Statistical mechanics of nucleation: a review

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Abstract: The principles of statistical mechanics have been used to develop a theory of the nucleation of a phase transition, but a number of subtle questions remain and are highlighted in this review. A central issue is the cluster definition, the mathematical scheme which distinguishes a molecular cluster from a collection of separate molecules. There is also the question of whether thermodynamic transition state theory is suitable to describe the process, or whether the development of kinetic rate equations describing cluster growth and decay is a better approach. The classical theory of nucleation is flawed but appears to provide useful estimates in some cases, including water. Phenomenological extensions of the classical theory can improve matters. However, improvements in the theory from microscopic considerations are not simple to apply, require major computational effort and suffer from uncertainties due to lack of knowledge of the fundamental intermolecular interactions. Calculations of the nucleation rate of water droplets are especially difficult since this substance is notoriously difficult to model. Nevertheless, as capabilities improve, accurate calculations should come within reach, which will offer better understanding of the process for practical applications such as the transition from dry to wet steam.

Keywords: statistical mechanics, nucleation

NOTATION

A	parameter in the fit to experimental data
B	parameter in the fit to experimental data
f	mean force on the molecule
f_0	free energy per molecule in the metastable phase
$F(i)$	free energy of an i-cluster
$\mathscr{F}$	Langevin force
$H(N)$	system Hamiltonian
i	cluster size in molecules
i^*	critical size
I_1, I_2, I_3	principal moments of inertia of cluster
I_1^m, I_2^m, I_3^m	principal moments of inertia of the molecule
J	nucleation rate
k	Boltzmann constant
m	molecular mass
M	cluster mass
n_i	population of i-clusters
n_i^{ce}	constrained equilibrium cluster populations
n_i^e	equilibrium cluster populations in subsaturated vapour
n_i^s	i-cluster population in saturated vapour
n_i^{ss}	steady state cluster population in supersaturated vapour
n_1^s	monomer population in saturated vapour
p_v	vapour pressure
p_v^s	saturated vapour pressure
$P_{i \to j}$	transition probability in population dynamics
q	sticking coefficient
q_0	parameter in the Dillmann–Meier model
r	radial position from the cluster centre of mass
r_e	escape radius
S	supersaturation
t	time
T	temperature
$U_0(i)$	cluster potential energy at rest
U_0^m	molecular potential energy at rest
V	system volume
$\mathscr{W}$	molecular probability density in space
Z_d	Zeldovich factor
Z_i	i-cluster canonical partition function
$\mathscr{Z}_i$	modified i-cluster canonical partition function
α_i	parameter in the Dillmann–Meier model
β_i	growth rate of an i-cluster

γ	Langevin friction coefficient
γ^{kin}	cluster decay rate in the Langevin model
γ_i	decay rate of an i-cluster
ΔF	change in free energy
ΔW	work of cluster formation
ΔW_{cl}	classical work of cluster formation
θ_i	parameter in the Dillmann–Meier model
κ_i	parameter in the Dillmann–Meier model
μ	chemical potential
μ_{s}	chemical potential in saturated vapour
Ξ	grand canonical partition function
ρ_{l}	liquid phase density
ρ_v	vapour phase density
ρ_v^{s}	saturated vapour density
σ	planar surface tension
τ	parameter in the Dillmann–Meier model
ω_k	cluster vibrational angular frequency
ω_k^{m}	molecular vibrational angular frequency

1 INTRODUCTION

One of the most remarkable properties of matter is its ability to take different physical forms for different values of parameters such as temperature or pressure. For example, a vapour will condense by the nucleation of droplets when its pressure is raised above the supersaturated vapour pressure, or when its temperature is reduced below the dew point. Such metamorphoses are fundamentally a consequence of the second law of thermodynamics, a principle that can be characterized as a desire on the part of physical systems to minimize their free energy by any available means. This can include the repositioning of molecules on a grand scale: a phase change. Phase transformations are the statistical consequences of the ability of large physical systems, and any environment with which they interact, to explore a huge range of microscopic configurations. This dynamical behaviour, underpinning the second law, remains only partially understood [1], but it seems to be universal.

A practical situation where a change in phase creates problems is the behaviour of steam in turbines. The temperature and pressure gradients are such that water droplets might nucleate with undesirable effects on the performance of the machine, including the erosion of the turbine blades. On the other hand the steam must be expanded as much as possible to extract the most work from it. Some of the drawbacks can be avoided if the phase change can be controlled.

The need for an understanding of the transition from dry to wet steam in turbines has motivated this review, but this is just an example of a process which affects many aspects of the world. The formation of droplets in

a turbine presents practical difficulties, but without atmospheric clouds, which form by a similar process [2], the global climate would be rather different from what it is at present [3]. Aerosol formation in the atmosphere and dust in space [4], and in the case of condensed phases, the freezing of liquids, all proceed by the same basic mechanism. The principal idea is that there exists a bottleneck in the transformation, which is passed through only by fragments, or molecular clusters, of the new phase. The bottleneck is narrowest when the clusters reach a so-called critical size, and therefore the properties of these critical clusters are central to the theory of nucleation [5].

Experimental progress in understanding droplet formation in turbines has been significant [6, 7], but at first sight it would appear that progress on the theoretical side has been less impressive. The tool used most often in modelling studies [8] remains the classical nucleation theory (CNT), derived many decades ago and based on the most primitive ideas of the properties of the critical cluster [9–13]. The capillarity approximation is employed, whereby the critical cluster, however small, is considered as a scaled-down macroscopic droplet of the condensed phase. The model is a version of transition state theory (TST), in which a realization of the system is identified which is in unstable thermodynamic equilibrium, equally able to develop with time into the initial or the final phase. How is it that this model is still employed, when developments in microscopic modelling have proceeded so rapidly in recent years? Why has no better model been developed?

One reason is pragmatism. It is very surprising that the classical theory successfully predicts nucleation rates within a couple of orders of magnitude in the case of water, perhaps the most important substance to understand, for a temperature range of about 210–260 K and a range of supersaturations. Evidence for this has been collected through various studies over the last 20 years [14–20]. This level of agreement is good in the field of nucleation theory! However, in these conditions, the critical cluster consists of only a few tens of molecules, and the capillarity approximation is questionable in the extreme.

However, if a broader view is taken and data for other materials are considered, the failure of CNT is more apparent. The nucleation rate seems to have a dependence on supersaturation suggested by CNT, but the temperature dependence does not agree. Often a temperature range where classical theory is reasonably consistent with experiment does not exist.

Experimental data gathered during recent years can be reviewed briefly. Some early data on n-nonane showed deviations from CNT of four orders of magnitude either way [21]. A study of several members of the n-alkane series [22] confirmed the need for correction factors of again up to four orders of magnitude. Early data for a range of alcohols showed

deviations from CNT of over five orders of magnitude [23]. In an effort to acquire definitive data for a single substance, the nucleation of *n*-pentanol was given particular attention by a number of research groups in the late 1990s and early 2000s. For temperatures in the range 260–290 K most data lie three orders of magnitude above the CNT predictions [24] although some measurements lie between one and three orders of magnitude below [25]. Further results for *n*-pentanol show good agreement with the CNT at 273 K [26], but with deviations away from this temperature. In the light of the reasonable success of CNT in explaining water data, it is disappointing to find that hydrogen-bonded organic materials such as a series of glycols disagree very strongly with the temperature dependence of the nucleation rate suggested by CNT [27]. Similarly, the organic species dibutyl phthalate deviates by up to six orders of magnitude from the model [28]. The situation becomes even more unsatisfactory for the nucleation of two or more species together. Strong deviations from binary CNT are found for the ethanol–water system [29] and for a range of *n*-nonane–*n*-alcohol mixtures [30]. However, it is with metals that the failure of CNT is most dramatic, examples in the literature being caesium [31], mercury [32] and lithium [33]. For caesium, the critical supersaturation (that required to drive nucleation at a specified rate) is between two and ten times larger than the CNT predictions. The difference between measured and predicted nucleation rates is astronomical. Although in most materials the deviation is less severe than this, it is certainly not the case that a small correction to CNT is all that is needed to account for all data.

