J. Phys. A: Math. Gen. 26 (1993) 529–548. Printed in the UK

Energy fluctuations in homogeneous nucleation theory for aerosols

J C Barrett, C F Clement and I J Ford

Theoretical Studies Department, Materials and Manufacturing Technology Division, B424.4, AEA Industrial Technology, Harwell Laboratory, Oxon OX11 0RA, UK

Received 5 May 1992

Abstract. For the analysis of the release of fission product aerosols from reactor cores in a severe accident, it is necessary to understand the process of homogeneous nucleation of droplets from a supersaturated vapour, including the dependence on system pressure, which can vary greatly depending on the type of accident. A model of the effect of carrier gas on the nucleation process is presented, based on the changes to the energy distribution of nucleating vapour molecule clusters induced by collisions with carrier gas molecules. The rate of nucleation is altered since the cluster decay rate is strongly energy dependent. The approach is compared with previous treatments of the problem, illustrating the importance of using an equilibrium cluster energy distribution which goes beyond a Gaussian approximation, and clarifying previous confusion between cluster temperature and cluster energy in the literature. Calculations of nucleation rates are performed for *n*-nonane in argon and water vapour in air, and show that an analytic approximation gives a reasonable approximation to numerical results. However, the resulting pressure dependence of the nucleation rate is weaker than has been observed experimentally suggesting that additional mechanisms operate.

1. Introduction

The initial formation of clouds by aerosol nucleation is a process which is most manifest in the atmosphere. It generally occurs in a heterogeneous fashion by growth on existing tiny nuclei in the nanometre size range. Homogeneous nucleation, where existing nuclei are not involved, can only occur if large supersaturations can build up in vapours. This can happen generally if large temperature differences, and consequently very large changes in equilibrium vapour pressure, exist in a system. It would therefore be an important process in possible nuclear accidents where fission product vapours released from an overheated core would condense into an aerosol in the large temperature gradients surrounding the core. There is presently no satisfactory theory with which to calculate nucleation rates. In this paper, we obtain and solve equations which describe thermal fluctuations as well as number fluctuations in the nucleation process.

With improved techniques using expansion and diffusion chambers, a number of measurements of homogeneous nucleation rates have been made in recent years [1–6]. Collectively for nonane [7], the results show that the temperature dependence of the rates differ widely from predictions of classical theory [8], and those of the statistical mechanical treatments of Lothe and Pound [9] and Reiss *et al* [10]. Furthermore, there have been strong experimental indications that the nucleation rates can be dependent on the presence and pressure of a carrier gas. Steinwandel and Buchholz [11] found a dependence of the argon nucleation rate on the presence of helium, and both an increase [12] and a decrease [7] have been reported in the nucleation rate with an increase in pressure.

As the predictions of classical nucleation theory allow for practically no dependence of the nucleation rate on pressure, the experimental results suggest that a new element is needed in the theory. This could be energy fluctuations arising from the balance between energy transfers to nucleating clusters from colliding (but non-sticking) carrier gas and vapour molecules, and latent heat transfers from condensation and evaporation. The pressure dependence of the nucleation rate could come from changes in the energy distribution of the clusters when the number of gas molecules is changed. The sensitivity to temperature of the cluster decay rate suggests that a considerable effect could arise from relaxing the requirement that clusters should acquire the ambient gas temperature, the characteristic of the existing 'isothermal' theories [8–10].

The initial treatment of energy fluctuations for clusters by Feder *et al* [13] led to only a relatively small correction to isothermal theory with the nucleation rate increasing with pressure. Recently, a different treatment was proposed [14, 15] in which there would be a large suppression in the isothermal rate. The treatment starts with rate equations for the concentration of clusters of a given number of molecules and energy, and similar equations, albeit with energy transfers partly treated by the Fokker–Planck approximation, have been given by Grinin and Kuni [16].

The contrast between the treatments has led us to re-examine the basis of two-dimensional rate equations for nucleation theory. We shall find that all existing treatments have deficiencies connected with the relation between energy and temperature for small clusters. Basically, the assumption of a Gaussian representation of a fluctuating energy is shown to be inadequate. This has a more serious consequence for the treatment of Ford and Clement [14, 15] whose conclusion that there are large reduction factors from classical nucleation rates, is found to be incorrect. The expansion method adopted by Feder *et al* [13] gives cluster decay rates which violate the requirement that they should be independent of the temperature of the surroundings, but we find that their overall results for nucleation rates are close to numerically calculated values.

Homogeneous nucleation theory suffers from uncertainties in its starting point, and in section 2 we attempt to remove some of the uncertainty by describing the basic physical assumptions necessary to set up a rate theory. These apply especially to the nature and definition of a cluster and the relationship between temperature and energy. Whilst many of our results apply in general, we need a specific model with which to perform calculations. The model chosen here involves cluster molecules interacting via a square well potential which gives results which can be interpreted on the basis of the familiar liquid drop model and its capillarity assumption. The statistical mechanics of this model has been investigated elsewhere [17], and we quote the results to be used in this paper.

In section 3 we obtain rate equations for cluster growth in the two dimensions of number of molecules and cluster energy. The rate at which the cluster energy is changed by collisions with gas and vapour molecules is carefully specified. The spontaneous decay rate of a cluster, which also describes the associated energy change, is obtained from the time reversal invariance of an equilibrium state at the cluster energy. This requires a knowledge of the equilibrium cluster population which, in our square well model, is specified in section 2 from statistical mechanics. The resulting decay rate satisfies the important requirement that it is independent of the properties of the surrounding vapour, namely temperature and supersaturation.

