Abstract. It is of great interest to study how the change of state from the monomer (atomic or molecular) state to the condensed matter state arises. For this cause we pay attention to changes of physical properties from the monomer state to the condensed matter state by examining the binding energy and the energy of formation of atomic and molecular clusters as a function of cluster size. We then show how phase transitions from the gaseous monomer states to the condensed matter states arise through the formation of intermediate cluster states leading to homogeneous or heterogeneous nucleation processes. In addition, we discuss how the onset of the Bose-Einstein condensation in high temperature superconductors may occur by showing some resemblance to the nucleation processes despite intrinsic physical differences between the two processes.

1. Introduction

Phase transition is a widely spread phenomenon which occurs in both nature and technological applications. A bulk (condensed matter) phase from a gaseous phase may arise with the process of nucleation. That is, nucleation initiates the onset of phase transition to the condensed matter (bulk) state by allowing stable growth of atomic or molecular clusters beyond a critical cluster size. There exist two kinds of nucleation processes for the onset of phase transition to the bulk phase, the homogeneous nucleation process and heterogeneous nucleation process [1, 2]. Such formation of the bulk phase via the nucleation processes is an interesting subject for both basic sciences and industrial applications, which encompass numerous areas such as physics, chemistry, bio-science, surface science, micro-electronics engineering, materials science and technology and atmospheric science.

As mentioned above, nucleation initiates the onset of phase transition which starts in a small region of real space requiring a nucleation site. The homogeneous nucleation refers to the onset of phase transition which occurs in the absence of foreign particles or surfaces by overcoming the barrier height of the energy of formation by thermal fluctuations, while the heterogeneous nucleation arises in the presence of the foreign particles or surfaces. In both nucleation processes stable growth of particles (clusters) arises owing to a continuous decrease in the energy of formation by overcoming the energy barrier height after a critical size is reached. In figures 1 and 2 we display schematic diagrams to reveal such variation of the energy of formation $\Delta U$, as a function of cluster size $n$ for the homogeneous nucleation and heterogeneous nucleation process respectively.
Using our earlier quantum statistical mechanical approach [3-9] we plan to examine the change of physical properties of both the atomic and molecular clusters as a function of cluster size and discuss how both the homogeneous and heterogeneous nucleation processes arise after an initial process of atom or molecule clustering at small sizes. For this study we first examine how physical properties vary from the monomer (atomic or molecular) states to the cluster states which are shown to be intermediate states between the monomer and bulk states. We then show how the onset of phase transition to the macroscopic bulk (condensed matter) states arises through the formation process of intermediate state clusters. In addition, we discuss how the onset of the macroscopic bulk phase of Bose-Einstein condensation in high temperature superconductors may arise, showing some similarity to nucleation processes despite intrinsic physical differences between the two.
2. From atomic and molecular states to condensed matter states

We first present a study on the variation of physical properties with cluster size with an illustration of molecular clusters. As well-known, the accurate Ab initio calculations for the atomic and molecular clusters of sufficiently large size are currently inaccessible owing to the requirement of excessive computational time. For this reason, we resort to the computationally efficient semi-empirical method of MNDO (modified neglect of differential overlap) [10] and its modified scheme [8, 9, 11] to properly treat hydrogen bonding of water molecular clusters.

To remedy the problems of poor predictions with MNDO for the physical properties of hydrogen bonded water clusters, earlier we developed an improved method, HMNDO [9] or IMNDO [11] to describe the physical properties of hydrogen bonded water clusters and found that the computed results of ionization potentials and binding energies [11] for small water clusters tested are in good agreement with the Ab initio calculations of Tomoda and Kimura [12]. The selected geometric configurations of water clusters of size up to \( n=8 \) are the same as the ones used in the Ab initio study [12]. In figures 3 and 4 we show the computed results of larger clusters beyond \( n=8 \) based on geometry optimization. In figure 3 the predicted hydrogen bond strength (binding energy) of water molecular clusters is seen to increase with cluster size \( n \). The solid squares represent the computed values of the average binding energy (bond strength) and the solid line, the linear least square fit to the predicted values. Interestingly, a tendency of rapid saturation is shown to occur at relatively small molecular clusters of nano scale as shown in the figure.