The usual CNT expression for the rate is

$$J_{\mathrm{CNT}} = q\left(\frac{2\sigma}{\pi m}\right)^{1/2}\frac{\rho_v}{\rho_1}\frac{p_v V}{kT}$$
$$\times \exp\left[-\frac{16\pi\sigma^3}{3(kT)^3\rho_1^2(\ln S)^2}\right] \qquad (1)$$

where q is a sticking or accommodation coefficient, m is the molecular mass, k is Boltzmann's constant, σ is the surface tension of a planar interface between the condensate saturated vapour, p_v is the vapour pressure, and ρ_1 and ρ_v are the densities of the bulk condensed phase and the vapour respectively in molecules per unit volume. S is the supersaturation, defined by $S = p_v/p_v^s$, where p_v^s is the saturated vapour pressure at the temperature T. Note that J in this expression is the number of particles formed per second, and it is proportional to the system volume V. There are good reasons to insert a factor of $1/S$ into the prefactor of the above expression, but this is the often-quoted form. Calculations are easy, agreement is reasonable and so why should anyone bother to develop the theory further?

The problem in employing this formula for water is that the laboratory data for water are taken at low temperatures and need to be extrapolated to high temperatures for application to turbine conditions. As already noted, water seems to be a lucky case where theory and experiment actually agree for a particular set of conditions, namely at a temperature of about 240 K, and for a range of supersaturations. Unfortunately, a discrepancy appears and grows as the temperature is raised and, at 260 K, the theory overpredicts the rate by an order of magnitude [18]. The ratio of measured nucleation rate to CNT prediction has been fitted to a simple function by Wölk and Strey [18]:

$$J_{\exp}(T, S) = J_{\mathrm{CNT}}\exp\left(A + \frac{B}{T}\right) \qquad (2)$$

where $A = -27.56$ and $B = 6500$ K. This formula fits data in the temperature range 220–260 K but has also been found to account for data at temperatures some tens of kelvins higher (B. Wyslouzil, personal communication, 2003).

Nevertheless, caution must be exercised in extrapolating to temperatures around 370 K for steam turbines. Developments in the theory are certainly needed. It is a challenge to understand why CNT works reasonably well at 240 K for water: what terms are cancelling out and why? How can measured data be extrapolated with confidence?

In this review the determination of the properties of molecular clusters using the tools of statistical mechanics is again considered. Similar accounts of the wider picture have been given in various reviews and books [34, 35]. Starting from very general arguments, attempts are made to discern how a theory such as the CNT might emerge. The subtleties of defining a cluster precisely in terms of the positions and momenta of its constituents are discussed. It is noted that the transition state theory, based on equilibrium cluster properties, is equivalent to an approach based on the kinetic theory of cluster decay, at least in certain circumstances. Some phenomenological models developed from CNT are reviewed and, finally, a perspective of future developments in this field is given.

By the very nature of a review, the discussion is rather broad, while at the same time some of the technicalities are outlined. The intention is to give a reasonably complete picture of the current state of nucleation theory, at least from the point of view of the present author, and to show that significant progress has been made in the approximately 80 years of its history, while more is still clearly necessary.

2 TRANSITION STATE THEORY

A theory of nucleation based on statistical ideas is necessary since direct simulation of the process from a

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microscopic point of view is very laborious and has been realized in only a very few example cases [36–39]. The time scales involved make a nucleation event simply too slow to follow directly, for realistic conditions and with current computational resources.

The simplest statistical treatment of the nucleation process comes from TST, within a framework of the theory of free energy fluctuations. According to thermodynamics, a system with externally fixed temperature and pressure (or volume) will adjust any internal properties in order to minimize its Gibbs (or Helmholtz) free energy [40, 41]. Such adjustments will include changes in phase. Nevertheless, statistical fluctuations in system properties will naturally take place, and it is useful to interpret these as fluctuations in the free energy of the system away from the minimum. Considering constant-volume conditions for the moment, general arguments [42–45] suggest that the probability of a fluctuation ΔF in Helmholtz free energy is proportional to $\exp[-\Delta F/(kT)]$.

The physical fluctuations that are important in the nucleation process are those where a molecular cluster of new phase is formed temporarily from the original phase. The change in free energy accompanying the formation of a cluster of i molecules in the new phase is written $\Delta F = \Delta W(i) \equiv F(i) - if_0$, where $F(i)$ is the free energy of the i cluster and f_0 is the free energy per molecule in the old phase. This is also called the 'work of formation' since it corresponds in thermodynamics to the external work needed to insert an additional cluster reversibly into the system, while maintaining the overall temperature and pressure (or volume). Note that this insertion of a new cluster while maintaining such constraints is a theoretical operation since it would be hard to achieve in practice!

For a metastable initial phase, the magnitude of the free-energy fluctuation ΔF peaks at the so-called 'critical size' i^*. This is illustrated in Fig. 1. The perturbed state with the additional critical cluster is therefore a thermodynamic transition state, since reversible changes in size of the extra cluster are accompanied by reductions in free energy. It is presumed that this means that the new cluster has equal probabilities of growing or decaying and that the rate of nucleation is therefore related to the rate of formation of these critical clusters.

The probability of forming the critical cluster, according to this picture, is proportional to $\exp[-\Delta W(i^*)/(kT)]$, but the proportionality constant (essentially a time scale) is not yet determined. To introduce this, simple kinetic theory [46] can be used to calculate the collision rate β_i between single molecules (monomers) and an i-cluster, modelled as a sphere with bulk condensed phase molecular density ρ_1:

$$\beta_i = \frac{qp_v}{(2\pi mkT)^{1/2}}\left[\left(1+\frac{1}{i}\right)^{1/2}\left(1+i^{1/3}\right)^2\right]\frac{(36\pi)^{1/3}}{\rho_1^{2/3}}$$

(3)

where m is the molecular mass. It is more usual to replace the expression in square brackets with $i^{2/3}$, the limit for large i. The simplest TST expression for the
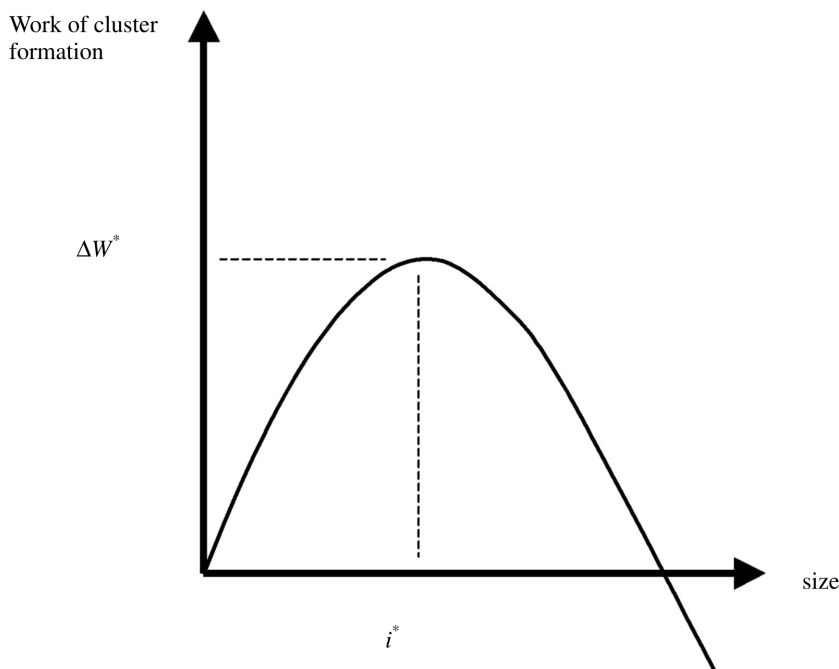

