On the Physical Cluster of Nucleation Theory: Generalized Hill Cluster

Rasmus A. X. Persson

Department of Chemistry, University of Gothenburg, Sweden

Abstract

The physical cluster originally conceived by Hill (J. Chem. Phys, 23, 617) is generalized for the case \( N > 2 \) in a novel way. Contrary to Hill’s pairwise generalization, this definition assures that all constituent molecules of the cluster have insufficient kinetic energy to escape, and avoids the spurious implication of Hill’s generalization that the molecular velocities are to be increasingly equal.
I. INTRODUCTION

The rate of a phase transition obviously depends to a large extent on the rate at which the molecules can rearrange themselves, and in the case of condensation especially, this rate is much smaller than the typical rate of molecular translation. A condensation process necessitates diffusion along the concentration gradient and would be thermodynamically forbidden were it not for the decrease of chemical potential associated with the transformation, due to the attractive interactions dominating in the condensed phase. However, in the very early stage of the phase transformation, insufficient condensed phase is present to afford this stabilization. In these cases, the transport of matter must occur along the chemical potential gradient. The great reluctance by which this fluctuation takes place is one bottleneck in the condensation process and was first identified by Gibbs, who expressed the free energy of a small cluster as the sum of a surface and a bulk term, taking the surface term to be proportional to the specific surface free energy of the bulk liquid [1]. This approach was further extended into a theory for the kinetics of the process by a number of authors [2–4]. This classical nucleation theory, as it has since become known, predicts a nucleation rate in fortuitous accord with experiment for water condensation in a narrow temperature interval.

In efforts to side track the assumptions of bulk properties for small clusters on the order of 50-100 monomers, much computer simulation, following the pioneering work of Lee et al. [5], has been carried out over the years, and new theories developed. However, the concept of a cluster has in these simulations often been quite arbitrary. Most often based on a simple distance criterion, as in e.g. the Stillinger [6] or LBA [5] cluster, there is no compelling argument \textit{a priori} for the particular dimension of the cluster. The same problem of arbitrariness is faced when exchanging the distance criterion for one of potential energy [7].

Of particular elegance is then the definition due to Hill [8], who regarded molecules in regions of phase space of negative total energy to form a cluster, in analogy with how “bound states” are usually defined in the rest of physics, for instance between atoms in molecules, or between celestial bodies and satellites in astronomy. Moreover, the concept of the critical temperature follows directly from this notion, as the effective temperature where the kinetic energy is so great that no bound states can be formed, even for the infinite cluster, \textit{i.e.} bulk. Following Hill, we denote such a cluster, a “physical cluster.” However, Hill’s generalization
of his cluster definition past the dimer is based on a pairwise expansion in which monomers are not bound to the cluster as a whole, but to each other, and while rigorous, is not completely intuitive. In fact, for large clusters, his definition entails that the velocities of the monomers become increasingly harmonized [9]. In the author’s view, nevertheless, one of the most important concepts of the Hill cluster is its inherent non-locality. Such non-locality has been exploited in other theories of nucleation, the most prominent being the density-functional approach of Oxtoby and Evans [10].

Consider the set $\mathbb{D}_N$ of $N$ particles ordered from 1 to $N$. The particles have positions $\{\vec{r}_i\}_1^N$, velocities $\{\vec{v}_i\}_1^N$ and masses $\{m_i\}_1^N$. Let $U(\{\vec{r}_i\})$ denote the potential energy of the system and let $U(\{\vec{r}_i\})$ have the property that $U(\{\vec{r}_i\}) \to 0$, when the smallest mutual distance in $\{\vec{r}_i\}$ approaches positive infinity. Let us first recall Hill’s definition of the physical dimer.

**Definition 1.** The two particles $i$ and $j$ constitute a physical dimer if $\frac{1}{2}\mu(\vec{v}_i - \vec{v}_j)^2 \leq -U(\vec{r}_i, \vec{r}_j)$ where $\mu = \frac{m_i m_j}{m_i + m_j}$.

Let us now define two ordered subsets of $\mathbb{D}_N$ denoted by $A$ and $B$ such that $A \cup B = \mathbb{D}_N$. We shall denote the mutual energy of interaction between these two subsets as $U(A, B)$ for conciseness. Furthermore, we define $m_A$ to be the sum of the elements of $\{m_i\}$ corresponding to the particles of $A$. Likewise, let $\vec{v}_A$ denote the mass-weighted average velocity of the elements of set $A$. Our generalized definition of Hill’s dimer to the cluster is given below.