![Figure 3. Average hydrogen bond strength, Kcal/mole vs. water cluster size, n](image)

In figure 4, we display the computed vertical ionization potential (eV) as a function of cluster size for the same geometric configurations of water clusters chosen in the above study. Initially a rapid drop of ionization energy at small molecular cluster sizes is predicted with the trend of slower variation at larger clusters. The predicted values of both the binding energy and ionization potential of water molecular clusters are similar in behavior in that they show a propensity of rapid convergence to their bulk limit values. It is, thus, of great interest to see whether the onset of phase transitions or nucleation processes can arise with the presence of such small molecular clusters as intermediate physical states between the monomer and bulk.
states.

![Graph showing Vertical Ionization Potential as a function of water cluster size](image)

**Figure 4.** Vertical Ionization Potential eV as a function of water cluster size n based on HMNDO method (Ref. 9). The computed results are based on the geometric configurations of Ab initio calculations of water clusters [Ref. 10].

We now examine atomic clusters of silicon by paying attention to the variation of binding energy per atom [6] with cluster size. In order to estimate the bulk limit of binding energy (cohesive energy) of silicon crystal, in figure 5 we display the average binding energy of silicon atomic cluster, that is, the binding energy per atom as a function of the inverse of cluster size n. The solid square denotes the average binding energy (eV) of each cluster and the solid line, the linear least square fit up to cluster size n = 20. Earlier we found that the analytic function of average binding energy which best represents the results of the linear least square fit is given by $B_n = B_{\infty} (1 - n^{-\alpha})$ where $B_{\infty}$ is the average binding energy of cluster size n; $B_{\infty}$, the predicted bulk limit value and $\alpha = 0.623$, a fitting parameter [6]. The predicted bulk value is $B_{\infty} = 4.785$ eV compared to the observed cohesive energy of silicon crystal, 4.63 eV [13]. As shown in the figure, we note a rapid initial increase of the average binding energy $B_n$ at smaller cluster sizes followed by a slower increase at larger cluster sizes. At size n=20, the computed average binding energy is 4.25 eV, suggesting that the small atomic clusters of nano-size tend to get quickly close to bulk physical properties.
As can be easily understood from the schematic diagrams of nucleation processes shown in figures 1 and 2, the homogeneous nucleation process involves an initial increase of the energy of formation (or free energy) to reach a substantially high energy barrier height, thus requiring a substantially high supersaturation ratio or vapor pressure for the stable growth of clusters beyond the critical cluster size to allow for nucleation process to take place. On the other hand, the heterogeneous nucleation process can readily occur with an initial decrease in the energy of formation followed by an energy barrier height at a critical size, as is shown in figure 2, thus demanding a lower supersaturation ratio compared to the case of the homogeneous nucleation process. Earlier, from the use of a quantum statistical mechanical method based on multistate-kinetics approach [5] we found that the computed results of homogeneous nucleation rates as a function of both temperature and supersaturation ratio are consistent with the cloud chamber measurements of Miller et al. [14]. The derived energy of formation (see Eq. 2.24b in reference [5]) is given by,

\[
\Delta U_\alpha = \Delta E_\alpha - kT(\ln \xi'_\alpha - n \ln \xi'_1) - (n-1)kT \ln\left(\frac{P}{kT}\right)
\]

where \(\Delta U_\alpha\) is the energy of formation for the molecular cluster size \(n\) at temperature \(T\) and pressure \(P\); \(\Delta E_\alpha\), the total binding energy of the molecular cluster of size \(n\) at \(T = 0\) K; \(\xi'_\alpha\), the volume averaged partition function of clusters of size \(n\) involved with the translational, rotational and vibrational degrees of freedom and \(\xi'_1\), that of monomer. The nucleation rate \(J\) is written [1],

