Two-state approximation for aggregate states of clusters

R. Stephen Berry
Department of Chemistry, University of Chicago, 5735 South Ellis Avenue, Chicago, Illinois 60637

Boris M. Smirnov
Institute of High Temperatures, Izhorskaya 13/19, Moscow 127412, Russia

The concepts of the phase and change of state for clusters are analyzed. The connection between a phase or state change and the thermodynamic parameters of a cluster is analyzed within the framework of a two-state model. This model aggregates the excited configurational states of each state of the cluster. The model allows one to estimate parameters of clusters and bulk in the range of the phase or state change. The approach has sufficient generality to be applicable not only to order–disorder changes and evaporation but also to such processes as ionization and vibronic (electronic-to-thermal) energy conversion. The last of these raises a question regarding one step in the interpretation of some recent experimental studies of cluster melting. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1354185]

INTRODUCTION

Phase changes in clusters differ from the traditional phase transitions for bulk systems. A phase transition of a single-component bulk system occurs only at points along its coexistence curve, a function of temperature and pressure. At this curve, the thermodynamic parameters of a bulk system vary in a stepwise way.[1–3] Clusters, in contrast, may display dynamically-coexisting phases in equilibrium throughout bands of temperature and pressure.[4–10] Correspondingly, cluster thermodynamic parameters vary continuously with the temperature and pressure within such a band. Any property that becomes discontinuous or infinite along the phase coexistence curve for a bulk system has a finite-system counterpart in clusters whose value exhibits a resonancelike peak. (To distinguish the traditional behavior of bulk systems from the much less familiar behavior of clusters, we use the term ''phase transition'' for the former, and the weaker expression ''phase change'' for the latter.)

A necessary condition for the dynamic coexistence of phases or states of clusters is the requirement that each of the phases has a persistence time long enough to establish equilibriumlike properties characteristic of those phases, properties that may somehow be observed experimentally. This translates, at the microscopic level, to a requirement that there be a sufficient free energy barrier between the regions of phase space corresponding to those phases or states.

Furthermore there is nothing to prevent the coexistence of more than two phases of clusters. In fact the distinction between ''phase'' and ''component'' is lost with clusters. As a result, ensembles of clusters may contain systems in two or more different phaselike forms; the probability of finding a cluster in an intermediate state of transition between phases is small.[10] This last observation is the basis of the two-state model for coexistence of two phases of clusters.[11–13] Here we analyze thermodynamic parameters of a cluster in the region of a phase or state change, within the framework of the two-state approximation. This approximation has been used previously to describe clusters[11–13] but in more phenomenological ways, either to demonstrate general properties of phase changes of these systems,[11,12] or to rationalize results of simulations.[13] The loss of distinction between ''phase'' and ''component'' also makes this two-state approach sufficiently general to apply it to processes such as ionization and energy exchange between electronic and vibrational degrees of freedom. This generality is illustrated by application of the method to two phenomena not usually classed with phase changes: The first application described here, of ionization, and by the final example, of exciton quenching in sodium clusters.

''PHASE'' EQUILIBRIA OF FINITE SYSTEMS: IONIZATION

Investigations of clusters compel us to generalize the classical concept of ''phase,'' expanding it to encompass microscopic systems with finite numbers of degrees of freedom. This allows us to consider known physical objects from new standpoints. We define a phase of a microscopic system as a group of states in a well-defined band of energies that is separated from other states by both the energy and other qualitative characteristics, e.g., the value of some quantifiable distinction which serves as an order parameter and may also be characteristic of bulk phases such as the diffusion coefficient or the density of very-low-frequency modes. Because the distinction between phase and component is lost in small systems, we can use the same approach to treat phase changes and some other changes of state in the same context. We now illustrate our two-state approach with the example of the ionization equilibrium between neutral and singly-charged clusters.

Let us place n atoms in a closed volume V, so that the temperature of our atoms is determined by the temperature T of the walls or inert bath molecules of this thermostat. If T is high enough, a fraction of these atoms is singly ionized, so that the equilibrium ensemble consists of n_a atoms, n_e elec-

trons and n_i ions; under these conditions we have $n=n_a+n_e$, $n_i=n_e$. The Saha formula quantifies this,

$$\frac{n_e^2}{n_a}=K_{eq}(T),\tag{1}$$

and the equilibrium constant in this case is given by[14]

$$K_{eq}(T)=\frac{g_e g_i}{g_a}\frac{1}{V}\left(\frac{mT}{2\pi\hbar^2}\right)^{3/2}\exp\left(-\frac{J}{T}\right).\tag{2}$$

Here g_e, g_i, g_a are the statistical weights of the electronic states of the electron, ion, and atom, respectively; m is the electron mass; J is the ionization energy of the atom, and the temperature T is expressed in energy units, i.e., as kT.