Methods of solution of the rate equations are described in section 4 and the appendix and we obtain numerical results for *n*-nonane in argon and water droplet nucleation in air. These are compared to the predictions of the theory of Feder *et al* [13] and approximate methods for solving the equations are discussed.

2. The physics of clusters

2.1. Analogy with nuclear structure

The nature of liquid microclusters which occur in a vapour, particularly during nucleation, continues to attract theoretical attention. A thermodynamic formalism has been developed by Nishioka [18], and Reiss and his co-workers [19] continue to approach the problem from a statistical mechanics point of view. In addition to describing other approaches, their paper [19] addresses the central problem of the exact definition of a cluster. This problem also affects our dynamical approach in which we require rate equations for cluster populations. The use of a cluster density for *i*-molecule clusters presupposes that these objects are well defined.

It may be useful to make an analogy to nuclear physics where the study of unstable clusters (compound nuclei) is more advanced than in molecular physics. This is because an unstable nucleus of $n+1$ nucleons can readily be made experimentally by firing a high energy projectile, usually a nucleon, onto a target of stable nuclei with *n* nucleons. Analogous scattering experiments in molecular physics would require atomic or molecular beams. Both in nuclear and molecular physics, there are short-range attractive forces with shorter-range repulsion, and a liquid drop model has been used successfully to describe heavy nuclei. Both forces saturate so that, above a minimum number of particles, the droplet volume is approximately proportional to the cube of the radius and the binding energy consists mainly of a volume term and a surface term.

The concept of a 'compound nucleus' was introduced by N Bohr and the theory of compound nucleus reactions is described in Blatt and Weisskopf [20]. The essential points, which have been directly verified by experiment, are:

(*a*) After an initial collision in which a nucleon is captured its energy is rapidly shared out amongst all available modes. Grinin and Kuni [16] give an argument that the same applies to molecular clusters. The possibility that the initial nucleon is scattered and escapes directly (a 'direct reaction' in nuclear physics) is analogous to allowing for a sticking probability less than unity in molecular physics.

(*b*) In the shared energy state, all the nucleons essentially occupy bound states in a common potential well. When internal collisions result in a nucleon reaching an unbound state with an energy significantly larger than the average, it can then escape. However, this takes many collisions so that the lifetime of the state is much longer than the transit time of a nucleon across the nucleus. This results in exponential decay with a decay probability independent of time, an essential requirement for rate equations for an unstable object.

(*c*) Because of the energy sharing, the decay probabilities of a compound nucleus do not depend on its mode of formation, only on the energy of the state. Decay rates are related to formation rates by time reversal invariance and are mainly given by the densities of states at the appropriate energy.

Experimentally, these ideas are well verified for compound nucleus reactions. We believe that the same physics applies to molecular clusters relevant to the nucleation process above a certain minimum size. Sequential collisions affecting the clusters are independent because of the low density of the vapour-gas system, and the decay probability at any given time depends only on the energy of the cluster. It can be related to the formation rate by time-reversal invariance, or detailed balance, as shown explicitly in section 3.2.

For a few molecules, as for a few nucleons, the description can break down as scattering molecules do not stay together long enough to form energy-shared states. Of course, bound dimers and trimers, etc may be formed which can be treated explicitly, but it is not obvious that bound states, rather than multiparticle scattering states, are the main stepping stones to larger clusters. If the energetics and kinetics of few-molecule clusters play an important part in the nucleation process in general, it would indeed be a formidable task to calculate the relevant quantities for most molecules.

2.2. *Equilibrium cluster populations*

If the above physics does apply, it is legitimate to consider a cluster concentration $C_i(E)$, of clusters containing i vapour molecules at a total energy E in a vapour–gas mixture. The evolution of $C_i(E)$ in time is considered in the next section, and we can obtain growth rates from collisions with vapour molecules. In the absence of any other information, however, decay rates can only be obtained from detailed balance and concentrations in an equilibrium state. For this we turn to statistical mechanics but, since the equilibrium is then defined by a temperature, T, we first have to discuss the relation between energy and temperature in the present context.

We want to describe a system with a very large number of molecules in which there is a much smaller, but still large, number of clusters. In an overall equilibrium, the system has a well-defined temperature, T, so that there is a partition over energy solely according to the partition function and density of states at a given energy. The formal separation of the partition function into those for clusters is a problem addressed in [19], but here we generally write

$$C_i^{\mathrm{eq}}(E) = \Omega_i(E)\exp(-E/kT)c_i^{\mathrm{eq}}/q_i \qquad (2.1)$$

where k is Boltzmann's constant, $\Omega_i(E)$ is the density of states appropriate to a cluster of i molecules, and c_i^{eq} is the total cluster concentration for size i so that the cluster partition function is

$$q_i = \int_{E_{\min}(i)}^{\infty} \mathrm{d}E\, \Omega_i(E)\exp(-E/kT). \qquad (2.2)$$