\[
J = \beta A_\alpha F Z_\alpha \exp(-\Delta U_\alpha / kT)
\]
Here $\beta$ is the sticking coefficient (often assumed to be 1); $A_n$, the surface area of the critical cluster size $n^*$; $F$, the monomer flux; $Z_n$, the Zeldovitch factor and $\Delta U_n$, the energy of formation for the clusters of critical size $n^*$, i.e., the energy barrier height. Employing the statistical mechanical multi-kinetics approach [5] for homogeneous nucleation process the critical cluster size of water clusters is found to range between $n = 25 \text{ and } 50$ for the temperature range of 260 K to 300 K at large supersaturation ratio, $S = 5$. This indicates that the formation of such small clusters of nano size as physically intermediate state clusters in the gas phase can lead to the onset of phase transition to the condensed matter phase.

Using a similar approach [3] [9] of quantum statistical mechanics, we now examine the heterogeneous nucleation process of water molecules in the presence of a foreign particle and a foreign surface by choosing a cesium ion, $\text{Cs}^+$ [3] for the former and a silicon oxide surface for the latter [9]. As shown in figure 6 for the heteromolecular clusters of $\text{Cs}^+ (\text{H}_2\text{O})_n$, we note that the energy of formation $\Delta U_n$ at the supersaturation ratio of $S = 1$ initially decreases in agreement with the generic nature of the heterogeneous nucleation process schematically shown in figure 2 and that the predicted minimum energy of formation occurs at a cluster of small size around $n = 10$.

![Figure 6](image)

**Figure 6.** Energy of formation Kcal/mole as a function of water cluster size $n$ for $\text{Cs}^+ (\text{H}_2\text{O})_n$.

For the heterogeneous nucleation on the silicon oxide surface we avoid reproduction of the phase diagrams (see figures 3 to 6 in reference [9]) which show the energy of formation vs. temperature at various supersaturation ratios. Instead, here we discuss new observations which were missed in the our previous study [9]. The heterogeneous nucleation processes occur with much lower barrier heights compared to the case of homogeneous nucleation, accompanying an initial decrease of the energy of formation, similarly to the above case of heterogeneous nucleation involving the foreign particle of $\text{Cs}^+$ ion. We find that the higher the saturation ratio, the more rapid the initial decrease of the energy of formation takes place with its minimum at a smaller cluster size. Another point of interest is that with increasing temperature the energy of formation tends to change from negative to positive values as the cluster size further increases to a critical size, while maintaining the robustness of initial decrease at small clusters. In both
the homogeneous and heterogeneous nucleation processes we find that the presence of preformed clusters in the gas phase is essential for the onset of phase transition or the initiation of nucleation process. The physical properties (binding energy and the energy of formation at finite temperature) are seen to be intermediate between the monomer (atomic or molecular) state and the condensed matter (bulk) state, as mentioned earlier.

Finally, we explore an entirely different system concerned with the physics of Bose-Einstein condensation (BEC) for high temperature superconductors in order to see correlation between the preformed phase of ‘molecular’ clusters, i.e., the Cooper pairs and the superconducting phase. They are believed to preexist before the onset of superconducting phase transition [15]. Lately, in order to study the high temperature superconductivity which is involved with the two-dimensional systems of strongly correlated electrons, namely, the doped Mott insulators [16] we proposed an advanced slave-boson theory of superconductivity [17] which differs from other slave-boson theories [18-21]. This will be briefly discussed below.

The t-J Hamiltonian for the two-dimensional systems of strongly correlated electrons is given by

$$H = -t \sum_{\langle i,j \rangle} (c^+_{i\sigma} c_{j\sigma} + c^+_{j\sigma} c_{i\sigma}) + J \sum_{\langle i,j \rangle} (S_i^+ S_j - \frac{1}{4} n_i n_j)$$

where $t$ is the hopping energy of electron; $c^+_{i\sigma}$ ($c_{i\sigma}$), the creation (annihilation) operator of electron with spin $\sigma$ at site $i$; $J$, the antiferromagnetic Heisenberg coupling constant; $S_i$, the spin operator at site $i$ and $n_i$, the number operator of electron at site $i$. $\langle i,j \rangle$ denotes summation over the nearest neighbor sites.

