \quad (56)$$

Taking account of the constraints $\Gamma_1^-/N_1^- > 0$ and $\Gamma_1^+/N_1^+ > 0$, we get the solution

$$\frac{\Gamma_1^-}{N_1^-} = \frac{\Gamma_1^+}{N_1^+}. \quad (57)$$

This result shows that the mean grow width for a growing resonance Γ_1^-/N_1^- , is equal to the mean decay width for a decaying resonance Γ_1^+/N_1^+ for the system AC . From the relations of Eqs. (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

$$\frac{\Gamma_1^-}{N_1^-} = \frac{\Gamma_1^+}{N_1^+} = \frac{\Gamma_2^-}{N_2^-} = \frac{\Gamma_2^+}{N_2^+} \quad (58)$$

are obtained. These relations indicate that a kind of balance such as 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.

VII. DISCUSSION

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 Eq. (4), the mean value of the quantity $A(\Gamma)$ is obtained by

$$\bar{A} = \frac{\int A(\Gamma) e^{-\beta \text{Im}\Gamma} W^{\text{Im}}(\Gamma) d\Gamma}{\int e^{-\beta \text{Im}\Gamma} W^{\text{Im}}(\Gamma) d\Gamma}. \quad (59)$$

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

$$\frac{d\bar{A}}{dt} = \frac{2}{\hbar} \left\{ \frac{-\int \Gamma A(\Gamma) e^{-\beta \text{Im}\Gamma} W^{\text{Im}}(\Gamma) d\Gamma}{\int e^{-\beta \text{Im}\Gamma} W^{\text{Im}}(\Gamma) d\Gamma} + \frac{\int A(\Gamma) e^{-\beta \text{Im}\Gamma} W^{\text{Im}}(\Gamma) d\Gamma \int \Gamma e^{-\beta \text{Im}\Gamma} W^{\text{Im}}(\Gamma) d\Gamma}{\left[\int e^{-\beta \text{Im}\Gamma} W^{\text{Im}}(\Gamma) d\Gamma \right]^2} \right\} = \frac{2}{\hbar} (-\overline{\Gamma A} + \bar{\Gamma} \bar{A}). \quad (60)$$

For $A = \Gamma$ we have the equation

$$\frac{d\bar{\Gamma}}{dt} = -\frac{2}{\hbar} (\Delta\Gamma)^2 < 0, \quad (61)$$

where $(\Delta\Gamma)^2 = \overline{\Gamma^2} - (\bar{\Gamma})^2$. This equation means that $\bar{\Gamma}$ 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 Γ are independently determined. Gel'fand triplets, however, contain many other solutions such that the real and imaginary eigenvalues ϵ and γ have some correlations. In such processes the thermodynamical weight cannot be obtained by the simple product of W^{Re} and W^{Im} as given in Eq. (2) [14]. Study of such processes is still an open question in the present SMGT.

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