**Definition 2.** The ordered set $\mathbb{D}_N$ of $N$ particles constitutes a physical cluster if for all sets $A \neq \emptyset$ and $B = \mathbb{D}_N \setminus A \neq \emptyset$, we have that $\frac{1}{2}\mu_{AB}(\vec{v}_A - \vec{v}_B)^2 \leq -U(A, B)$ where $\mu_{AB} = \frac{m_A m_B}{m_A + m_B}$.

**II. PARTITION FUNCTION OF THE HILL ENSEMBLE**

To treat the physical cluster in the theory of statistical mechanics, we need to derive its partition function. For the sake of notational simplicity, we shall concern ourselves only with the cluster at rest ($\vec{v}_{cm} = 0$). Center-of-mass motion will be assumed separable from the internal degrees of freedom. Hill [8] gives the partition function for the dimer and the explicit expression for the probability

$p[-\beta U(\vec{r}_i, \vec{r}_j)] = \text{erf} \left( \sqrt{-\beta U(\vec{r}_i, \vec{r}_j)} \right) - \frac{2}{\sqrt{\pi}} e^{\beta U(\vec{r}_i, \vec{r}_j)} \sqrt{-\beta U(\vec{r}_i, \vec{r}_j)}$ (1)
that two molecules a physical cluster at inverse temperature $\beta = 1/kT$, where $k$ is Boltzmann’s constant and $T$ is the absolute temperature. Because of the strong analogy between Definitions 1 and 2 we are motivated to apply this probability function to each term in Definition 2 but care must be exerted so as to avoid double counting. We first consider the sets $A_j$ that contain the only element molecule $j = 1, 2, \ldots, N$. The probability that molecule $j$ is part of the cluster is

$$p_j \equiv p[-\beta U(A_j, D_N \setminus A_j)]$$  \hspace{1cm} (2)$$

Next we consider the sets $A_{jk}$ that contain only the elements $j$ and $k$. The probability that the dimer $j, k$ is part of the cluster is

$$p_{jk} \equiv p[-\beta U(A_{jk}, D_N \setminus A_{jk})]$$  \hspace{1cm} (3)$$

We continue to define probabilities like these, over greater and greater subsets $A_{jk, \ldots}$ until we reach the subset that has $N/2$ elements where we must stop to avoid double-counting.

The partition function for the cluster now follows upon substituting the canonical probability function $e^{-\beta U(\{\vec{r}_i\})}$ by $e^{-\beta U(\{\vec{r}_i\})} \prod_j p_j \prod_{j<k} p_{jk} \ldots$ in the definition of the partition function. In the quantum case, we must deal with the subtle issues raised by the Heisenberg uncertainty principle, but in the classical case, this immediately gives

$$Q_{cm} = \frac{V}{N! \Lambda^3 N} \int d\{\vec{r}_i\} e^{-\beta U(\{\vec{r}_i\})} \prod_j p_j \prod_{j<k} p_{jk} \prod_{j<k<l} p_{jkl} \ldots$$  \hspace{1cm} (4)$$

This partition function in essence defines a new ensemble: the ensemble of the physical cluster, or “bound” states. Its probability distribution is not of Boltzmann form. We shall refer to this new ensemble as the “Hill ensemble” in his honor.

### III. CONCLUSION

Definition 2 is very general and encompasses both clusters of molecules or atoms, or the molecules themselves. However, the physical cluster is not defined for all potentials. For instance, the harmonic spring does not satisfy the requirement that the potential energy vanish for large distances. In physical reality, however, such an unbounded potential is never encountered, and all molecules, and especially their clusters, are prone to disintegration at high enough temperature.
Because the products run over all dimers, trimers, . . ., N/2-mers, the numerical complexity in verifying whether N molecules constitute a cluster according to Definition 2 is (N/2)!. Hence, numerical experiments on the physical cluster are prohibitively expensive beyond the very smallest ones. However, generally it is clear that for T → 0, we have

\[ p[-\beta U(\cdot)] \rightarrow 1. \]

Therefore, the Hill ensemble will reduce to the canonical ensemble for low temperatures. This explains the observation by Lee, Barker and Abraham [5] that the thermodynamic properties of Lennard-Jones clusters are largely independent of the choice of cluster constraining radius at low temperature.

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