In this way we define the equilibrium of the neutral and ionized ''phases'' or states. The definition of the neutral state includes the ground and excited states of the atom. The ionized state includes the spin states of the free electrons as well as whatever electronic states of the ion may occur at the temperature T. Because we lump electronic and spin states together to define these states as aggregates, rather than specific quantum states, they can, in the context of clusters, equally well be called phases. In order to express Eq. (2) in a more general form, we introduce two parameters for the phases, that is, J the excitation energy of the higher-energy form, the ionization energy of the atom in the above example, and g the ratio of statistical weights of these states. Then formula (1) takes the form

$$\frac{n_e}{n_a}\equiv K(T)=g\exp\left(-\frac{J}{T}\right).\tag{3}$$

In such a state change, it is important that $g\gg1$; in the case of ionization equilibrium the high degeneracy of the higher-energy phase is provided by the large volume V available to the ionized system compared with a typical atomic volume $(mT/2\pi\hbar^2)^{-3/2}$. For this reason, this state change proceeds at temperatures very low compared to the ionization potential. The same is true of dissociations; it is the entropy of the high-energy phase that determines the lowest temperatures at which that phase becomes observable. This consideration allows us to neglect excited states of both ions and neutral atoms that have only small populations relative to the total number of neutral atoms and ions.[15]

In a general case one can represent the equilibrium constant $K(T)$ in the form

$$K(T)=\exp\left(-\frac{\Delta F(T)}{T}\right),\tag{4}$$

where $\Delta F(T)$ is the free energy change of this phase transition. For the above example we have

$$\Delta F(T)=\Delta E-T\ln g=\Delta E-T\Delta S,\tag{5}$$

where the energy variation is $\Delta E=J$, and $\Delta S=\ln g$ is the entropy change resulting from this transition; in the general case the free energy depends on additional variables and conditions, such as the contributions of internal degrees of motion and on rotations. Nevertheless, whenever new translational degrees of freedom appear as a consequence of the change, they dominate the entropy change of the transition.

One can use the partition functions Z_0 and Z_{ion} for the neutral and ionized states of the system. If we evaluate the free energy in the usual way, we include the contributions of the excited atomic and ionic states. In terms of these variables, relation (3) takes the form

$$\frac{Z_{ion}}{Z_0}=\exp\left(-\frac{\Delta F}{T}\right)=\exp\left(-\frac{\Delta E}{T}+\Delta S\right).\tag{6}$$

The equilibrium constant is itself a kind of order parameter. Below we use a simple transform of $K(T)$ as our order parameter, a form especially convenient for a two-phase system. We define the distribution $D(T)$ to have the form,[10]

$$D(T)=\frac{K-1}{K+1}=\frac{n_e-n_a}{n_e+n_a};\tag{7}$$

this function varies from -1 to $+1$, as the system passes from the neutral to the ionized state.

Transition to a bulk system corresponds to the limit of very large g; in this limit the range of temperatures in which both phases coexist in observable quantities becomes unobservably narrow, at any given pressure. Hence, the range of temperature and pressure in which one may observe the coexistence of phases consists, effectively, of just a curve in p, T-space for bulk systems, while the width of the coexistence region should be clearly observable for small finite systems. As said previously, within the framework of this analysis, we may consider the ionization and dissociation transitions in gases to be phase changes because the distinction between ''component'' and ''phase'' is lost in small systems. This usage is obviously outside the classical definition, because under bulk conditions, equilibria of components may be observed over wide ranges of composition, while phase transitions are sharp.

THE ORDER–DISORDER PHASE CHANGE

We now consider the phase change between ordered and disordered states, thinking primarily of the transition between the solid and liquid states. We define the cluster states in the following way. The (or, if there are structural isomers, a) solid state of the cluster consists of the ground and low-lying configurationally excited states of a given structural variety, e.g., icosahedral or face-centered cubic (fcc). As the liquid state we take a group of configurationally excited, nonrigid cluster states near the corresponding entropy-determined maximum of the partition function. Restricting ourselves to these two aggregate states, we can use the two-state cluster approximation. Formally, the above relations that describe the components of a chemical transition are valid for the phaselike forms of this phase change. But the order–disorder transition differs in principle from a chemical transition; we analyze this difference here. Indeed, in the case of the ionization or any chemical transition, the states of interest are independent of the number of particles comprising the system. In an order–disorder transition, the state of each atomic particle depends on the positions of the nearby atomic particles with which it interacts. Hence, collective effects are very important in this case, and the parameters of

the transition, ΔF, ΔE, and ΔS, are proportional, at least in lowest order, to the total number of particles.