Fig. 1 Sketch of the cluster work of formation for a range of (constrained) cluster sizes. The maximum in the curve defines the critical size i^* and the critical work of formation, $\Delta W(i^*)$

nucleation rate is then $J \propto \beta_{i*} n_{i*}$, where n_{i*} is the mean number of critical clusters in the system.

More sophisticated treatments of thermodynamics can provide the time scale without recourse to the above kinetic argument, which is reasonably valid for gas-to-particle conversion but not for freezing, for example. Attempts based on linearized non-equilibrium thermodynamics [47, 48] originate from the work of Onsager [49].

The next step is crucial, and it is to relate the population n_{i*} to the probability of a fluctuation and to an explicit model of the critical work of formation. The assumption in classical nucleation theory is that

$$n_{i*} = n_1 \exp\left[\frac{-\Delta W_{\text{cl}}(i^*)}{kT}\right] \qquad (4)$$

where $\Delta W_{\text{cl}}(i)$ is the classical work of formation given by

$$\Delta W_{\text{cl}}(i) = 4\pi R^2 \sigma - ikT \ln S \qquad (5)$$

and $\Delta W_{\text{cl}}(i^*)$ is the maximum of this function. The cluster is envisaged to be a sphere of radius R given by $4\pi R^3 \rho_1 / 3 = i$.

Unfortunately, some uncertainty accompanies these steps in the derivation. The theory is flawed on several counts. The work of formation contains a term associated with the creation of a spherical interface (characterized by the bulk value of surface tension), and a change $-kT \ln S$ in free energy per molecule due to the change in phase from supersaturated vapour to condensate. Moreover, the factor n_1 appearing in equation (4) appears to have been introduced heuristically. Might it not instead be the monomer population in the saturated vapour? How does $\Delta W_{\text{cl}}(i)$ compare with the actual work of formation, $\Delta W(i)$? Is the droplet really spherical with a sharp interface? Have any important factors been left out? Furthermore, should there be concern that equation (4) is inconsistent when $i^* = 1$? This has been a controversial issue [50–54].

3 KINETIC INTERPRETATION

The expression for the classical rate of nucleation given in equation (1) emerges from the models in equation (4) and (5) when the thermodynamic transition state analysis is embellished by a kinetic interpretation [11]. Instead of using the probability of fluctuations away from the equilibrium state (the TST route), a set of rate equations is introduced to describe the dynamics of cluster populations.

The evolution of cluster populations is modelled using the following equations:

$$\frac{\mathrm{d}n_i}{\mathrm{d}t} = \sum_j n_j P_{j \to i} - n_i \sum_j P_{i \to j} \qquad (6)$$

where $P_{j \to i}$ is the mean rate at which a j cluster converts into an i cluster. The transition processes are assumed to be Markovian, so that the rate coefficients depend on the properties of the cluster and its environment, but not on their history.

The kinetic interpretation can be taken a step further by assuming that the only important transitions are those involving the addition or loss of single molecules to or from the cluster. The scheme of transition processes is illustrated in Fig. 2. The only non-zero rate coefficients are then $\beta_i = P_{i \to i+1}$ for cluster growth, and $\gamma_i = P_{i \to i-1}$ for cluster decay. The rate equations

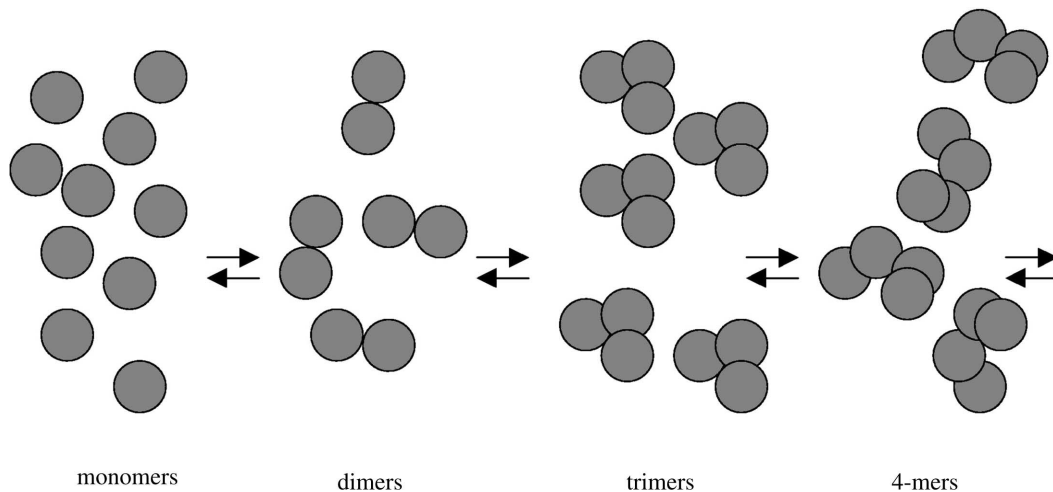| monomers | dimers | trimers | 4-mers |

Fig. 2 The scheme of the birth and death of clusters: addition of a monomer to a cluster will take it up the chain, towards the right, while the loss of a monomer will take it in the opposite direction. Attachment and detachment of dimers and larger clusters are usually ignored

reduce to

$$\frac{\mathrm{d}n_i}{\mathrm{d}t} = \beta_{i-1}n_{i-1} - \gamma_i n_i - \beta_i n_i + \gamma_{i+1}n_{i+1} \qquad (7)$$

These are the Becker–Döring equations [11], and they provide a useful reinterpretation of the TST approach. There are two steady state solutions. In the first, the populations satisfy equation (7) and also the detailed balance condition

$$\beta_{i-1}n_{i-1}^{\mathrm{e}} = \gamma_i n_i^{\mathrm{e}} \qquad (8)$$

and the $\{n_i^{\mathrm{e}}\}$ are taken to represent the cluster populations in an equilibrium vapour at or below the saturated vapour pressure. For true thermal equilibrium, the monomer population has to be less than or equal to its value for the saturated vapour n_1^{s}. The cluster populations in a saturated vapour are denoted $\{n_i^{\mathrm{s}}\}$. Nevertheless, a situation can be invented which is known as 'constrained equilibrium' where the detailed balance condition is still satisfied but with $n_1 > n_1^{\mathrm{s}}$. Since $\beta_i \propto p_v \propto S$, while γ_i is independent of vapour pressure, equation (8) then defines so-called constrained equilibrium populations

$$n_i^{\mathrm{ce}} \approx S^i n_i^{\mathrm{s}} \qquad (9)$$

for a supersaturated vapour. It has been assumed that $S = p_v/p_v^{\mathrm{s}} \approx n_1/n_1^{\mathrm{s}}$.

