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# Molecular dynamics study of phase transition and nucleation in supercooled clusters of potassium iodide

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## Abstract

In a series of molecular dynamics (MD) runs on (KI)<sub>108</sub> clusters, the Born–Mayer–Huggins potential function is employed to study structural, energetic, and kinetic aspects of phase change and the homogeneous nucleation of KI clusters. Melting and freezing are reproducible when clusters are heated and cooled. The melted clusters are not spherical in shape no matter the starting cluster is cubic or spherical. Quenching a melted (KI)<sub>108</sub> cluster from 960 K in a bath with temperature range 200–400 K for a time period of 80 ps both nucleation and crystallization are observed. Nucleation rates exceeding 10<sup>36</sup> critical nuclei m<sup>−3</sup> s<sup>−1</sup> are determined at 200, 250, 300, 350, and 400 K. Results are interpreted in terms of the classical theory of nucleation of Turnbull and Fisher and of Buckle. Interfacial free energies of the liquid–solid phase derived from the nucleation rates are 7–10 mJ m<sup>−2</sup>. This quantity is ~0.19 of the heat of transition per unit area from solid to liquid, or about two-thirds of the corresponding ratio which Turnbull proposed for freezing transition. The temperature dependence of  $\sigma_{sl}(T)$  of (KI)<sub>108</sub> clusters can be expressed as  $\sigma_{sl}(T) \propto T^{0.34}$ . © 1999 Elsevier Science B.V. All rights reserved.

## 1. Introduction

Clusters have become increasing popular subjects for investigation, partly because of their novel status intermediate between molecular and bulk systems but partly because they are particularly tractable systems to be treated by molecular dynamics (MD) simulations. Although a considerable number of computer simulations of clusters have presented in the literature, most of the detailed studies of transitions in clusters to date have been concerned with small atomic and molecular systems [1–5]; only a

few MD simulations have been reported so far for ionic systems [6–8].

Quantitative investigations of homogeneous nucleation have proven to be troublesome to perform. For reasons discussed by Turnbull [9,10] and others, deductions based on pure theory are hampered by the complexity of the problem. Many years ago, Turnbull began the first systematic studies of the kinetics of homogeneous nucleation in the freezing of liquids. He and his collaborators devised both an effective experimental technique [10] and a reasonable theoretical framework for interpreting experimental results. Experiments proved to be sufficiently difficult so that relatively few studies have been carried out with

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fully convincing precision. Interfacial free energies are very difficult to measure directly when one of the phases is solid. The most direct method that has yielded apparently valid results is that of Hobbs and Ketcham [11] for water. This method requires a long time for equilibrium interfacial contact angles to develop between the liquid and two small crystals separated by a grain boundary. Therefore, it has been worthwhile to turn to computer simulations of phase transitions to explore what insights they may convey. Although the rate of homogeneous nucleation studied on a microsecond time scale could be followed by electron diffraction [12], it is possible to follow certain aspects of transformations in computer simulations that are extremely difficult to monitor in cluster and bulk systems by existing techniques.

Alkali halide clusters are good model systems because their interaction potential parameters are quite well known [13]. Furthermore, no experimental method of preventing crystallization of the liquid alkali halides has been found and it is possible to freeze the melt into microcrystals in MD simulation even at unrealistically fast cooling rates [6]. In the present paper, our investigation includes the features of phase transition of  $(\text{KI})_{108}$  clusters, the determination of nucleation rates from MD simulations, how they vary with temperature, and what can be inferred from the rates according to classic nucleation theory.