In order to demonstrate this relationship, we consider the solid–liquid transition within the framework of the Bragg–Williams lattice gas model.[16,17] Let the system consists of n interacting particles placed in the unit cells of a crystal. For simplicity, we take this crystal to be a square net containing $2n$ cells. Let the interaction energy of particles in nearest cells be equal to $-\epsilon$ and suppose the energy depends only on interactions between nearest neighbors. Then the ground state of this system corresponds to a compact array of particles. The densest array possible is characterized by the energy $-4\epsilon n$. Assuming $n \gg 1$, we neglect the edge effects. Formation of one vacancy inside this structure leads to the loss of four bonds, corresponding to the energy of formation of one vacancy 4ϵ.

Now we define the ordered state of the solid as this compact state with at most a small number k of vacancies. We shall assume that k is larger than unity, perhaps even much larger, but much smaller than n, so that we may assume there are many isolated vacancies. The partition function of a state with k vacancies, when $k \ll n$, is given by

$$Z_k = C_n^k \exp\left(-\frac{4\epsilon k}{T}\right), \quad k \ll n.$$

Assuming $k \gg 1$, we have

$$\ln Z_k = -\frac{4\epsilon k}{T} + n \ln n - (n-k)\ln(n-k) - k \ln k$$

$$= -\frac{4\epsilon k}{T} + k + k \ln\frac{n}{k}.$$

This partition function has its maximum at k_0, given by

$$k_0 = n \exp\left(-\frac{4\epsilon}{T}\right), \quad (8)$$

and near that maximum we have

$$\ln Z_k = \ln Z_{\max} - \frac{(k-k_0)^2}{2k_0}, \quad Z_{\max} = e^{k_0}.$$

We here neglect the preexponential factor. These equations yield the solid partition function

$$Z_{\text{sol}} = \int_0^\infty Z_k dk \sim Z_{\max} \sim e^{k_0}.$$

We see that the dominant contributions to the solid state partition function are terms corresponding to excitation with a number of vacancies that contribute to the partition function near k_0. Since the melting point is low, $T \ll \epsilon$, the typical number of vacancies for the solid states is relatively small; $k_0 \ll n$. The entropy of the solid state is

$$S_{\text{sol}} \approx k_0 = n \exp\left(-\frac{4\epsilon}{T}\right) \ll n. \quad (9)$$

Now we address the liquid state. Analyzing the disordered states in which the number of vacancies is comparable to n, we find that the maximum excitation energy of this system corresponds to each particle being surrounded entirely by vacancies, i.e., the total energy of this state is $E = 0$ and the excitation energy is $4\epsilon n$. From symmetry considerations, the mean excitation energy for this system is $2\epsilon n$. The total number of ways to place n particles and n vacancies in $2n$ cells is

$$g = \exp S_{\text{liq}} \approx 2^{2n}.$$

The entropy of the disordered or liquid state is $S_{\text{liq}} \approx 2n \ln 2 \gg S_{\text{sol}}$. One can construct the partial partition function of the liquid state in the form

$$Z_{\text{liq}} = S_{\text{liq}} \exp\left(-\frac{\bar{E}}{T}\right),$$

where $\bar{E} \approx T_m \cdot 2n \ln 2 < 2\epsilon n$ is the excitation energy that gives the greatest contribution to the partition function of the disordered state, and T_m is the temperature of the order–disorder phase change. (Strictly, for a small system, this is the temperature at which the free energies of the two forms are equal. In the following discussion, we shall denote this temperature by the term ''melting point''.) Although within the framework of this model we cannot generally find this value, one can draw a general conclusion about the behavior of the partial partition function at the point where the phase change takes place. The partial partition function as a function of the excitation energy has a maximum in the range of excitations at which the number of vacancies is comparable to the number of particles. The states near this maximum belong to the disordered or liquid aggregate states. Because these are the occupied states of the system near the maximum of the partition function, we may infer that the corresponding disordered aggregate states are separated from the ordered states by an energy gap. The probability of occupancy of intermediate states is small. This rationalizes the suitability of the two-state approximation for this state.