The second steady state solution to the Becker–Döring equations is more realistic. It is not meant to represent thermal equilibrium. The supersaturation is set to a value greater than unity, and a boundary condition of zero population at some cluster size $i_{\max}$ is imposed. These conditions will drive a steady production rate of large clusters from the vapour. The approach is for mathematical convenience only, and the same steady state cluster populations n_i^{ss} and nucleation rate would emerge if $i_{\max}$ was sent off to infinity. The detailed balance condition (8) is replaced by $J = \beta_{i-1}n_{i-1}^{\mathrm{ss}} - \gamma_i n_i^{\mathrm{ss}}$, defining the nucleation current J, which can then be calculated analytically, as shown in another paper in this volume [55]. To a good approximation,

$$J = Z_{\mathrm{d}}\beta_{i^*}n_{i^*}^{\mathrm{ce}} \qquad (10)$$

which involves the constrained equilibrium population at the critical size i^*, the size with the lowest constrained equilibrium population. The condition $i_{\max} \gg i^*$ must hold. Z_{d} is the so-called Zeldovich factor [12] given approximately by

$$Z_{\mathrm{d}} = \left\{ \frac{1}{2\pi}\left[\frac{\partial^2(\ln n_i^{\mathrm{ce}})}{\partial i^2}\right]_{i=i^*} \right\}^{1/2} \qquad (11)$$

When equations (4) and (5) are used to specify n_i^{ce} and the result is substituted into equations (10) and (11), then the classical nucleation rate given in equation (1) is recovered, as long as the large i limit of the attachment rate coefficient in equation (3) is taken. It is also possible to derive an expression for J purely in terms of the rate coefficients β_i and γ_i. This possibility is considered again in section 8.

The main assumptions used in this derivation of the classical theory, principally the validity of equations (4) and (5), are now examined. In order to explore this, it is necessary to see how the equilibrium cluster populations n_i^{e} in subsaturated vapours may be calculated using statistical mechanics.

4 CLUSTER STATISTICAL MECHANICS

The statistical mechanical treatment of a vapour is best developed using a grand canonical ensemble [56–59]. The system is placed in contact with a particle reservoir at a chemical potential μ and temperature T, so that the number of molecules, N, in the system can change. The grand partition function of the system, Ξ, is then proportional to the integral of $\exp\{-[H(N) - N\mu]/(kT)\}$ over all possible configurations of molecular positions and momenta, where $H(N)$ is the Hamiltonian of the system.

Evaluating Ξ exactly is exceedingly difficult, and it is much simpler to proceed by considering the configurations of the system as arrangements of molecular clusters. The vapour then is viewed as a mixture of ideal gases, each composed of clusters of different sizes. The grand partition function of the system can be reconstructed from partition functions for single i-clusters. In order to do this, however, a cluster must be defined in a unique way in terms of molecular positions and velocities. An example of such a definition would be to require the separation between molecules in a cluster to be less than a maximum distance R_{c} [60], as illustrated in Fig. 3.
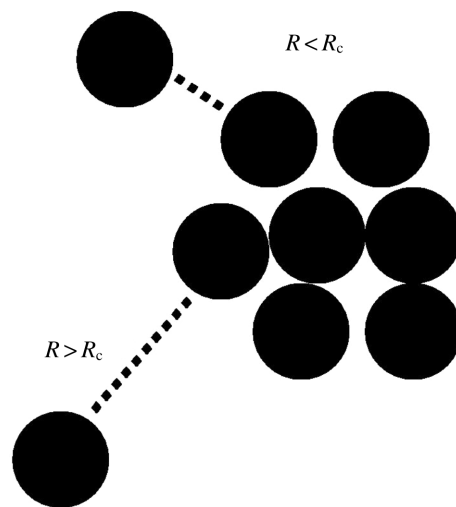

Fig. 3 According to the Stillinger definition, a molecule is considered part of a cluster if it lies closer than a distance R_{c} from a constituent molecule of the cluster

At first sight the cluster definition is completely arbitrary: a means of categorizing and resumming all the elementary configurations of the system. However, accurately representing the system as a mixture of ideal gases requires the interactions between molecules lying in different clusters to be minimized. The cluster definition affects whether a particular interaction is regarded as intercluster or intracluster, and so it plays a crucial role. This will be discussed further in section 6. Residual cluster–cluster interactions can be taken into account in the form of a virial series [61].

These ideas are now put into practice. Define a modified canonical partition function $\mathcal{Z}_i$ for a cluster containing i molecules. This is simply the integral of $\exp\{-[H_c(i) - i\mu]/(kT)\}$ over configurations involving molecules in the cluster alone, with H_c the Hamiltonian of the i molecules comprising the cluster. Using the picture of a mixture of ideal gases, the grand partition function of the complete system can then be expressed as

$$\Xi \approx \sum_{\{n_i\}} \left(\prod_{i=1}^{\infty} \frac{\mathcal{Z}_i^{n_i}}{n_i!} \right) \tag{12}$$

where the sum is over all possible cluster population distributions $\{n_i\}$. This is demonstrated rigorously in appendix A of reference [57].

The next step is to determine the distribution $\{n_i^e\}$ that dominates the sum in equation (12). The logarithm of the summand is extremized:

$$\frac{\partial}{\partial n_i} \sum_{i=1}^{\infty} \ln\left(\frac{\mathcal{Z}_i^{n_i}}{n_i!} \right) = 0 \tag{13}$$

which gives the following very simple expression for the most probable, or equilibrium, cluster size distribution for the given conditions T and μ:

$$n_i^e = \mathcal{Z}_i(\mu, T) = Z(T)\, e^{i\mu/(kT)} \tag{14}$$

which is equivalent to the so-called law of mass action

$$n_i^e = Z_i \left(\frac{n_1^e}{Z_1} \right)^i \tag{15}$$

where $Z_i(T) = \exp[-F(i)/(kT)] = \mathcal{Z}_i \exp[-i\mu/(kT)]$ is the canonical partition function for an i cluster, and $F(i)$ is the i-cluster Helmholtz free energy. This relationship is often used as the starting point in models of cluster populations.

The vapour pressure is now given by a sum of partial pressures

$$p_v V = kT \sum_{i=1}^{\infty} n_i^e = kT \sum_{i=1}^{\infty} \mathcal{Z}_i(\mu, T) \tag{16}$$

and this series will only converge if the equilibrium populations or the $\mathcal{Z}_i$ decrease sufficiently quickly for large i. This limits the statistical mechanics approach to

the study of saturated or subsaturated vapours. However, as in the preceding section, the equilibrium populations n_i^e in equation (14) (for $S < 1$) can be extrapolated into constrained equilibrium populations n_i^{ce} (with $S > 1$) for use in equation (10). Saturated vapour corresponds to a particular chemical potential μ_s, and the saturated vapour cluster populations are n_i^s. The constrained equilibrium populations are obtained by inserting into equation (14) the chemical potential of the supersaturated vapour, which is $\mu = \mu_s + kT \ln S$, giving $n_i^{ce} = S^i n_i^s$, which is consistent with the result obtained in equation (9), for dilute vapours.