The basic detailed balance relation (see (3.14)) is expressed in terms of cluster concentrations at given energies and must lead to decay rates which are independent of any overall temperature. Indeed, it is only in equilibrium that clusters can be regarded as having a distribution of energy states corresponding to a specific temperature. In a nucleating situation, whilst it is probably legitimate to describe the monomers and gas as having a well-defined temperature, the same may not be true for clusters. We know that large growing nucleated droplets can have a temperature above this value [21], but it is not necessarily true, as was assumed previously in [13] and [14], that small clusters have a well-defined temperature, or even if they do, that the detailed balance relation can be expressed in terms of temperature rather than energy. The question is related to the adequacy of the following Gaussian expression for a cluster population with a mean energy $\bar{E}$ corresponding to a temperature T:

$$C^{\mathrm{eq}}_{iG}(E) = (2\pi i c_{\mathrm{vv}} k T^2)^{-1/2} c_i^{\mathrm{eq}} \exp\left[-\frac{(E-\bar{E})^2}{2 i c_{\mathrm{vv}} k T^2} \right] \tag{2.3}$$

where c_{vv} is vapour molecule heat capacity at constant volume for molecules in the cluster. We return to this subject in section 5.

According to the law of mass action [10], the total number of i-clusters in equilibrium is given by

$$c_i^{\mathrm{eq}} = q_i (c_1/q_1)^i \tag{2.4}$$

where c_1 is the monomer concentration and the monomer partition function is

$$q_1 = \left(\frac{2\pi m_{\mathrm{v}} k}{h^2} \right)^{3/2} q_1^{\mathrm{int}} \tag{2.5}$$

with m_{v} the molecular mass, h Planck's constant and q_1^{int} an internal molecular partition function.

To proceed further, we adopt a cluster model (shown in figure 1) which corresponds to a mean field treatment [22] of two-body potentials of a square well form giving a cluster potential energy

$$U_i = -ai + bi^{2/3}. \tag{2.6}$$

Details of this model and its uncertainties as far as potential energies are concerned are discussed elsewhere [17]. In the spirit of classical nucleation theory, we can identify a and b with the bulk volume and surface energies per molecule, i.e. $a = m_{\mathrm{v}} L$ and $b = A_1 \sigma$ where L is the latent heat, σ the bulk surface tension, $A_1 = (36\pi v_0^2)^{1/3}$ the effective surface area per molecule and $v_0 = m_{\mathrm{v}}/\rho_\ell$ where ρ_ℓ is the bulk liquid density.

The model leads to the following form for q_i

$$q_i = q_1^i \frac{v_0^{i-1} i^{i+2-\delta}}{i!} \mathrm{e}^{-U_i/kT} \tag{2.7}$$

where v_0 is the volume per molecule in the cluster and the value of δ depends on the exact definition of the cluster ($\delta = 3$ for a cluster centred on the centre of mass and $\delta = 0$ for a cluster centred on an individual monomer [17]). We assume that each vapour molecule has $2c_{\mathrm{vv}}/k = 2\tilde{c}_{\mathrm{vv}}$ independent degrees of freedom, so the density of states is proportional to $(E - U_i)^{i\tilde{c}_{\mathrm{vv}}-1}$. From (2.1) and (2.2) we then obtain

$$C_i^{\mathrm{eq}}(E) = c_i^{\mathrm{eq}} \frac{(E-U_i)^{i\tilde{c}_{\mathrm{vv}}-1}}{(kT)^{i\tilde{c}_{\mathrm{vv}}} \Gamma(i\tilde{c}_{\mathrm{vv}})} \mathrm{e}^{-(E-U_i)/kT}. \tag{2.8}$$

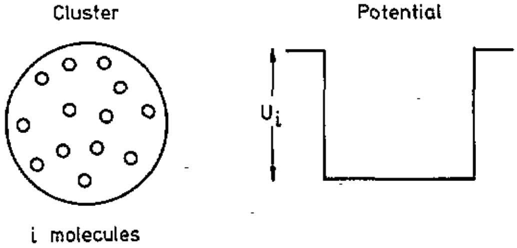

Figure 1. Liquid drop cluster model with square well potential.

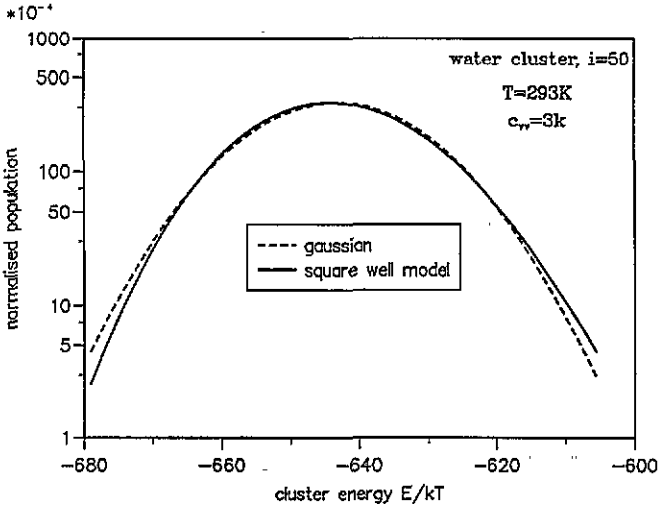

Figure 2. Comparison between exact energy distribution of a cluster based on the square well model, and a Gaussian approximation.

Multiplying (2.8) by E and integrating (for $U_i \leqslant E \leqslant \infty$) gives the mean i-cluster energy, $\bar{E}_i = ic_{vv}T + U_i$. In figure 2 we compare equilibrium distributions from (2.3) and (2.8) at $i = 50$. We have taken $a = 18.14kT$, $b = 8.38kT$, $c_{vv} = 3k$, and $v_0 = 3 \times 10^{-29}$ m^3, corresponding to the bulk properties of liquid water at 20 °C. The Gaussian form deviates from the exact form towards the extremities of the distribution. The implications of this will become apparent later. The $C_i^{eq}(E)$ are used in the next section to derive coefficients in the evolution equations for the cluster populations.