We now note the principal differences in the ionization energy, dissociation energy and energies of other chemical transitions that accompany the order–disorder phase transition. In the first case the state of each particle does not depend on the states of others, and the transition parameters do not depend on the number of particles in the system. On the contrary, in the case of the order–disorder phase transition, we cannot neglect this dependence, and the parameters ΔF, ΔE, and ΔS in formula (6) are proportional to the total number of particles.

HEAT CAPACITY OF A CLUSTER NEAR THE PHASE TRANSITION POINT

The heat capacity of a bulk system of bound atoms goes to infinity at the melting point and has a strong maximum for clusters. Therefore we first analyze the behavior of this property near the melting point, within the two-state model. The probabilities for the system to be in the solid w_{sol} and liquid w_{liq} states are, according to formula (6),

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$$w_{sol} = \frac{Z_{sol}}{Z} = \frac{1}{1+p}, \quad w_{liq} = \frac{Z_{liq}}{Z} = \frac{p}{1+p},$$

$$p = \exp\left(-\frac{\Delta F}{T}\right) = \exp\left(-\frac{\Delta E}{T} + \Delta S\right), \tag{10}$$

where $Z = Z_{sol} + Z_{liq}$ is the total partition function, and $w_{sol} + w_{liq} = 1$. Evidently, the melting point is determined by the relation $w_{liq}(T_m) = w_{sol}(T_m)$, or

$$\exp\left(-\frac{\Delta E}{T_m} + \Delta S\right) = 1, \quad \text{or} \quad \Delta E = T_m \Delta S. \tag{11}$$

Let us introduce the cluster's internal vibrational energies $U_{v,sol}(T)$ and $U_{v,liq}(T)$ for the solid and liquid states, respectively. We assume thermodynamic equilibrium for the motion of cluster atoms and characterize the internal energy of the cluster by a temperature T. In particular, in the case in which the thermal vibrational energy of a cluster atom far exceeds the Debye energy, these values are determined by the Dulong–Petit Law. The liquid, however, resides in a region of the potential surface with a mean potential energy somewhat higher than that of the solid, just because of the energy required to produce the vacancies and defects that make the liquid compliant and mobile. We assume that mean difference is the constant, ΔE; strictly, the regions of the potential surface accessible to the liquid may expand and go to higher energies as the temperature increases, but we neglect this change of ΔE. Then $U_{v,sol}(T) = U_{v,liq}(T) = 3nT$, where n is the number of atoms in the cluster. Because we have assumed that the dynamic equilibrium between the phases localizes the cluster in both the solid and liquid states for observable intervals of time, we can take appropriately time-weighted averages to compute the cluster's mean internal energy in each phase, and the overall average. Then that overall average internal energy of the cluster is

$$U(T) = U_{v,sol}(T)w_{sol} + [U_{v,liq}(T) + \Delta E]w_{liq}. \tag{12}$$

From this we have for the heat capacity of the system of atoms $(U_{v,sol}(T) \approx U_{v,liq}(T))$,[11]

$$C(T) = \frac{dU}{dT} = C_0(T) + \frac{\Delta E^2}{T^2} \cdot \frac{g \exp(-\Delta E/T)}{[1 + g \exp(-\Delta E/T)]^2}$$

$$= C_0(T) + \frac{\Delta E^2}{T^2} \frac{p}{(1+p)^2}. \tag{13}$$

Here the heat capacity is taken at constant volume or pressure depending upon external conditions, and $C_0(T)$ is the part of the heat capacity which is not related to the phase transition. We assume $U_{sol}(T) \approx U_{liq}(T)$ and a weak (power) temperature dependence for these values, as it takes place in reality. Above we used formulas (2) for the probability of the solid and liquid cluster state. As we see, this expression has a maximum at the melting point T_m, equal near that maximum to[9]

$$C_{max} = C_0 + C_{max}e^{[-\alpha(T-T_m)^2]},$$

where

TABLE I. Parameters of condensed, pure inert gases.