The constrained equilibrium populations are therefore expressed as

$$\begin{aligned} n_i^{ce} &= S^i \mathcal{Z}_i(\mu_s, T) \\ &= \exp\left\{ \frac{-[F(i) - i\mu_s - ikT \ln S]}{kT} \right\} \end{aligned} \tag{17}$$

and the correspondence with CNT can be made closer by introducing the n_1 prefactor:

$$n_i^{ce} = n_1 \exp\left\{ \frac{-[F(i) - i\mu_s + kT \ln n_1 - ikT \ln S]}{kT} \right\} \tag{18}$$

The next task is to explore how the combination $F(i) - i\mu_s + kT \ln n_1$ might be approximated by the CNT result $4\pi R^2 \sigma$. This can be explored most easily for solid rather than liquid clusters.

5 SOLID CLUSTERS

The partition function of a solid cluster of i molecules can be factorized into translational, rotational and vibrational parts through a transformation to suitable relative positions and momenta [62–64]. Starting with the vibrational degrees of freedom, the atom positions are defined with respect to their mean positions, which are determined by a fixed centre of mass and set of lattice vectors. It is assumed that the potential energy part of the Hamiltonian is quadratic in the displacements from these mean positions. Now the partition function is worked out for configurations of the particles restricted to having zero total linear and total angular momentum about the centre of mass. This is written Z_{vib}, corresponding to a product of partition functions for $3ji - 6$ independent oscillators (if there are j atoms per molecule, and therefore a total of $3ji$ degrees of freedom, if the molecule is not linear), each of which in the classical limit takes the form $kT/(\hbar\omega)$, where ω is the angular frequency of the specific vibrational mode. The partition function has an additional factor of $\exp[-U_0(i)/(kT)]$, where $U_0(i)$ is the system potential energy evaluated at the mean atom positions. A

different expression applies for low temperatures, when the oscillator is not classically activated [65].

The rotational and translational degrees of freedom are next. The previous restriction of the configurations to zero angular momentum is lifted. The approximate (classical) rotational partition function is

$$Z_{\text{rot}} = \pi^{1/2} \left(\frac{8\pi^2 kT}{h^2} \right)^{3/2} (I_1 I_2 I_3)^{1/2} \qquad (19)$$

where I_k are the principal moments of inertia about the centre of mass, for atoms fixed in their mean positions.

Finally, the translational free energy of the centre of mass of the cluster is given by the partition function

$$Z_{\text{trans}} = V \left(\frac{2\pi MkT}{h^2} \right)^{3/2} \qquad (20)$$

where V is the system volume and $M = im$ is the cluster mass. The free energy of the cluster (plus $kT \ln n_1$ for convenience) is therefore

$$
\begin{aligned}
F(i) &+ kT \ln n_1 \\
&= -kT \ln \left(\frac{Z_{\text{trans}} Z_{\text{rot}} Z_{\text{vib}}}{n_1} \right) \\
&= U_0(i) - kT \ln \left[\frac{(2\pi MkT)^{3/2}}{S\rho_v^{\text{s}} h^3} \pi^{1/2} \left(\frac{8\pi^2 kT}{h^2} \right)^{3/2} \right. \\
&\qquad\qquad \left. \times (I_1 I_2 I_3)^{1/2} \prod_{k=1}^{3ji-6} \frac{kT}{\hbar \omega_k} \right] \qquad (21)
\end{aligned}
$$

where $\rho_v^{\text{s}} = n_1^{\text{s}}/V$ is the molecular density of dilute saturated vapour.

By similar arguments, the chemical potential of dilute saturated vapour is

$$
\begin{aligned}
\mu_{\text{s}} = U_0^{\text{m}} - kT \ln &\left[\frac{(2\pi mkT)^{3/2}}{\rho_v^{\text{s}} h^3} \pi^{1/2} \left(\frac{8\pi^2 kT}{h^2} \right)^{3/2} \right. \\
&\left. \times (I_1^{\text{m}} I_2^{\text{m}} I_3^{\text{m}})^{1/2} \prod_{k=1}^{3j-6} \frac{kT}{\hbar \omega_k^{\text{m}}} \right] \qquad (22)
\end{aligned}
$$

where U_0^{m} is the potential energy of a molecule when the atoms are at their mean positions, I_k^{m} are the three principal moments of inertia of the molecule about the centre of mass and ω_k^{m} are the oscillatory frequencies of molecular internal vibrations.

The classical work of formation, $\Delta W_{\text{cl}}(i)$, should now correspond to the leading-order contribution to the difference between equation (21) and i times equation (22). Calculations [54, 64, 66–68] demonstrate that the leading term is indeed roughly proportional to $i^{2/3}$, thus justifying the form of the classical model. The suitability of the capillarity approximation depends on the extent to which the coefficient of this leading term corresponds numerically to the planar surface free energy. However, the full statistical mechanical expression for the work of

formation contains additional terms, and these will be important for small clusters and need to be taken into account. In order to evaluate them, the various structural and energy properties of cluster are required, all of which can be obtained from microscopic models, and they can then be inserted into the formulae for the thermodynamic properties [equations (21) and (22)], the constrained equilibrium populations [equation (18)] and ultimately the nucleation rate [equation (10)]. Following this route employs the almost universally held assumption that equilibrium properties such as free energies can be used to describe non-equilibrium properties, specifically the cluster decay rate. This assumption is re-examined in section 8.

6   LIQUID DROPLETS AND THE CLUSTER DEFINITION

Defining what was meant by a solid cluster in the previous section was not an issue. Within the assumptions of the model (harmonic interactions) it was impossible for a molecule to escape from the cluster! The cluster definition in the case of liquids cannot be dismissed so easily. Liquids are more volatile than solids, and the molecules in a cluster are much more mobile. It is imperative now to characterize a cluster using the molecular positions and velocities, and perhaps some time scale and length scale too.

The traditional microscopic method for defining a cluster is to impose a geometric constraint on molecular positions. An example is to restrict molecules to a sphere centred on the centre of mass [69–71], or to impose a maximum allowable separation between the molecules (the Stillinger criterion [60]). More sophisticated treatments exist, such as the n/v Stillinger cluster introduced by Reiss and co-workers [72–75]. Here, the confining volume v used to define the cluster is considered to be an additional defining characteristic, on the same level as the cluster size n. As time progresses, a cluster changes its confining volume as the component molecules follow their respective trajectories, just as they change their size with the gain and loss of molecules. The association of a molecular configuration with a precise confining volume is complicated but tractable. The dependence of the free energy on v determines the statistical dynamics of this cluster volume. A similar attempt to associate a cluster with a specified volume within a grand canonical ensemble description was developed by Kusaka and co-workers [58, 59, 76]. The simulation box was taken to be the confining cluster volume. Many of these ideas may be viewed as a treatment of the cluster definition (e.g. the Stillinger radius) as a variational parameter in the representation of the partition function. Further

refinement of this point of view, using a treatment of cluster–cluster interactions to optimize the defining cluster volume, has been presented [77]. A review of recent progress in this area and the application of these ideas to nucleation theory has been provided by Senger *et al.* [78].

Such geometric constraints can be implemented, but their realism is questionable. Situations better regarded as close encounters between separate clusters would be classed as snapshots of single larger clusters. It should be recalled that the cluster definition is an internal feature of the model which is to be optimized to reduce cluster–cluster interactions and to improve the representation of the grand partition function. Misclassifying configurations is fraught with consequences. A second issue to consider is that, for convenience, the clusters should behave in a manner that can be modelled with Becker–Döring equations. This means that the growth and decay rates should be free of memory effects; i.e. the transition processes should be Markovian. The extent to which this is satisfied (if indeed it is physically realistic) depends on the cluster definition.