Introducing proper Hubbard-Stratonovich transformations involved with hopping, spin (spinon) pairing, and charge (holon) pairing order parameters for the t-J Hamiltonian above, the effective Hamiltonian is derived to be [17],

$$H_{eff} = \frac{J(1-\delta)^2}{4} \sum_{\langle i,j \rangle} \left[ |\Delta_f|^2 + |\chi|^2 \right] + \frac{J}{2} \sum_{\langle i,j \rangle} \left[ |\Delta_f|^2 - \frac{1}{4} n_i n_j \right]$$

$$-J(1-\delta)^2 \sum_{\langle i,j \rangle} \left[ \chi^* f_{i\uparrow} f_{j\downarrow} + c.c. \right] - \frac{J(1-\delta)^2}{2} \sum_{\langle i,j \rangle} \left[ \Delta_{ij}^* (f_{i\uparrow} f_{j\downarrow} - f_{i\downarrow} f_{j\uparrow}) + c.c. \right]$$

$$-\mu \sum_{i,\sigma} f_{i\sigma}^+ f_{i\sigma} - \mu' \sum b_i^+ b_i$$

$$-t \sum_{\langle i,j \rangle} \left( \chi_i^* b_j^+ b_i + c.c. \right)$$

$$-\frac{J}{2} \sum_{\langle i,j \rangle} \left( \Delta_{ij}^* b_i^+ b_j^+ + c.c. \right)$$

Here $\delta$ is the hole concentration; $f$, the spinon (spin) annihilation operator and $b$, the holon (charge) annihilation operator. The first bracketed term represents the minimum energy corresponding to the saddle point of the order parameters, $\Delta_f^*$, $\Delta_{ij}^*$, and $\chi_{ij}$. Thus, this term contains no contribution from the fluctuations of the order parameters. The second term is a
correction term which arises as a result of coupling between the spin (spinon) singlet pairing channel and the charge (holon) pairing channel. The third term represents the kinetic energy of the spinons and the fourth term, the spinon pairing interaction for the binding of the spinon pairs. The fifth and sixth terms represent the effective chemical potentials of the spinons and the holons respectively. The seventh term represents the kinetic energy of the holons and the last term, the holon pairing order $\Delta^b_{\mu}$ coupled with the spinon pairing order $\Delta^f_\nu$. It is important to realize from the last term that the Cooper pairs are formed owing to the coupling of the spinon pairing order to the holon pairing order, which is responsible for the superconductivity of high temperature cuprates.

Using the above theory here we present an interesting finding based on the study of Bose-Einstein condensation in high temperature superconductors. From their exact diagonalization calculations for the Cooper pairing of two holes with the square lattice size up to 32, Chernyshev et al. [22] found that the pairing energy (binding energy) of the Cooper pair is proportional to the Heisenberg coupling constant $J$ and inversely proportional to the lattice size. Paying attention to the Cooper pairs of coherent phase in association with the Bose-Einstein condensation, we calculated the ratio of the pairing (binding) energy of the Cooper pair to the lattice size. From this study we find that the pairing energy in the superconducting phase is independent of hole concentrations, revealing a trend of proportionality to $J$ and inverse proportionality to the lattice size. Surprisingly, this trend is consistent with their exact diagonalization calculation [22] of the pairing energy of the Cooper pair based on the presence of only two holes in the square lattice. This is equivalent to the presence of preformed Cooper pairs with no phase coherence which exist before the onset of superconducting phase transition. Thus we claim that there exist preformed Cooper pairs acting as ‘molecular clusters’ of critical size in the normal state to cause the onset of the superconducting phase transition, similarly to the case of the nucleation process for the onset of the phase transition which arises from the preformed clusters of critical size in the gas phase.