3. Rate equations for cluster growth

The evolution equation for $C_i(E)$ can be written

$$\begin{aligned}\frac{\partial C_i(E)}{\partial t} = &\int s_A \beta_{i-1}(E-E_1, E_1) C_{i-1}(E-E_1)\,\mathrm{d}E_1 \\ &+ \int \alpha_{i+1}(E+E_1, E_1) C_{i+1}(E+E_1)\,\mathrm{d}E_1 \\ &- (s_A \bar{\beta}_i(E) + \bar{\alpha}_i(E)) C_i(E) \\ &+ \left[\int \bar{\beta}_{ig}(E') P_g(E' \to E) C_i(E')\,\mathrm{d}E' - \bar{\beta}_{ig}(E) C_i(E)\right] \\ &+ (1-s_A)\left[\int \bar{\beta}_i(E') P_v(E' \to E) C_i(E')\,\mathrm{d}E' - \bar{\beta}_i(E) C_i(E)\right]. \qquad (3.1)\end{aligned}$$

The first term on the right represents the increase in $C_i(E)$ from clusters of size $(i-1)$ gaining a monomer. $\beta_i(E, E_1)$ is the rate at which monomers with energy E_1 collide with i-clusters of energy E and s_A is the sticking probability (in general this is also a function of E and E_1, but here it is assumed independent of energy). The second term on the right represents the increase due to clusters of size $(i+1)$ losing a monomer,

$\alpha_i(E, E_1)$ being the rate constant for the emission of a monomer of energy E_1 by an i-cluster of energy E. The third term represents the decrease in $C_i(E)$ from i-clusters gaining or losing a monomer. The $\bar{\alpha}_i(E)$ is related to $\alpha_i(E, E_1)$ by

$$\bar{\alpha}_i(E) = \int \alpha_i(E, E_1)\,\mathrm{d}E_1 \tag{3.2}$$

and the same relationship holds between $\bar{\beta}_i(E)$ and $\beta_i(E, E_1)$. The fourth term represents the change in $C_i(E)$ due to collisions with gas molecules; $\bar{\beta}_{ig}(E)$ is the collision rate for gas molecules with an i-cluster of energy E and $P_g(E' \to E)$ is the probability that a cluster with initial energy E' has energy E after the collision. Similarly, the final term represents the change due to collisions with the fraction $(1-s_A)$ of vapour molecules that do not stick to the i-cluster but which may exchange energy with it, $P_v(E' \to E)$ being the probability that a non-sticking collision with a vapour molecule causes a transition in cluster energy from E' to E.

Some care must be taken in specifying the limits of integration in (3.1), since there is a minimum allowable i-cluster energy, equal to the minimum interaction potential energy $U_i^{\min}$ which in our model is simply U_i. Provided we specify that

$$C_i(E) = 0 \qquad \text{for } E < U_i^{\min} \tag{3.3}$$

and also that $E_1 \geq 0$, we can allow the limits to range from minus infinity to plus infinity. Note, however, that in $\alpha(E, E_1)$ we must have $0 \leq E_1 \leq (E - U_{i-1}^{\min})$ and these limits should be used in determining $\bar{\alpha}_i(E)$ from (3.2).

3.1. *Energy transfer from gas molecules*

We now consider the determination of $\bar{\beta}_{ig}$ and $P_g(E' \to E)$ from equilibrium statistical mechanics. Individual gas molecules are treated as classical systems with $2c_{vg}/k$ independent degrees of freedom, where c_{vg} is the gas molecular heat capacity. The gas-cluster collision rate depends on cluster energy since the clusters are in motion. However, for cluster sizes of interest ($i \geq 10$), this dependence is weak and we ignore it, so $\bar{\beta}_{ig}$ is independent of E and equal to the total number of gas molecules striking a stationary cluster with surface area A_i per second. This is given by the usual kinetic expression

$$\bar{\beta}_{ig} = A_i n_g \left(\frac{kT}{2\pi m_g}\right)^{1/2} = \frac{A_i p_g}{\sqrt{2\pi m_g kT}} \tag{3.4}$$

where $p_g = n_g kT$ is the gas pressure and m_g the mass of a gas molecule.

The rate at which gas molecules with total energy between E_1 and $E_1 + \mathrm{d}E_1$ collide with a cluster is

$$\text{constant} \times \mathrm{e}^{-E_1/kT}\,\mathrm{d}E_1 \int_0^{E_1} \mathrm{d}\varepsilon\, \varepsilon (E_1 - \varepsilon)^{c_{vg}/k - 5/2} = \frac{E_1^{\tilde{c}_{bg}-1}}{\Gamma(\tilde{c}_{bg})(kT)^{\tilde{c}_{bg}}}\, \mathrm{e}^{-E_1/kT}\,\mathrm{d}E_1 \tag{3.5}$$