An intuitively reasonable choice of definition, which addresses both these points, is that a cluster should consist of molecules that are bound energetically. This should minimize the cluster–cluster contributions to the total energy. According to such a definition, if a molecule interacts strongly with a cluster, then it is likely to be regarded as part of that cluster. Also, an energetically bound cluster is likely to decay by thermal fluctuation in a stochastic Markovian fashion, rather than by the separation of passing, poorly bound fragments.

Ideas have been proposed which require the cluster to be energetically bound (in a loose sense, since a cluster is intrinsically prone to decay). The time evolution of a molecular configuration, and not simply the set of instantaneous positions of its component molecules, is of central importance. Hill [79] introduced a cluster definition requiring the total energies of pairs of molecules in a cluster to be negative (in their centre of mass frame). The intention was to exclude situations where a molecule could leave the cluster within the time it would take for a molecule to travel a typical linear dimension of the cluster. Soto and Cordero [80] have developed Hill's criterion, and Barrett [81] has performed Monte Carlo modelling of molecular configurations, excluding those which decay in molecular dynamics within a given period. A number of other energy-based criteria have been developed [82–85].

Harris and Ford [86] have recently proposed a new energy-based cluster definition. As with Barrett's approach, it is based on the requirement that a molecular snapshot is energetically bound for a chosen subsequent period. Evaporation according to this scheme requires not only that a molecule should make a positive energy excursion but also that the subsequent

dynamics carry it far away from the cluster. Only perhaps one in eight molecules manage to avoid recapture, once having satisfied the positive energy criterion [86]. A snapshot of a cluster, in this case surrounded by a carrier gas, is shown in Fig. 4. The history of the energy of a molecule in such a cluster is illustrated in Fig. 5; three excursions into positive energy occur in this sequence, but only one leads to actual escape, corresponding to the maintenance of positive energy for a significant time. The instant of escape is taken to be the point at which the energy goes positive for the third and final time.

Cluster definitions implemented in molecular dynamics and Monte Carlo codes allow cluster free energies, and hence the decay rate, to be calculated. An enormous amount of simulation work has been carried out, and calculations can be laborious. Many different schemes and approximations have been made to ease the evaluation of these properties. The principal conclusion from various studies, using a range of cluster definitions and interaction models [49, 57, 58, 70, 85, 87–92], seems to be that the work of formation of liquid critical clusters does indeed contain a dominant contribution proportional to $i^{2/3}$, consistent with the classical work of formation. Hale and collaborators present cluster free energies for water and other species in a way that makes this particularly clear; indeed it is surprising how dominant the surface term can be for even very small clusters [70, 93, 94]. Nevertheless, further contributions exist; small clusters are not characterized just by scaled-down properties of large clusters, and it is impossible to escape the need to determine the additional terms.

In all the above discussion, it has been assumed that the intermolecular interactions are accurately specified. This is a situation that is rarely possible. Although first-principles quantum-mechanical models could be
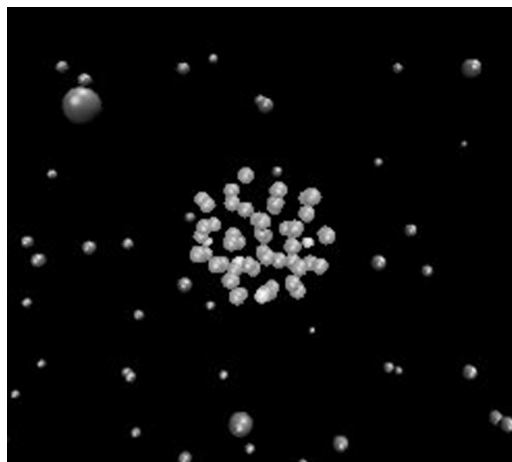

Fig. 4 Snapshot of a cluster of 50 argon atoms (bright spheres) bathed in a gas of helium (darker spheres)
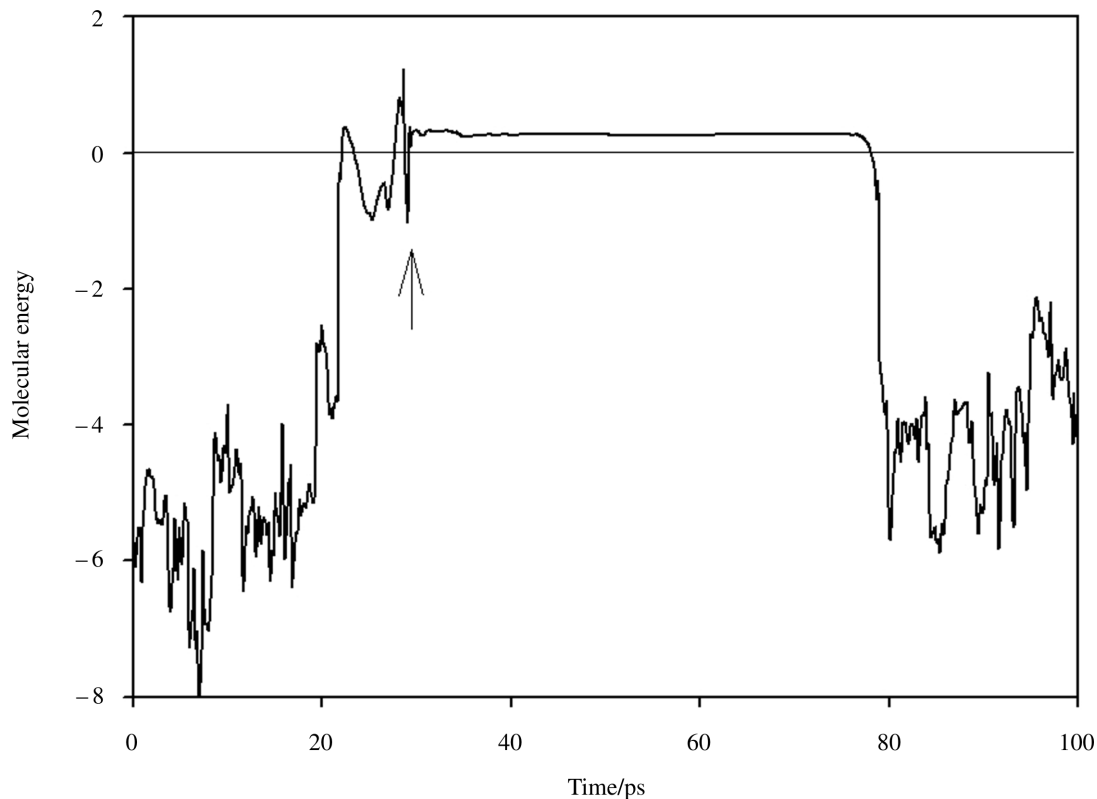
Fig. 5 The energy of a molecule in the centre-of-mass frame of a cluster occasionally becomes positive, but this does not necessarily lead to escape. Only the third positive energy excursion in this sequence, indicated by an arrow, results in particle escape. A cluster definition must capture this behaviour

developed, in practice, empirical potentials are developed on the basis of physical intuition, containing parameters fitted to the measured properties of the substance in question [95]. Usually these are bulk properties, and it is not always clear that the same interactions can be used for the very different circumstances of a molecular cluster [96]. In view of the sensitivity of nucleation rates to the thermodynamic properties of clusters, this is perhaps a crucial failing. Progress can be made, however, by computing known cluster properties, where they are available, and by refining the potentials to suit. Extraction of cluster properties through use of the so-called nucleation theorems (which relate derivatives of the nucleation rate to properties of the critical cluster [16, 56, 97–99]) may provide just this sort of experimental information.