3. Conclusion
In the present study, we examined how changes of physical properties occur from the monomer (atomic or molecular) state to the condensed matter (bulk) state by paying attention to the binding energy and the energy of formation of clusters as a function of cluster size. It is shown that the physical properties of both the atomic and molecular clusters smoothly vary as intermediate states between the monomer state and the macroscopic bulk state. We noted that the critical cluster size for the onset of phase transition is a nano scale for both the homogeneous and heterogeneous nucleation processes. To put it otherwise, for the onset of phase transition or nucleation, there exist the preformed clusters of nano size in the gas phase which will lead to the clusters of critical size, by having intermediate physical properties between the monomer state and the macroscopic bulk (condensed matter) state. In addition, we discussed that as a macroscopic bulk phase the Bose-Einstein condensation in high temperature superconductors can occur by first requiring the presence of preformed Cooper pairs as the “molecular clusters” of critical size in the normal state for the onset of the superconducting phase transition, similarly to the case of nucleation processes in which the presence of the preformed clusters in gaseous phase (‘normal phase’) is essential for causing the onset of the phase transition to the state of the macroscopic bulk (condensed) matter.

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References
[1] Abraham, F F 1974, Homogeneous Nucleation Theory (New York, Academic Press) p 4-29
[2] Dimo Kashchiev, Nucleation : Basic Theory with Applications (Woburn, MA, Oxford) p 17-29
[3] Salk Sung-Ho Suck 1981, J. Chem. Phys. 75, 5090
[4] Salk Sung-Ho Suck 1987, J. Chem. Phys. 87, 636
[5] Salk Sung-Ho Suck and Lutrus, C K 1990 Phys. Rev. A 42, 6151
[6] Salk Sung-Ho Suck, Lutrus C K, Hagen D E, Oshiro T, Beck S and Loper G. L. 1992, Phys. Rev. B 45, 1458
[7] Lutrus, C K, Oshiro T, Hagen D E and Salk Sung-Ho Suck 1993 Phys. Rev. B 48, 15086
[8] Oshiro, T, Lutrus, C K, Hagen D E, Beck S, and Salk Sung-Ho Suck 1993 Solid State Comm. 87, 801
[9] Lutrus C K, Hagen D E and Salk Sung-Ho Suck 1993 J. Chem. Phys. 99, 9962
[10] Dewar M J S and Thiel W 1977 J. Am. Chem. Soc. 99, 4899
[11] Lutrus C K and Salk Sung-Ho Suck 1986 Theor Chim Acta 70, 3
[12] Tomoda, S and Kimura K 1983 Chem. Phys. Lett. 102, 560
[13] Moore C E 1965, Atomic Energy Levels, U. S. National Bureau of Standards Reference Data Series (Washington, D. C. U. S. GPO) Vol. 35
[14] Miller R C, Anderson J R, Kassner Jr. J L and Hagen D E 1983 J. Chem. Phys. 78, 3204
[15] Carlson E W, Emery V J , Kivelson S A and Orgad D 2004, The Physics of Conventional and Unconventional Superconductors (Berlin, Springer, Berlin, 2004); references therein.
[16] Anderson P W 1987 Science 237, 1169
[17] Lee S S and Salk Sung-Ho Suck 2001 Phys. Rev. B 64, 052501; Lee S S and Salk Sung-Ho Suck 2005 Phys. Rev. B 71, 13451
[18] Kotliar G and Liu J 1988 Phys. Rev. B 38, 5142
[19] Suzumura Y, Hasekawa Y and H. Fukuyama 1988 J. Phys. Soc. Jpn, 57, 2768
[20] Ubbens M U and Lee P A 1994 Phys. Rev. B 49, 6853
[21] Anderson P W J et al, 2004 Phys.: Condens. Matter 16, R755 (2004); References therein.
[22] Chernyshev A L, Leung P W and Gooding R J 1998 Phys. Rev. B 58, 13594