where ε is the gas molecule kinetic energy, and $\tilde{c}_{bg} = c_{bg}/k = c_{vg}/k + \frac{1}{2}$, the extra $\frac{1}{2}$ arising because molecules with kinetic energy ε have speed $(2\varepsilon/m_g)^{1/2}$, so fast molecules collide more frequently. The gas molecule and cluster are assumed to form a microcanonical (constant energy) system so the probability of any decay is proportional to the density of states of that decay. The density of states of the gas molecule to be emitted with total energy between E_2 and $E_2 + \mathrm{d}E_2$ is proportional to $E_2^{\tilde{c}_{bg}-1}\,\mathrm{d}E_2$ and that for the cluster to have energy E is $\Omega_i(E)$ so the correctly normalized probability that the system with energy $(E'+E_1)$ decays to this final state is

$$\frac{\Omega_i(E)E_2^{\tilde{c}_{\mathrm{bg}}-1}\,\mathrm{d}E_2}{\int_0^{E'+E_1-U_i^{\min}}\Omega_i(E'+E_1-E_3)E_3^{\tilde{c}_{\mathrm{bg}}-1}\,\mathrm{d}E_3}. \tag{3.6}$$

Our final expression for $P_{\mathrm{g}}(E'\to E)$ is found by multiplying (3.5) and (3.6) and integrating over all values of E_1 and E_2 that satisfy $E'+E_1=E+E_2$,

$$P_{\mathrm{g}}(E'\to E)=\frac{1}{\Gamma(\tilde{c}_{\mathrm{bg}})(kT)^{\tilde{c}_{\mathrm{bg}}}}\int_0^\infty \mathrm{d}E_1 \times\int_0^\infty \mathrm{d}E_2\,\frac{\Omega_i(E)(E_1E_2)^{\tilde{c}_{\mathrm{bg}}-1}\,\mathrm{e}^{-E_1/kT}\delta(E'+E_1-E-E_2)}{\int_0^{E'+E_1-U_i^{\min}}\mathrm{d}E_3\,\Omega_i(E'+E_1-E_3)E_3^{\tilde{c}_{\mathrm{bg}}-1}}. \tag{3.7}$$

We can use the properties of the delta function $\delta(x)$ to perform one of the integrals, say over E_1, but this affects the lower limit of the remaining integral:

$$\begin{aligned}P_{\mathrm{g}}(E'\to E)&=\frac{1}{\Gamma(\tilde{c}_{\mathrm{bg}})(kT)^{\tilde{c}_{\mathrm{bg}}}}\\&\quad\times\int_{\max(0,E'-E)}^\infty \mathrm{d}E_2\,\frac{\Omega_i(E)(E+E_2-E')^{\tilde{c}_{\mathrm{bg}}-1}E_2^{\tilde{c}_{\mathrm{bg}}-1}\,\mathrm{e}^{-(E+E_2-E')/kT}}{\int_0^{E+E_2-U_i^{\min}}\Omega_i(E+E_2-E_3)E_3^{\tilde{c}_{\mathrm{bg}}-1}\,\mathrm{d}E_3}\\&=\frac{1}{\Gamma(\tilde{c}_{\mathrm{bg}})(kT)^{\tilde{c}_{\mathrm{bg}}}}\,\frac{\Omega_i(E)\Omega_i(E')}{C_i^{\mathrm{eq}}(E')}\,\frac{q_i}{c_i^{\mathrm{eq}}}\\&\quad\times\int_{\max(E,E')}^\infty \mathrm{d}x\,\frac{[(x-E')(x-E)]^{\tilde{c}_{\mathrm{bg}}-1}\,\mathrm{e}^{-x/kT}}{\int_0^{x-U_i^{\min}}\mathrm{d}E_3\,\Omega_i(x-E_3)E_3^{\tilde{c}_{\mathrm{bg}}-1}}.\end{aligned} \tag{3.8}$$

Since the integrand is symmetric in E and E', it follows that the detailed balance condition is satisfied in equilibrium, i.e.

$$P_{\mathrm{g}}(E'\to E)C_i^{\mathrm{eq}}(E')=P_{\mathrm{g}}(E\to E')C_i^{\mathrm{eq}}(E). \tag{3.9}$$

Using our square well model of a cluster, with $\Omega_i(E)$ obtained from (2.1) and (2.8), we can evaluate the integral in the denominator of (3.7) and obtain

$$\begin{aligned}P_{\mathrm{g}}(E'\to E)&=\frac{1}{(kT)^{\tilde{c}_{\mathrm{bs}}}}\,\frac{\Gamma(i\tilde{c}_{\mathrm{vv}}+\tilde{c}_{\mathrm{bg}})}{\Gamma(\tilde{c}_{\mathrm{bg}})^2\Gamma(i\tilde{c}_{\mathrm{vv}})}\\&\quad\times\int_0^\infty \mathrm{d}E_1\int_0^\infty \mathrm{d}E_2\,\frac{(E-U_i)^{i\tilde{c}_{\mathrm{vv}}-1}(E_1E_2)^{\tilde{c}_{\mathrm{bg}}-1}\,\mathrm{e}^{-E_1/kT}}{(E'+E_1-U_1)^{i\tilde{c}_{\mathrm{vv}}+\tilde{c}_{\mathrm{bg}}-1}}\\&\quad\times\delta(E'+E_1-E-E_2).\end{aligned} \tag{3.10}$$

This form is the most convenient for evaluating integrals over E, which is the procedure used in solving the rate equations. In particular, the mean energy transfer from an i-cluster with energy E' is

$$\int (E'-E)P_{\mathrm{g}}(E'\to E)\,\mathrm{d}E=\frac{c_{\mathrm{bg}}}{ic_{\mathrm{vv}}+c_{\mathrm{bg}}}(E'-\bar{E}_i) \tag{3.11}$$

where $\bar{E}_i=ic_{\mathrm{vv}}T+U_i$ is the i-cluster mean energy at temperature T.