Parameter	Average value
a/R_e	1.005 ± 0.013
ϵ/D	6.4 ± 0.2
T_{tr}/D	0.579 ± 0.07
$\Delta H_{fus}/D$	0.98 ± 0.02
Δs	1.68 ± 0.03
$p_{tr}R_e^3/D$, 10^{-3}	1.9 ± 0.2
$p_{tr}\Delta V/\Delta H_{fus}$, 10^{-4}	2.2 ± 0.4
v_{sol}/n, 10^{-5}	1.9 ± 0.8
v_{liq}/n	0.320 ± 0.001
$\Delta\epsilon_{liq}/D$	3.3 ± 0.2
g_{liq}	71 ± 5
γ_{liq}	2.91 ± 0.01

$$C_{max} = \frac{\Delta E^2}{4T_m^2} = \left(\frac{\Delta S}{2}\right)^2, \quad \alpha = \frac{\Delta E^2}{4T_m^4} = \left(\frac{\Delta S}{2T_m}\right)^2. \tag{14}$$

This relation is valid under the condition $\Delta E \gg T_m$. One can see that the "resonance" or peak corresponds to a narrow range of temperatures $\Delta T \sim \alpha^{-1/2} \sim T_m/\Delta S \ll T_m$. Since the value C_0 is proportional to n, the number of atoms in the cluster, and the fusion energy ΔE is proportional to the number of voids inside the cluster, a number of the order of n, the influence of the phase transition on the heat capacity grows roughly as $\sim n$. For a bulk system of bound atoms this contribution at its maximum tends to infinity. Indeed, the ratio of the second term of formula (14) to the first is $\sim n$, and the resonance width is $\sim 1/n$. Hence determination of the heat capacity of a large cluster reveals its melting point with a high accuracy.

The entropy of a system of bound atoms near its melting point is given by

$$S = w_{liq}\Delta S = \Delta S \frac{p}{1+p} = \frac{\Delta S}{1 + \exp\left(\frac{\Delta E}{T} - \Delta S\right)}, \tag{15}$$

where we approximate the entropy of the solid cluster near the melting point to be zero. In this case the entropy of the system varies from zero to ΔS when the system of bound atoms is heated, and its temperature passes through the melting point.

PARAMETERS OF MELTING FOR BULK AND CLUSTERS WITH PAIR INTERACTIONS BETWEEN ATOMS

Simple models do not allow us to determine the parameters of the order–disorder phase transition. We give these parameters[17,18] in Table I for a system of classical atoms with a short-range interaction, i.e., in which only nearest-neighbor interactions determine the properties of the bound system. Because condensed inert gases satisfy this condition with moderate accuracy, their parameters may be used. The similarity laws show the accuracy of this assumption for condensed inert gases.

Here D is the depth of the potential well for the pair interaction potential of identical atoms of inert gases, R_e is the equilibrium interparticle distance for this pair interaction

potential, a is the distance between nearest neighbors of the crystal lattice at zero temperature, T_{tr} and p_{tr} are the temperature and pressure at the triple point, ϵ is the binding energy per atom for the solid rare gas at the melting point, ΔH_{fus} is the fusion energy per atom, ΔV is the volume variation per atom accompanying melting, Δs is the corresponding entropy change per atom, n is the number of atoms, v_{sol} is the number of vacancies for the solid state at the melting point, v_{sol} is the number of voids for the solid state at the melting point, γ_{liq} is the average number of atoms removed from nearest neighbor sites around a test atom being removed as the system starts to transform to the liquid state from the solid. Dimensioned quantities are in units of the length and energy parameters of the pair potential.

Let us comment now on the data in Table I. If the interactions are restricted to nearest neighbors, the distance a between neighboring atoms of the crystal at zero temperature coincides with the equilibrium distance R_e between atoms at the minimum of the pair interaction potential, and the crystal binding energy ϵ per atom is equal to the energy of breaking 6 bonds, that is, $6D$. This is satisfied for condensed inert gases within an accuracy of several percent. If we extend the model so the interaction obeys the Lennard-Jones potential, the specific binding energy of the crystal increases due to the long-range contributions to the interaction and is $8.6D$.[19]

According to the data of Table I, the pressure at the triple point p_{tr} is relatively low, and the mechanical work due to expansion on melting, $p\Delta V$, is small in comparison with the change of the internal energy of the system $T\Delta S$. This allows us to neglect the pressure dependence for parameters of the system of bound atoms in the absence of a strong external pressure, and, correspondingly, we can neglect any pressure dependence of the parameters of this system.