A technique that has not yet been described is the use of density functional theory (DFT) to model the properties of liquid droplets [100–104]. This powerful application of statistical mechanics promises to avoid laborious computations at the microscopic level, by instead focusing on the density profile of molecules making up the droplet. This profile may be regarded as the average distribution of molecules about the cluster centre of mass. Although this might appear to involve coarse-graining and approximation, it is a well-founded approach and in principle can be exact. In practical implementations, however, a mean field approach is taken, such that the constituent molecules move in an effective potential well created by the other molecules in the cluster [105]. Also, the interactions are assumed to be characterized by strong repulsive cores and weakly attractive tails.

Considerable analytical work has been carried out [104, 106]. Various developments have been made to describe droplets consisting of simple atoms as well as chain-like molecules [107] and polar molecules [108]. The main drawback in these implementations is that specific interactions such as hydrogen bonds are hard to represent. Certain details of the modelled system are neglected [109, 110] and the (implicit) cluster definition used is geometric and not energetic [111]. On the other hand, quite sophisticated systems have been modelled, including multi-component droplets. The method has been compared with other approaches [112, 113], and certain features are better described, particularly the approach to spinodal conditions, where the nucleation barrier vanishes. DFT calculations can be performed relatively easily, and they can provide a qualitative and perhaps quantitative insight into quite complicated clustering problems. They provide an intermediate-level description between the simple capillarity approximation and a microscopic description.

7 PHENOMENOLOGICAL MODELS

The reader might be dismayed by the mathematical complexity of the expressions for the work of formation of solid clusters in section 5, might be alarmed by the procedural complexity of implementing a cluster definition in section 6, may recoil from the difficulties in calculating free energies from molecular simulation methods and ultimately may give up in view of the uncertainties in the underlying intermolecular interactions. Considering these complications, it is tempting to try to develop phenomenological models of the work of formation. After all, if the capillarity approximation works reasonably well for water, then surely a minor correction to account for small cluster effects ought to be sufficient to improve matters?

However, after perhaps two decades of work, no model has emerged offering broad success across a range of different substances. It is perhaps asking too much to expect universal improvement; CNT works as a first approximation for water for a particular temperature range but, as discussed earlier, it possesses the wrong temperature dependence, so that predictions away from a temperature in the range 210–260 K are uncertain. A similar picture emerges for other substances, although in some cases the failure is even more severe.

The simplest phenomenological adjustment to equation (4), the basis for CNT, is to write

$$n_i^{ce} = n_1 \exp\left\{ \frac{-[\Delta W_{cl}(i) - \Delta W_{cl}(1)]}{kT} \right\} \tag{23}$$

where $\Delta W_{cl}(i)$ is given by equation (5). This amounts to a uniform downward shift of the classical free energy barrier illustrated in Fig. 1. At least now the expression is consistent at $i = 1$. The theory is known as internally consistent classical theory (ICCT) [51]. Unfortunately, it is not clear whether this constant shift in the work of formation should be a realistic representation of all the subleading terms in the work of formation [52]. It is an arbitrary modification, and its success in accounting for data is mixed. For example, nucleation rates for a range of alkanes [114] require further modification by factors of between one and nine orders of magnitude to come into agreement with ICCT.

It should be noted at this point that the correction term $-kT \ln S$, which appears in $\Delta W_{cl}(1)$, can be regarded as rigorous. There are good reasons for this, based on general considerations involving the nucleation theorems [56], or more simply the principles of chemical equilibrium represented by the law of mass action given in equation (15). The correction converts the prefactor n_1 in equation (4) into n_1^s and results in the insertion of a factor $1/S$ in the nucleation rate in equation (1).

The Fisher droplet model is a slightly more sophisticated scheme [115]. Here, the constrained equilibrium populations are modelled by

$$n_i^{ce} = n_1^s \exp\left\{ -\left[\theta_i i^{2/3} + \tau \ln i - \ln\left(\frac{q_0 kT}{p_v^s} \right) \right] + i \ln S \right\} \tag{24}$$

The term proportional to θ_i may be viewed as a surface term, while the other two are corrections of a type suggested by the free energy expressions developed in section 5. The parameters q_0, θ_i and τ are chosen to ensure that the model correctly reproduces known properties of clusters and vapours, including virial coefficients and critical properties; the theory is therefore phenomenological.

For large cluster sizes, and for temperatures well below the critical temperature, the free energy of formation should tend towards that of a macroscopic liquid droplet. θ_i should therefore approach $A_1 \sigma / (kT)$ for large i, where $A_1 i^{2/3}$ is the surface area $4\pi R^2$ of a spherical droplet containing i monomers at the bulk liquid density, so that $A_1 = (36\pi)^{1/3} \rho_1^{-2/3}$. Dillmann and Meier [116] suggested writing

$$\theta_i = \frac{\kappa_i A_1 \sigma}{kT} \tag{25}$$

with the *Ansatz*:

$$\kappa_i = 1 + \alpha_1 i^{-1/3} + \alpha_2 i^{-2/3} \tag{26}$$

The coefficients α_1 and α_2 can be found in terms of virial coefficients of the vapour. The form of this *Ansatz* was motivated by the curvature dependence of the bulk surface tension derived in classical thermodynamics by Tolman [117].

The initial success of the Dillmann–Meier theory was short lived, since modifications had to be made to overcome an internal inconsistency [118]. Virial expansions for the vapour pressure and density were used incorrectly to calculate the virial expansion of the ratio of the two. Correcting this error [61] changed predicted rates by several orders of magnitude. Nevertheless, the approach was very influential [119]. In a further development, Kalikmanov and van Dongen [120] set $\alpha_2 = 0$ (this term can be absorbed into q_0 anyway) and chose α_1 such that the experimental saturated vapour pressure p_v^s is reproduced by the model. The Dillmann–Meier model matched the first two virial coefficients only. The Kalikmanov–van Dongen theory should therefore approximate the (revised) Dillmann–Meier theory at low temperatures, but ought to provide a better description at higher temperatures.

Other phenomenological models have been proposed, including the Hale scaling relation [121]. This model, based on CNT but employing simplified models for the surface tension and liquid density based on scaling behaviour near the critical point, together with a rather

more straightforward rate prefactor, seems to be quite successful in accounting for data for a wide range of materials, even metals [122] and two-component systems [123]. Another phenomenological model is the diffuse interface theory [124], which is based on a treatment of the phase interface using simplified density profiles of thermodynamic properties. Another general class of model makes use of conditions at the vapour–liquid spinodal to constrain the form of the model free energy [125–128].

The main drawback in phenomenological models is the arbitrariness in the form of the proposed work of formation. The parameter fitting in practice ensures that the populations of small clusters, especially the monomer and dimer, are well represented by the model, but the properties of larger clusters depend on the expression assumed for the model and are therefore uncertain. Intuition suggests that phenomenological modelling is likely to have mixed success, and that microscopic calculations of cluster properties do matter. There might be better value in phenomenological models, however, if they were based securely on the results of microscopic calculations.