We use a similar model for energy transfer by non-condensing vapour molecules so $\bar{\beta}_i$ is given by (3.4) with the vapour pressure p_{v} in place of p_{g} and m_{v} in place of m_{g}. Similarly $P_{\mathrm{v}}(E'\to E)$ is given by (3.7) (or (3.10) for the square well model), with $\tilde{c}_{\mathrm{bv}}=c_{\mathrm{vv}}/k+\frac{1}{2}$ in place of $\tilde{c}_{\mathrm{bg}}$.

3.2. *Cluster growth and decay rates*

As in the previous subsection, we ignore cluster motion. The monomer–cluster collision rate $\beta_i(E, E_1)$ is then independent of E and is given by analogy with (3.5)

$$\beta_i(E, E_1) \equiv \beta_i(E_1) = \frac{A_i p_v}{\sqrt{2\pi m_v kT}} \frac{1}{\Gamma(\tilde{c}_{bv})(kT)^{\tilde{c}_{bv}}} E_1^{\tilde{c}_{bv}-1} e^{-E_1/kT} \tag{3.12}$$

where, as before, $\tilde{c}_{bv} = c_{vv}/k + \frac{1}{2}$. Equation (3.12) is normalized so that

$$\bar{\beta}_i = \int_0^\infty \beta_i(E_1)\, dE_1 = \frac{A_i p_v}{\sqrt{2\pi m_v kT}}. \tag{3.13}$$

The key step is to obtain the decay rate $\alpha_i(E, E_1)$ from the equilibrium detailed balance condition

$$s_A \beta_{i-1}(E_1) C_{i-1}^{eq}(E - E_1) = \alpha_i(E, E_1) C_i^{eq}(E). \tag{3.14}$$

Using (2.1), (2.4) and (3.12), we obtain from (3.14)

$$\alpha_i(E, E_1) = \frac{s_A A_{i-1}}{\sqrt{2\pi m_v}} \frac{q_1}{(kT)^{\tilde{c}_{vv}}} \frac{E_1^{\tilde{c}_{bv}-1}}{\Gamma(\tilde{c}_{bv})} \frac{\Omega_{i-1}(E - E_1)}{\Omega_i(E)}. \tag{3.15}$$

Since q_1 is proportional to $T^{\tilde{c}_{vv}}$, the decay rate is independent of both the vapour temperature and the supersaturation external to the cluster, as is required.

For our liquid drop cluster model, with $C_i^{eq}(E)$ given by (2.8), we obtain

$$\alpha_i(E, E_1) = \frac{s_A A_{i-1}}{\sqrt{2\pi m_v}\Gamma(\tilde{c}_{bv}) v_0} \left(\frac{i-1}{i}\right)^{i+1-\delta} \times \frac{\Gamma(i\tilde{c}_{vv})}{\Gamma((i-1)\tilde{c}_{vv})} E_1^{\tilde{c}_{bv}-1} \frac{(E - E_1 - U_{i-1})^{(i-1)\tilde{c}_{vv}-1}}{(E - U_i)^{i\tilde{c}_{vv}-1}} \tag{3.16}$$

(where we have used (2.4) and (2.7) to eliminate c_{i-1}^{eq}/c_i^{eq}). We can integrate (3.16) over E_1 (with $0 \leqslant E_1 \leqslant E - U_{i-1}$) to obtain

$$\bar{\alpha}_i(E) = \frac{s_A A_{i-1}}{\sqrt{2\pi m_v} v_0} \left(\frac{i-1}{i}\right)^{i+1-\delta} \frac{\Gamma(i\tilde{c}_{vv})}{\Gamma(i\tilde{c}_{vv} + \frac{1}{2})} \frac{(E - U_{i-1})^{i\tilde{c}_{vv}-1/2}}{(E - U_i)^{i\tilde{c}_{vv}-1}}. \tag{3.17}$$

Using the Gaussian approximation for $C_i^{eq}(E)$, equation (2.3) in (3.14), together with (3.12) for $\beta_i(E_1)$ gives the following approximate expression for the decay rate

$$\alpha_i^{GA}(E, E_1) = \frac{s_A A_{i-1}}{\sqrt{2\pi m_v}} \frac{1}{\Gamma(\tilde{c}_{bv})(kT)^{\tilde{c}_{vv}}} \left(\frac{i-1}{i}\right)^{1/2} \frac{q_1 q_{i-1}}{q_i} E_1^{\tilde{c}_{bv}-1} \times \exp\left[-\frac{E_1}{kT} - \frac{(E - \bar{E}_{i-1} - E_1)^2}{2(i-1)c_{vv}kT^2} + \frac{(E - \bar{E}_i)^2}{2ic_{vv}kT^2}\right]. \tag{3.18}$$

For the square well model, $\bar{E}_i = ic_{vv}T + U_i$ and $q_1 q_{i-1}/q_i = (1 - 1/i)^{i+1-\delta} \exp((U_i - U_{i-1})/kT)/v_0$. The integral of $\alpha_i^{GA}(E, E_1)$ over E_1, which we denote by $\bar{\alpha}_i^{GA}(E)$, can be performed analytically if $\tilde{c}_{bv}$ is an integer; alternatively, it can be evaluated numerically for any $\tilde{c}_{bv}$. Figure 3 shows the variation of $\bar{\alpha}_i(E)$ and $\bar{\alpha}_i^{GA}(E)$ (with $s_A = 1$) for the case shown in figure 2 (i.e. typical of water at 20 °C). Although the Gaussian approximation for the equilibrium energy distribution gives reasonable results in the region of the peak of $C_i^{eq}(E)$, it leads to an overestimation of the decay rate away from the peak, particularly at low energies. This has implications as regards the nucleation rate.