## 2. Procedure

The system is a cluster of 108 ion pairs whose starting configuration is based on the face center cubic cell with  $\text{K}^+$  at  $(0, 0, 0)$  and  $\text{I}^-$  at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ , and the fcc cell parameter is taken to be  $a = 7.0655 \text{ \AA}$  [14]. 108  $\text{K}^+$  and 108  $\text{I}^-$  ions are initially arranged in a cluster of cubic shape with  $3 \times 3 \times 3$  unit cells. Molecular dynamics simulations are carried out with a modified version of the program MDIONS [15]. The well-known Born–Mayer–Huggins [13,16] interaction potential function is adopted, that is,

$$U = \sum \left\{ q_i q_j / r_{ij} + A_{ij} \exp[(\sigma_{ij} - r_{ij})/\rho] \right\}, \quad (1)$$

where the first term is a simple Coulomb interaction and the second term is the short-range repulsive interaction caused from the overlap of the filled

electronic shells of the ions. Here  $r_{ij}$  is the distance between ions  $i$  and  $j$ , and  $q_i$  and  $q_j$  represent the charges on the ions  $i$  and  $j$ , respectively. The values of constants  $A_{ij}$  and  $\sigma_{ij}$  are calculated from the parameters given by Tosi and Fumi [13] and listed in Table 1. The value of constant  $\rho = 0.355 \text{ \AA}$  for KI is taken from Tosi and Fumi [13].

The MD simulation processes are as follows. In heating, the simulation starts with 5000 time steps in a bath of 298.15 K and follows by another 5000 time steps at constant energy, then repeats 5000 time steps in a bath at 298.15 K and 10000 time steps at constant energy. During the constant energy stages, thermodynamic averages of such quantities as potential energy and temperature are accumulated, and coordinates, quaternion parameters, etc., of all the ions are saved every 20 time steps. A series of heating stages begin at 400 K, each succeeding stage is 20 K warmer than the previous one. Every stage is first simulated at constant temperature for 1000 time steps and then by 4000 time steps at constant energy. In all the simulations the time step is set at 8 fs. Additional runs are performed that allow 10000 time steps in the heat bath and 5000 time steps at constant energy per 20 K increment close to the transition in order to obtain a more reasonable estimate of melting points. Heating is continued to 960 K, which is  $\sim 100 \text{ K}$  above the melting point of the  $(\text{KI})_{108}$  cluster. Freezing is simulated in a similar way as used in the melting process. In the cooling process, the melted clusters are cooled through a series of stages started from 960 K and each succeeding stage is 20 K cooler than the previous one until the temperature of the clusters reaches 410 K.

To acquire reasonable statistics for the stochastic process of nucleation, it is necessary to make many runs over a substantial temperature range. For this purpose, 90 independent cooling runs are carried out on liquid clusters of  $(\text{KI})_{108}$  to investigate the distribution of times of nucleation. First, 90 liquid clusters

Table 1  
Potential parameters for KI used in the simulation

Ionic pair	$\text{K}^+ - \text{K}^+$	$\text{K}^+ - \text{I}^-$	$\text{I}^- - \text{I}^-$
$\sigma \text{ (Å)}$	2.926	3.370	3.814
$A \text{ (kJ/mol)}$	25.628	20.358	15.268

are generated by fast heating the solid clusters from 400 to 960 K. Heating is continued at 960 K to form 90 clusters each with 2000 or more timesteps than the previous one that gives a set of melted systems