A two-step procedure is convenient for quantifying the description of the transformation of the solid state to the liquid for a system of atoms bound by a pair interaction. The first step is formation of vacancies in the crystal by removal of internal atoms to outside sites of the system. The second step is relaxation of this system as a result of compression and transformation of those vacancies into stable voids. The number of voids is equal to the number of initial vacancies, but the volume of a freshly-formed vacancy is approximately twice the volume of a stable void in the liquid state. Thus this method prepares locally stable excited configurational states of the system of bound atoms. However many of these are actually nonequilibrium states in the context of other such configurationally excited states, so one can allow the model to pass continuously between the solid and liquid state by varying the number of initial vacancies v. The parameter γ_{liq} in Table I is the number of nearest neighbors of a test vacancy which are vacancies at the first step of preparation of the liquid state.

One more example is the Lennard-Jones cluster consisting of 55 atoms which was studied by the methods of molecular dynamics.[20–24] Analysis of the results of such studies gives the following parameters for the cluster melting: $\Delta E = 17, T_m = 0.30$, and the parameters are expressed in units of the dissociation energy of one bond. From this we have $\Delta S = 57$, and the specific values are $\Delta H_{fus} = 0.31$ and $\Delta s = 1.0$.

One can see that the specific values for this cluster are smaller than those for the bulk system. In this case this is explained by the role of the surface in the cluster melting, because 42 of the 55 atoms of this cluster are located on its surface. The melting of a cluster is a more complex process than that of bulk systems, because the individual shells of a cluster may have significantly different melting properties, so that a cluster may exhibit several melting points as well as several caloric curves; see, for example, Refs. 9, 10, 25.

Continuing the analysis of the Lennard-Jones cluster of 55 atoms, we use our previous conclusion that, in the absence of a strong external pressure, one can neglect the pressure dependence of its parameters. Then the behavior of the cluster's heat capacity near the melting point is determined by formula (14). Using the above parameters of this cluster, formula (14) and the Dulong–Petit Law for the heat capacity far from the melting point, $C_0 \approx 3n$, we have $C_0 \approx 160, C_{max} \approx 810$, and the width of the melting range $\Delta T = \alpha^{-1/2} = 2T_m/\Delta S = 0.01$. That is, the melting of this cluster falls in the temperature range $T = 0.29$–0.31. This is in good agreement with the molecular dynamics analysis[22] of this cluster.

To pursue this analysis further, we separate the excitation due to vibrational degrees of freedom from that due to a change of configuration of cluster or bulk atoms. Were we to assume that the vibrational state is changed only slightly in the course of the phase transition, we could ascribe this melting phenomenon simply to configurational excitation of the system of bound atoms. In reality, the vibrational excitation in the melting region depends on cluster size (and perhaps on the instantaneous configuration of the solid) and differs for clusters and bulk systems. Hence vibrational excitation can play a significant role in determining the values of parameters of clusters in the region of the phase change.

Thus the order–disorder phase transition for clusters exhibits parallels with ionization, dissociation, and chemical transitions in gases. This phenomenon for clusters is more complex than for bulk systems and its description requires additional details. This is an illustration of how investigation of the phase changes of clusters gives a deeper understanding the nature of this phenomenon and links this with other processes.

EMISSION OF PARTICLES FROM A CLUSTER

Coexistence in a phase or state change influences the observable behavior of clusters and hence of various parameters describing that behavior. Two such parameters describe thermoemission of electrons from the cluster surface in its melting region and the character of atomic evaporation from its surface. In this section, we consider atom evaporation in the temperature range in which the solid–liquid phase change takes place. The total net evaporation rate is determined by the different temperature dependencies of the evaporation rates of the solid ν_{sol} and liquid ν_{liq} cluster states. The total evaporation rate in the cluster melting region has the form of an average,

$$\nu(T) = \nu_{sol}w_{sol} + \nu_{liq}w_{liq}, \tag{16a}$$

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TABLE II. Parameters of the evaporation rate of alkai metal clusters near the melting point.

	T_m, K	T_0, K	T_*, K
Li	454	312	11.0
Na	371	265	10.9
K	336	254	10.8
Rb	312	242	10.2
Cs	302	234	10.1

where w_{sol} and w_{liq} are the probabilities of finding the cluster in the solid and liquid states, respectively.

The cluster evaporation rate can be expressed in terms of the rate of atomic attachment to the cluster surface, on the basis of the principle of detailed balance. This gives the evaporation rate from the surface of a spherical bulk particle of radius r (Refs. 26, 27) as

$$\nu(T) = 4\pi r^2 \xi N_{sat}(T)\exp\left(-\frac{\Delta\epsilon}{T}\right), \qquad (16b)$$

where ξ is the sticking probability, i.e., the probability that contact of an incident atom with the particle surface leads to its attachment, $N_{sat}(T)$ is the number density of atoms at the saturated vapor pressure at the chosen temperature, $\Delta\epsilon$ is the difference of the binding energies of an atom on the surface of this bulk particle and on a planar bulk surface.