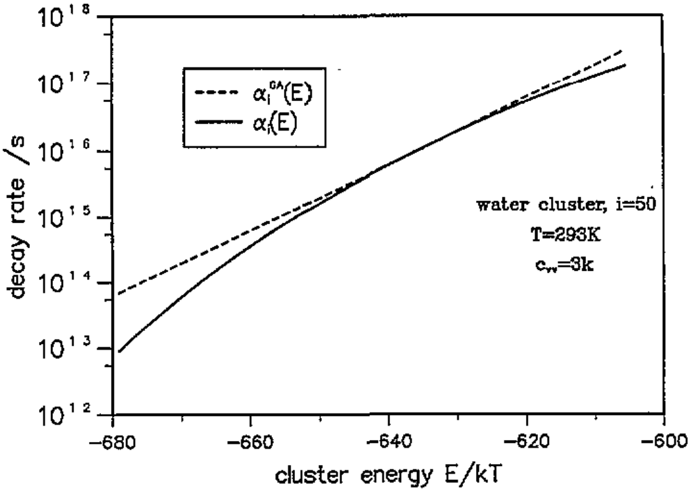

Figure 3. Comparison between exact cluster decay rate and form based on a Gaussian approximation (GA) for the cluster energy distribution.

It is interesting to consider the behaviour of $\bar{\alpha}_i(E)$ for large i. If we define τ by $ic_{vv}\tau = E - U_i$, we find for large i, from (3.17)

$$\bar{\alpha}_i(\tau) \simeq \frac{s_A A_i \sqrt{k\tau}}{\sqrt{2\pi m_v}\, e v_0} \exp((U_i - U_{i-1})/k\tau)$$

$$\simeq \frac{s_A A_i}{\sqrt{2\pi m_v k\tau}} p_{ve}(\tau) \exp(2b/(3k\tau i^{1/3})) \tag{3.19}$$

where the first right-hand side follows from (3.17) using the approximations, valid for large z, $\Gamma(1+z) \simeq z^z\, e^{-z}$ and $(1-x/z)^z \simeq e^{-x}$ and the final form follows using equation (2.6) for U_i, since the equilibrium vapour pressure for this model is $p_{ve}(T) = (kT/ev_0)\, e^{-a/kT}$ [17]. If we identify b with the bulk surface energy per molecule, $b = \sigma A_1$, then the final exponent in (3.19) is the Kelvin factor giving the modification of the vapour pressure over a curved surface of radius $r_i = (3v_0 i/4\pi)^{1/3}$. The decay rate given by (3.19) is just that from a droplet of radius r_i at temperature τ, as suggested previously [14]. Note however, that τ is simply a parametrization of the energy E, and not a true temperature.

Finally, it is useful to define here a quantity $\hat{\alpha}_i(T_i)$ by the relation

$$c_i^{eq}(T_i)\hat{\alpha}_i(T_i) = \int_{U_{i-1}^{\min}}^{\infty} \bar{\alpha}_i(E) C_i^{eq}(E, T_i)\, dE \tag{3.20}$$

where $C_i^{eq}(E, T_i)$ is the equilibrium cluster distribution in a vapour at temperature T_i (given by (2.1) with $T = T_i$, noting that c_i^{eq} and q_i should also be evaluated at $T = T_i$). Integrating the detailed balance condition, (3.14), over E and E_1 (bearing in mind the condition (3.3)) gives

$$\hat{\alpha}_i(T_i) = \bar{\beta}_{i-1} c_{i-1}^{eq}/c_i^{eq} \tag{3.21}$$

where the terms on the right-hand side are all evaluated at $T = T_i$.

Multiplying (3.14) by E and integrating over E and E_1 gives

$$\int_{U_{i-1}^{\min}}^{\infty} \bar{\alpha}_i(E) E C_i^{eq}(E, T_i)\, dE = \bar{\beta}_{i-1} c_{i-1}^{eq}(\bar{E}_{i-1}(T_i) + c_{bv} T_i) \tag{3.22}$$

where $\bar{E}_i(T_j)=kT_j^2\,\mathrm{d}(\ln q_i(T_j))/\mathrm{d}T_j$ is the mean energy of an i-cluster in equilibrium at temperature T_j. The results (3.20)–(3.22) are not restricted to any particular cluster model.

4. Nucleation rates

The steady-state cluster energy distribution $C_i^{ss}(E)$ is the solution of

$$\int \beta_{i-1}(E_1)C_{i-1}^{ss}(E-E_1)\,\mathrm{d}E_1+\int \alpha_{i+1}(E+E_1,E_1)C_{i+1}^{ss}(E+E_1)\,\mathrm{d}E_1$$
$$-[\bar{\beta}_i+\bar{\alpha}_i(E)]C_i^{ss}(E)+\bar{\beta}_{ig}\left[\int P_g(E'\to E)C_i^{ss}(E')\,\mathrm{d}E'-C_i^{ss}(E)\right]=0 \tag{4.1}$$

where, for simplicity, we have assumed $s_A=1$. Equations (4.1) must be solved subject to the boundary conditions $C_1^{ss}(E)=C_1^{eq}(E)$ (equilibrium energy distribution of monomers) and

$$\lim_{i\to\infty} C_i^{ss}(E)\to 0$$

(no large droplets present).