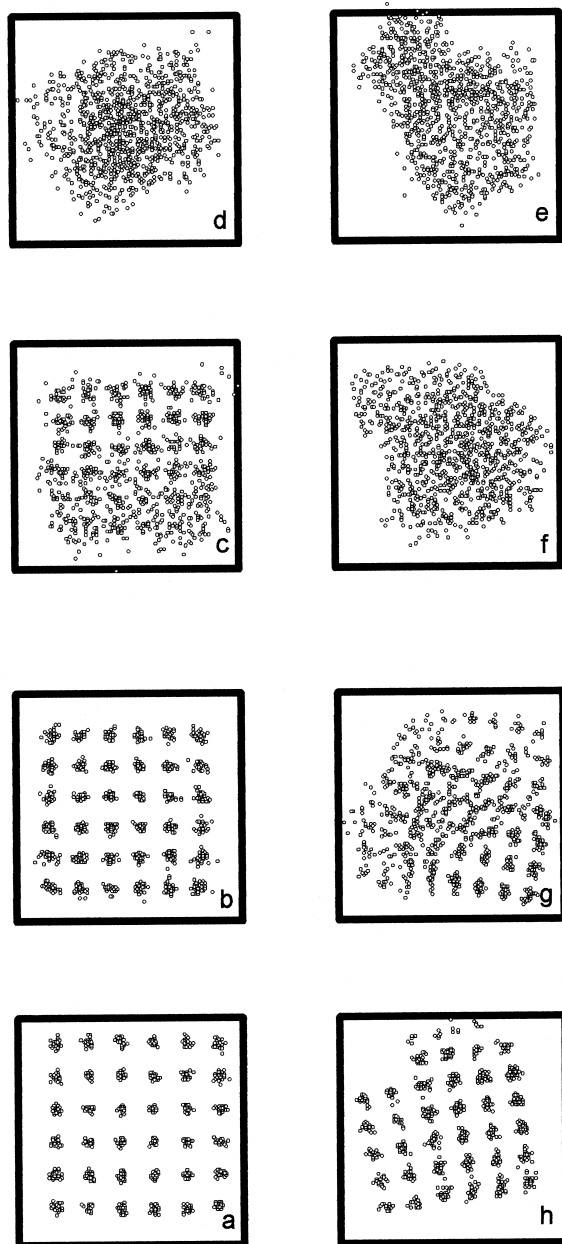


Fig. 1. Images of  $(\text{KI})_{108}$  clusters at various stages of heating and cooling. Heating stage: (a) 400 K, (b) 600 K, (c) 840 K, (d) 880 K; cooling stage: (e) 810 K, (f) 710 K, (g) 470 K, (h) 410 K.

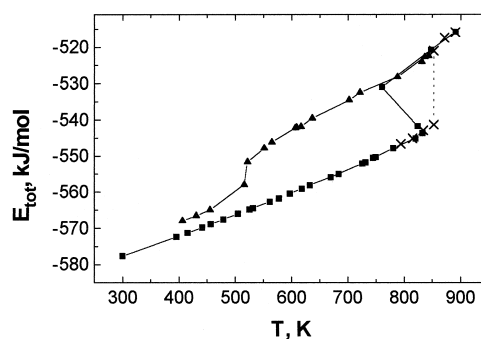


Fig. 2. Total energy per mole as a function of temperature during the heating (solid squares) and cooling (triangles) stages. The dashed line and crosses are with 10000 time steps allowed in the heat bath at each temperature.

with different thermal histories for crystal nucleation studies. Then, nucleation and crystallization of  $(\text{KI})_{108}$  cluster are examined by quenching a completely melted cluster to a certain temperature (200, 250, 300, 350, and 400 K) for a time period of 80 ps.

Various diagnostic tests are employed during the heating and cooling process to monitor the behavior of ions. Melting and freezing are ascertained by observing the temperature dependence of the caloric curve, the Lindemann index  $\delta$  and the pair-correlation function  $g(r)$ . The MACSPIN program written in Visual BASIC 4.0 provides a very efficient tool to view the image of the arrangement of ions and monitor the progress of a phase change.

Useful perspectives can be derived by analyzing nucleation data in terms of classical theory of homogeneous nucleation [9]. In order to carry out such analysis, it is necessary to know the cluster volume  $V_c$  application to nucleation events. For a molecular

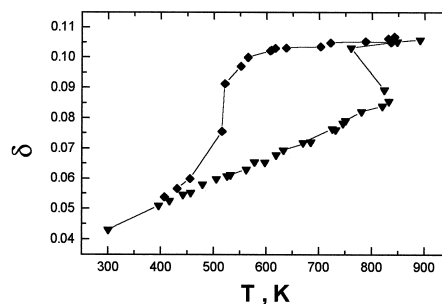


Fig. 3. Lindemann indices  $\delta(T)$  averaged over all  $\text{K}^+\text{I}^-$  ionic pairs in  $(\text{KI})_{108}$  cluster as a function of temperature during stages of heating (triangles) and cooling (solid squares).



index,  $\delta(T)$ , for the slow heating and slow cooling processes. The melting and crystallization temperatures located from the sharp changes in  $\delta(T)$  are consistent with those obtained from the caloric curves (Fig. 2). The melting and freezing of  $(\text{KI})_{108}$  cluster can be observed also by a careful examination of pair-correlation functions  $g(r)$  for K–I (Fig. 4). It is clear that when the cubic shape cluster constructed from  $108 \text{ K}^+$  and  $108 \text{ I}^-$  is heated from the fcc phase in the slow melting approach, it is melted at  $\sim 860 \text{ K}$ . When the melted cluster so formed is cooled from  $960 \text{ K}$ , it starts to freeze to the fcc phase at  $\sim 470 \text{ K}$ .