Note that the temperature dependence for $N_{sat}(T)$ is $N_{sat}(T) \sim \exp(-\epsilon/T)$, where ϵ is the atomic binding energy at the surface; this binding energy is different for the solid and liquid states. Nevertheless the number density $N_{sat}(T)$ is the same for the solid and liquid states at the melting point, i.e., at the triple point. The different temperature dependencies near the melting point of the evaporation rates of the solid and liquid states determines the peculiarity of the total evaporation rate.

For simplicity we assume the change from solid to liquid of atomic binding energy $\Delta\epsilon$ of the cluster changes in the same way as the difference of binding energies of the solid and liquid of the planar bulk surface. Then formula (15) near the melting point T_m can be represented in the form

$$\nu(T) = \nu_0(T_m)\left[1 + D(T)\frac{T-T_m}{T_0}\right], \qquad (17)$$

where $\nu_0(T_m)$ is the evaporation rate at the melting point which we assume is the same for the solid and liquid state, $D(T) = w_{sol}(T) - w_{liq}(T)$, the parameter T_0 is given by

$$\frac{1}{T_0} = \frac{1}{2\nu_0(T_m)}\frac{d}{dT}[\nu_{sol}(T) - \nu_{liq}(T)]\big|_{T_m}.$$

Table II contains the values of these parameters for the alkali metal clusters. The parameters of bulk alkali metals near their melting points are taken from Ref. 28. Because the melting range for clusters is relatively narrow, we shall assume that the variation of rate in this range due to the phase transition is negligible. For comparison, Table II shows the typical temperature T_* which characterizes the variation of each evaporation rate and is introduced as

$$\frac{1}{T_*} = \frac{d\ln}{dT}[\nu_{sol}(T) + \nu_{liq}(T)]\big|_{T_m}.$$

It follows from the data of Table II that the influence of the change of phase on the evaporation rate constant is weaker at least by one order of magnitude than that of the temperature dependence of this value in each channel.

QUENCHING OF EXCITONS IN SODIUM CLUSTERS: VIBRONIC RELAXATION

Metallic clusters are effective absorbers of light. Recently, optical absorption was used for measurement of the heat capacity of charged, thermalized sodium clusters of ~ 100 atoms.[29–31] In this method cluster ions of one size were selected and the initial temperature of the selected clusters in a beam was established by collisions with helium atoms of the chosen temperature. The size-selected, temperature-selected clusters were then irradiated, and were thereby heated to considerably higher internal temperatures, the precise temperature depending on the number of photons absorbed. These heated cluster ions decayed on the way to a mass analyzer and detector, each cluster temperature was associated with a final spectrum of cluster fragments. Comparison of the mass spectra of unexcited cluster ions with the spectra produced from the clusters of known initial size and temperature, together with knowledge of the possible numbers of photons the ions could absorb, allowed one to find the internal cluster energy. This required assuming that the energy of the absorbed photons is transformed into the thermal energy of cluster ions. From these data, one can infer the caloric curve of $E(T)$ and, from that, the heat capacity of the clusters and the temperature range in which melting occurs. The point at which the free energies of solid and liquid clusters are equal presumably coincides with the maximum of the heat capacity.

These experiments also give additional information that allows us to check the validity of the assumption that equilibrium is very quickly established between optical excitations of the clusters and the vibrational motion of the cluster atoms. Below we show that, on the basis of these measurements, this equilibrium is not necessarily established rapidly. Then one can analyze the character of transformation of cluster excitations and other cluster degrees of freedom. (We call them excitons by analogy with solids, but in alkali clusters, they may be called plasmons.)