8   KINETICS OR THERMODYNAMICS?

In section 3, kinetic equations representing the nucleation process were described. However, the coefficients in those equations were related to constrained equilibrium populations, and hence to the equilibrium statistical mechanics of clusters, through the detailed balance condition (8). Is it necessary to do this? Could a completely kinetic route be followed by evaluating the mean growth and decay coefficients β_i and γ_i directly, by some statistical approach? The main problem is, of course, the difficulty in performing such calculations, and this has restricted the development of such models [129–131]. It is expected that the kinetic coefficients will correspond to those derived from the detailed balance argument, for near-equilibrium conditions, but circumstances can be imagined where non-equilibrium effects are present, which cannot be dealt with within standard statistical mechanics.

The framework for evaluating kinetic coefficients of cluster decay can be briefly introduced [86, 132]. A molecular dynamics simulation of a cluster can be set up and evolved according to the interactions until, by chance, an evaporation event occurs. By extensive simulation, statistics for the mean evaporation rates γ_i can be amassed in this way. Similarly, molecular dynamics simulations where a single molecule is captured by a cluster could be performed, and the growth rates β_i determined. These will be functions of cluster energy and so would fit best into a rate equation scheme involving both size and energy [133].

This is a laborious approach, but statistical physics offers an approximate alternative representation of the escape and capture processes. The basic tool is the Langevin equation. The radial motion of a molecule in the cluster is described by [134]

$$m\ddot{r} = f(r) + \mathscr{F}(r, \dot{r}, t) \tag{27}$$

where r is the radial position, m is the molecular mass, f is the mean (time- and velocity-averaged) force on the molecule at position r, and $\mathscr{F}$ is the stochastic force. The latter is usually represented as a velocity-dependent friction term $-m\gamma\dot{r}$, where γ is the so-called friction coefficient, plus a fluctuating term $\tilde{f}(r, t)$ with zero mean and correlation in time $\langle \tilde{f}(r, t)\tilde{f}(r, t')\rangle = (2\gamma kTm)\delta(t - t')$, where k is Boltzmann's constant and where T has the characteristics of a temperature, as will be seen. It is a standard manipulation [135] to convert the Langevin description, in the large friction limit, into a Fokker–Planck equation:

$$\frac{\partial \mathscr{W}}{\partial t} = \frac{1}{m\gamma}\left[-\frac{\partial(f\mathscr{W})}{\partial r} + kT\frac{\partial^2 \mathscr{W}}{\partial r^2} \right] \tag{28}$$

which represents the evolution of $\mathscr{W}(r, t)$, the probability density that the molecule should lie at the radial position r. It should be noted in passing that Fokker–Planck equations have often been used to describe the stochastic dynamics of a cluster in *size* space [48, 136]. In contrast, the use of the method described above refers to motion of a molecule in real coordinate space, relative to the centre of mass of the cluster.

The steady state equilibrium solution of equation (28) is

$$\mathscr{W}(r) \propto \exp\left[-\frac{\Phi(r)}{kT} \right] \tag{29}$$

where $\Phi(r)$ is called the potential of mean force, related to the mean force on the molecule, f, through $f = -d\Phi/dr$. It can now be seen how the parameter T in the stochastic force plays the role of temperature, since equation (29) looks like a Boltzmann distribution. This solution is not what is sought, however. The escape problem is characterized by a boundary condition $\mathscr{W}(r_e) = 0$, where r_e is the radius at which a particle escapes from the system. The resulting escape rate may be shown to be [134]

$$\gamma^{\text{kin}} = K(r_e, T, m, \gamma)\exp\left(-\frac{\Delta\Phi}{kT} \right) \tag{30}$$

where the prefactor K depends on the parameters listed as well as the shape of the potential of mean force. The principal feature of equation (30) is the exponential dependence on the depth $\Delta\Phi$ of the potential of mean force. Therefore, if the potential of mean force $\Phi(r)$ can
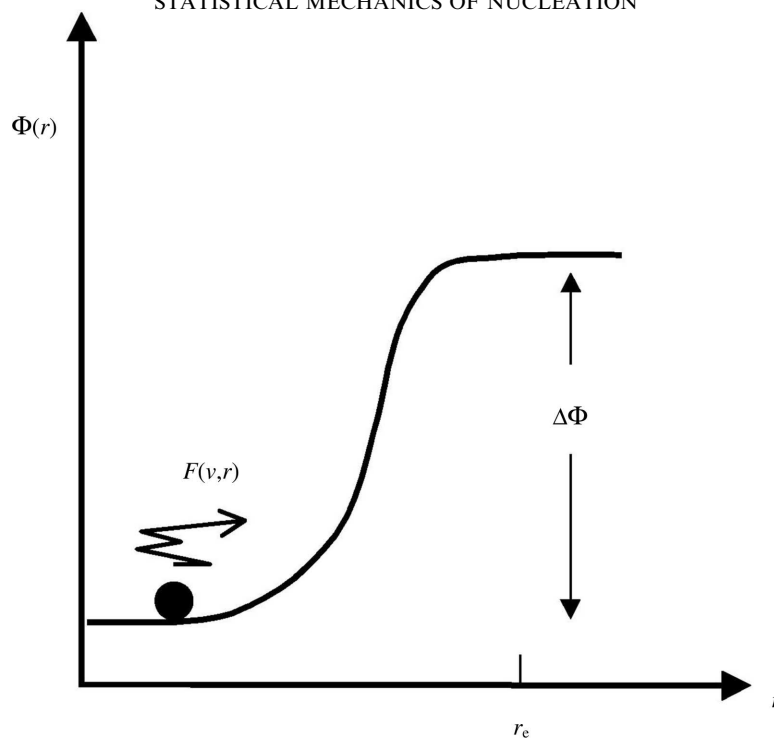
Fig. 6   A molecule in a cluster may be considered to be confined within it by a potential of mean force $\Phi(r)$. It can escape by reaching a radial position r_e, driven by a phenomenological stochastic force

be evaluated by studying a molecular dynamics trajectory, for example, then the kinetic decay rate can be determined. This could be extended to account for a radially dependent temperature and friction coefficient, both of which might be determined from simulation. A sketch of a potential of mean force is given in Fig. 6.

Kinetically determined cluster growth and decay rates, γ_i^{kin} and β_i^{kin} respectively, could provide a new route for the determination of nucleation rates, independent of assumptions about detailed balance and the use of equilibrium statistical mechanics in a non-equilibrium situation.

9   CONCLUSIONS

This review has been brief and in some ways partisan to the personal views of the author. It attempts to sketch a coherent picture of nucleation theory, and how the various disparate strands relate to one another. One of the fascinations of nucleation theory is the variety of approaches, and the number of difficult issues that are encountered. How well does free energy fluctuation theory represent a real non-equilibrium process? How well does the idea of detailed balance provide a framework for determining non-equilibrium decay coefficients from equilibrium statistical mechanics? How well do various methods perform in the evaluation

of cluster free energies? Can cluster growth and decay rates be calculated directly without the need for such a framework? How exactly are clusters to be defined?

The theoretical problems are many, but the issues can be resolved to various degrees of satisfaction. There remains, of course, the fundamental task of choosing an intermolecular potential that adequately represents the physical interactions. Without this, all the finer points of cluster definition and treatments of non-equilibrium processes are unimportant. Modelling many problems in science relies on the availability of an accurate microscopic description, and so nucleation rate calculations are not unique in this respect. Most empirical molecular potentials are fitted to the properties of bulk and surface properties and, in the very best examples, attention is given to their transferability to more unusual environments such as clusters. In view of these capabilities and modern theoretical developments in nucleation theory, it seems likely that successful microscopic models of the nucleation process, based on statistical physics, are at last coming within reach.

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