According to standard nucleation theory, the nucleation rate of crystallization can be estimated from the fraction  $f(t)$  of clusters crystallized into solid phase at time  $t$ , i.e.

$$\ln[1 - f(t)] = -JV_c(t - t_0), \quad (2)$$

where  $t_0$  is the time at which  $N_2$  (the number of clusters in solid phase) is zero,  $V_c$  is the effective volume in which nucleation can occur, and  $J$  is the rate of production of critical nuclei per unit volume per unit time once a steady state of embryonic precursors has been established. The time  $t$  at which a critical nucleus appears in each run is somewhat subjectively identified as the time step at which the instantaneous configurational energy begins a concerted descent toward a new phase. To get a more detailed diagnosis we have applied the criterion adopted in the past [7]. Potassium iodide crystallizes into a fcc structure and the iodine coordinate number to the nearest neighbour in the unit cell is 12. If the

coordination number is 12 and a cutoff distance taken to be the first minimum of a fcc pair-correlation function [4] are used as the criterion of the fcc structure, it will be able to tolerate large displacements. In all, 90 cooling runs are carried out on  $(\text{KI})_{108}$  during which 10 runs were nucleating at  $200 \text{ K}$ , 12 at  $250 \text{ K}$ , 15 at  $300 \text{ K}$ , 12 at  $350 \text{ K}$  and 10 at  $400 \text{ K}$ , as represented in Table 2. The remaining 31 runs did not transform to the fcc phase. Rates  $J$  determined from the data of Table 2 at various temperatures are plotted in Fig. 5.

#### 4. Discussion

As mentioned above, it is very difficult to determine the interfacial free energy between the solid and its liquid directly from experiment. Most of the solid–liquid interfacial free energy data are derived from nucleation rates. According to the classical theory of homogeneous nucleation, the rate of nucleation can be expressed by [20,21]

$$J(T) = A \exp(-\Delta G^*/k_B T), \quad (3)$$

where  $A$  is the prefactor,  $k_B$  is the Boltzmann constant,  $T$  is the temperature, and  $\Delta G^*$  is the free energy barrier to the formation of a critical nucleus from the liquid.  $\Delta G^*$  can be calculated in terms of

$$\Delta G^* = 16\pi\sigma_{sl}^3/[3(\Delta G_v)^2] \quad (4)$$

if the strain energy between the old and new phases is neglected. In Eq. (4),  $\sigma_{sl}$  is the interfacial free energy between solid and liquid and  $\Delta G_v$  represents the free energy of freezing per unit volume. It is a common approximation to calculate  $\Delta G_v$  by taking  $\Delta C_p$  to be zero for the phase change,

$$\Delta G_v(T) = -\Delta H_{fus}(T_m - T)/T_m V_m, \quad (5)$$

where  $\Delta H_{fus}$  is the molar heat of fusion at the melting point  $T_m$  and  $V_m$  is the molar volume. In the present paper we adopt the standard thermodynamic relation

$$\Delta G_v(T) = \frac{1}{V_m} \int_{T_m}^T \Delta S_{fus}(T) dT, \quad (6)$$

where  $V_m$  is the molar volume,  $\Delta S_{fus}$  represents the molar entropy change of fusion at temperature  $T$ ,

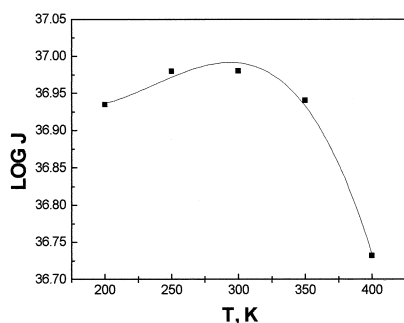


Fig. 5. Nucleation rates at various temperatures. The five points were derived from the present simulations. The solid line is the fitting curve.