Now, from the standpoint of the two-state approximation, we analyze the transformation of photon-induced excitonic energy into heat in metallic clusters. We will be guided by the experiments of Schmidt et al.[29] in which the heat capacity of clusters Na_{139}^+ was measured on the basis of the following concept. When such clusters pass from a source to the detector, they decay, and the mass spectrum of the fragment clusters depends on the temperature of the optically-heated, initially-thermalized parent cluster ion. If a cluster of a given temperature absorbs one photon of energy $\hbar\omega$, its internal energy increases by $\hbar\omega$, if we assume the energy of an optically-generated exciton is transformed into heat. If the

mass spectrum produced from a parent cluster coincides with that associated with a temperature T', one can conclude that the cluster internal energy $U(T)$ is

$$U(T') - U(T) = \hbar\omega. \tag{18}$$

This allows one to determine the cluster's heat capacity $C(T) = dU(T)/dT$. Treatment of experimental results when Na_{139}^+ clusters have lost three atoms as a result of the thermal decay process leads to a heat capacity in the melting region in the form,[29] analogous to formula (14),

$$C(T) = C_0 + C_{max} \exp\left[-\frac{(T - T_m)^2}{2\Delta^2} \right], \quad C_{max} = \frac{\Delta E}{\Delta\sqrt{2\pi}}, \tag{19}$$

with parameters $T_m = 267$ K, $\Delta E = 1.98$ eV, $C_{max} = 730 = 0.063$ eV/K, $2\Delta = 12.6$ K. Note that the melting point of bulk sodium is 371 K, and the specific latent energy is $\Delta E/n = 27$ meV, while for this cluster we have $\Delta E/n = 14$ meV.

In the two-state approximation, with the cluster heat capacity given by formulas (14) and (19), the maximum and width of the ''resonance'' for the heat capacity are connected. The resonance width in formula (19) is expressed through the other parameters by the relationship,

$$\Delta = \frac{T_m^2}{\Delta E}\sqrt{\frac{\pi}{2}} = \frac{T_m}{\Delta S}\sqrt{\frac{\pi}{2}}. \tag{20}$$

Using the measured values of T_m, C_{max}, and Δ, we have $\Delta S = \sqrt{2 C_{max}} = 54$, and $\Delta S = T_m\sqrt{\pi}/(\Delta\sqrt{2}) = 52$. From this we obtain $\Delta E = T_m \Delta S = 0.61$ eV, which is only 31% of that obtained from the energy absorbed photons.

Analyzing this contradiction, we note that the formulas used are valid for the phase transition involving two cluster aggregate states or phaselike forms. In the interpretation of the experiment, it was assumed that the energy of absorbed photons converts entirely into the cluster's internal energy. The model introduced here suggests that, under conditions of this experiment, only 31% of the absorbed energy is transformed into internal cluster energy, and that the other portion passes into other degrees of freedom. In particular, this energy may be carried off by emitted photons or kinetic energy. A more accurate analysis of this problem will require additional experimental study.

Another reason for this contradiction may be due to a difference in how evaporation from a cluster occurs under equilibrium and nonequilibrium conditions. Under equilibrium conditions, an atom is released from a heated cluster when its fluctuating energy exceeds its binding energy. This process is slow relative to typical vibrational periods inside the cluster, and an atom so released has a typical thermal energy, close to the binding energy of the atom. On the contrary, under nonequilibrium conditions in the cluster, when some few degrees of freedom are excited, atoms may escape as a result of energy transfer from only these degrees of freedom. Under these circumstances, the energy of a released atom may be well above the thermal evaporation energy. Therefore, if the evaporation process occurs from a nonequilibrated cluster, the effective energy deposited as heat in the cluster will not be all that the photons deliver, and the interpretation of the experiments will have to be revised.

In the experiments under consideration,[29,31] the excitation energy from the photons exceeds the atomic binding energy by about a factor of 4. Hence if this process can be interpreted as quenching of excitons, the efficiency of the photon absorption as a heating process is approximately 25%. This is only a rough estimate; a more precise assessment of this will require a deeper understanding of the redistribution of energy from the exciton spectrum and the precise way energy passes from electronic to vibrational degrees of freedom, to dissociation of one or more surface atoms. Nevertheless, this estimate is of the same magnitude as the efficiency of the absorption process that we can infer from experimental data, 31%. Therefore as a rough approximation one can see justification to examine how excitations decay in the experiment under consideration.

CONCLUSION

The two-state approximation shows itself to be useful for the analysis of cluster behavior in the range of phase coexistence. This approximation classifies and restricts configurations of cluster atoms to two groups, one for the solid and the other, for the liquid. The differences of configurational energy and vibrational structure are neglected within each category, but the liquid differs from the solid both in energy and entropy, notably in configurational entropy. Configurationally excited cluster states that do not figure into the dominant contributions to either solid or liquid forms do not contribute significantly to cluster thermodynamic parameters and we neglect them. This approximation also requires thermodynamic equilibrium of the atomic motions in each of the phases. The two-state approximation, when it is valid, can be used for both canonical and microcanonical ensembles of clusters.

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