which can be estimated from the enthalpies and heat capacities of solid and liquid. The heat capacity of the solid phase [22] in  $\text{cal mol}^{-1} \text{K}^{-1}$  can be expressed in the temperature range 298–954 K by

$$C_p = 9.282 + 6.912 \times 10^{-3}T + 1.178 \times 10^{-5}T^2, \quad (7)$$

but no heat capacity of the supercooled liquid is available in the region of interest as far as we know. The difference of heat capacities  $\Delta C_p$  is derived from the difference between the slopes of the liquid and solid curves in Fig. 2 and listed in Table 3.

The kinetic prefactor  $A$  can be expressed as [25]

$$A = 2(\sigma_{\text{sl}}k_{\text{B}}T)^{1/2}[\exp(-\varepsilon/k_{\text{B}}T)]/(h\nu_{\text{m}}^{2/3}), \quad (8)$$

where  $\nu_{\text{m}}$  is the volume per molecule and the symbol  $\varepsilon$  represents the activation energy for motion of a molecule from the liquid into a growing embryonic crystal. According to the viscous flow model [26], the coefficient of viscosity  $\eta$  is given by

$$\eta = (h/\nu_{\text{m}})\exp(-\varepsilon/k_{\text{B}}T). \quad (9)$$

Therefore, Eq. (8) can be transformed into

$$A = 2(\sigma_{\text{sl}}k_{\text{B}}T)^{1/2}/(\nu_{\text{m}}^{5/3}\eta). \quad (10)$$

If all of the parameters in the prefactor  $A$  are known except for  $\sigma_{\text{sl}}$ , it is obvious that the interfacial free energy  $\sigma_{\text{sl}}$  is derivable from the nucleation rate  $J$ . Grant and Gunton [27] expressed the prefactor  $A$  as

$$A = 0.77\lambda(\sigma_{\text{sl}})^{7/2}/[(k_{\text{B}})^{3/2}T^{1/2}L^2(-\Delta G_v)\xi^4] \quad (11)$$

where  $\lambda$ ,  $L$ , and  $\xi$  represent the thermal conductivity, heat of fusion per unit volume of solid, and correlation length characterizing the thickness of the interface between the old and new phases, respectively.

Table 3  
Thermodynamic and physical properties used in analyses

Quantity	Value	Ref.
$T_{\text{m}}$ (K)	955	[23]
$\Delta H_{\text{fus}}$ ( $\text{J mol}^{-1}$ )	17 138	[23]
$C_p(\text{l}) - C_p(\text{s})$ ( $\text{J mol}^{-1} \text{K}^{-1}$ )	15.0	this work
$\log(\eta)$	$-4.3 + 2778/T$	[24]
$V_{\text{m}}$ ( $\text{m}^3 \text{mol}^{-1}$ )	$5.33 \times 10^{-5}$	[23]

As shown in Fig. 5, the derived nucleation rates from MD simulations are over  $10^{36}$  critical nuclei per cubic meter per second and exceed the rates measured in conventional nucleation experiments [28,29]. These results are in agreement with those of  $(\text{NaCl})_{108}$  clusters [7]. According to present MD simulations, the maximum nucleation rate is to be reached, which remains to be experimentally proven. At extreme supercooling (before the maximum of the curve in Fig. 5), the increasing viscosity prevails over the decrease cost in free energy barrier to nucleation ( $\Delta G^*$  of Eq. (3)) as the supercooling is increased, which leads to sluggish nucleation and explains the downturn in Fig. 5. For warm clusters (after the maximum of the curve in Fig. 5), the most important factor augmenting nucleation is the decrease in the free energy barrier with an increase in supercooling, which accounts for the upturn in Fig. 5.

In general, there are several sources of error in the nucleation analyses, one being the effective volume  $V_{\text{c}}$  for nucleation. We approximately use one-third of the total cluster volume as the  $V_{\text{c}}$  value, but this uncertainty can only influence the result within a fraction of an order of magnitude. Another source of error is the uncertainty in the starting transition time, which should affect the result by less than an order of magnitude. A major source of error is due to the statistical error caused by the comparatively small number of nucleation events. Fortunately, we have adopted many independent nucleation events to analyse nucleation rates.

$\sigma_{\text{sl}}$  is the derived parameter of greatest significance in nucleation theory. Fig. 6 shows that the solid–liquid interfacial free energies tend to increase slowly with increasing temperature as expected [29,30]. The magnitude of the solid–liquid interfacial free energy is plausible when considered in light of Turnbull's observation [28]. For a variety of metalloids and simple nonmetallic substance he observed that

$$\sigma_{\text{sl}} = k_{\text{T}}\Delta H_{\text{fus}}/(V_{\text{m}}^2N_{\text{A}})^{1/3}, \quad (12)$$

where  $V_{\text{m}}$  is the molar volume and  $N_{\text{A}}$  is Avogadro's number. Turnbull found that  $k_{\text{T}}$  tended to be  $\sim 0.32$ . The solid–liquid interfacial free energies  $\sigma_{\text{sl}}$  are derived by Eqs. (3), (4), (6) and (10) and the propor-

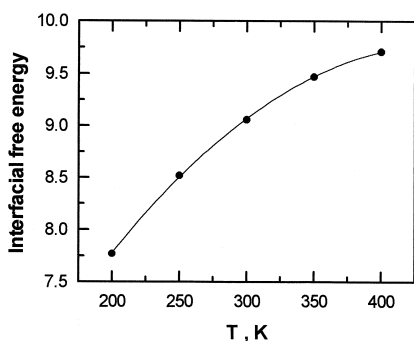


Fig. 6. Solid–liquid interfacial free energies ( $\text{mJ m}^{-2}$ ) derived from nucleation rates at various temperatures. The five points are from the present molecular dynamics simulations. The solid line represents the fitting curve.

tionality constant  $k_T$  for the  $(\text{KI})_{108}$  cluster system is 0.19. Bartell [3] suggested  $k_T$  tends to be perhaps 0.2–0.3 for many interfaces, including solid–solid as well as solid–liquid. This illustrates the interfacial free energies derived are not unreasonable, at least, it provides a useful order of magnitude for the solid–liquid interfacial free energy of KI in the absence of more complete information. If using Eqs. (3), (4), (6) and (11), the derived  $\sigma_{\text{sl}}$  ( $17.0 \text{ mJ m}^{-2}$ ) at 400 K is closer to Turnbull's value ( $19.0 \text{ mJ m}^{-2}$ ). Unfortunately, no thermal conductivities of KI are available below 400 K. The temperature dependence of  $\sigma_{\text{sl}}(T)$  has been taken as the following empirical expression [27]

$$\sigma_{\text{sl}}(T) = \sigma_{\text{sl}}(T_1)(T/T_1)^n, \quad (13)$$

where  $n$  is a number presumably rather smaller than unity. It is reasonable to relate the interfacial free energies of water [31] obtained at  $\sim 195$  and  $\sim 240$  K by using  $\sigma_{\text{sl}}(T) \propto T^{0.3}$ . A value between  $n = 0.3$  and  $n = 0.4$  was obtained from the freezing experiment of mercury [32]. In the case of the  $(\text{KI})_{108}$  cluster, the  $n$  value is 0.34, that is  $\sigma_{\text{sl}}(T) \propto T^{0.34}$ , which is consistent with that of water or mercury.

## 5. Conclusions

The phase transition and nucleation of  $(\text{KI})_{108}$  clusters are examined by MD simulations. The homogeneous nucleation rates exceed  $10^{36}$  critical nuclei  $\text{m}^{-3} \text{s}^{-1}$  at temperatures of 200–400 K. The

solid–liquid interfacial free energies  $\sigma_{\text{sl}}$  derived are  $\sim 7\text{--}10 \text{ mJ m}^{-2}$  at these temperatures.

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