Once $C_i^{ss}(E)$ is known, the steady-state flux J can be found from (noting the lower limit on E in $\alpha_i(E,E_1)$)

$$J=\int_{U_{i-1}^{\min}}^{\infty}[\bar{\beta}_{i-1}C_{i-1}^{ss}(E)-\bar{\alpha}_i(E)C_i^{ss}(E)]\,\mathrm{d}E. \tag{4.2}$$

We first discuss an approximate method to determine the nucleation rate which gives analytical results and then consider the numerical solution of (4.1).

4.1. *Approximate analytical solution*

We assume that the steady-state i-cluster distribution has the same energy dependence as an equilibrium distribution at temperature T_i, that is, we write

$$C_i^{ss}(E)=c_i^{ss}\frac{\Omega_i(E)\,\mathrm{e}^{-E/kT_i}}{q_i(T_i)}=\frac{c_i^{ss}}{c_i^{eq}(T_i)}\,C_i^{eq}(E,T_i). \tag{4.3}$$

Using this in (4.2) we obtain

$$J=\bar{\beta}_{i-1}(T)c_{i-1}^{ss}-\hat{\alpha}_i(T_i)c_i^{ss} \tag{4.4}$$

where we have used the definition of $\hat{\alpha}_i(T_i)$, equation (3.20). Multiplying (4.1) by E and integrating over all E gives a one-dimensional heat balance relation

$$\bar{\beta}_{i-1}(T)[\bar{E}_{i-1}(T_{i-1})+c_{bv}T]c_{i-1}^{ss}+\hat{\alpha}_{i+1}(T_{i+1})\bar{E}_i(T_{i+1})c_{i+1}^{ss}$$
$$-[\bar{\beta}_i(T)\bar{E}_i(T_i)+\hat{\alpha}_i(T_i)(\bar{E}_{i-1}(T_i)+c_{bv}T_i)]c_i^{ss}-Qc_i^{ss}=0 \tag{4.5}$$

where we have used (3.22). Q is the heat transfer away from the cluster due to gas molecule collisions, which for small temperature differences (T_i-T) can be written

$$Q=\lambda c_{bg}\bar{\beta}_{ig}(T_i-T). \tag{4.6}$$

The value of λ depends on the extent of thermal accommodation between clusters and colliding gas molecules: for complete accommodation, $\lambda = ic_{\mathrm{vc}}/(ic_{\mathrm{vc}} + c_{\mathrm{bg}}) \sim 1$ for large i (c_{vc} is the molecular heat capacity for molecules in the cluster).

Using (4.6) and (4.4), written for i and $(i+1)$, in (4.5) gives

$$\begin{aligned} J[\bar{E}_{i-1}(T_i) - \bar{E}_i(T_i) + c_{\mathrm{bv}}T_i] \\ &= \bar{\beta}_{i-1}(T)c_{\mathrm{bv}}(T_i - T)c_{i-1}^{\mathrm{ss}} + \bar{\beta}_{ig}\lambda c_{\mathrm{bg}}(T_i - T)c_i^{\mathrm{ss}} + \bar{\beta}_{i-1}(T) \\ &\quad \times [\bar{E}_{i-1}(T_i) - \bar{E}_{i-1}(T_{i-1})]c_{i-1}^{\mathrm{ss}} - \hat{\alpha}_{i+1}(T_{i+1})[\bar{E}_i(T_{i+1}) - \bar{E}_i(T_i)]c_{i+1}^{\mathrm{ss}}. \end{aligned} \tag{4.7}$$

The terms on the right represent the heat transfer from the cluster due to collisions with vapour and gas molecules and the energy required to heat up growing clusters and cool down evaporating clusters. Given a form for $\bar{E}_i(T_i)$, and assuming a maximum cluster size $i = N$, equations (4.4) and (4.7) form a set of coupled non-linear equations for the $2(N-1)$ unknowns $c_2^{\mathrm{ss}}, \ldots, c_N^{\mathrm{ss}}, T_2, \ldots, T_N$. We can obtain an approximate analytical solution by following the procedure used by Kantrovitz [23]. First we note from the law of mass action (2.4) and the definitions of $\hat{\alpha}_i(T_i)$ (equation (3.21)) and of $\bar{E}_i(T_i)$ that $kK' = \bar{E}_{i-1}(T_i) - \bar{E}_i(T_i) + \bar{E}_i(T_i)$ where

$$K' = T_i^2 \frac{\mathrm{d}}{\mathrm{d}T_i} \ln\left(\frac{\hat{\alpha}_i(T_i)}{\bar{\beta}_{i-1}(T_i)}\right). \tag{4.8}$$

With the asymptotic form of $\hat{\alpha}_i(T_i)$, equation (3.19), this K' is the same as that used in [14]. Using the Clausius–Clapeyron equation for p_{ve} this K' is

$$m_{\mathrm{v}}L/k - \left[\frac{4\pi}{3}\right]^{1/3} 2\sigma v_0^{2/3}/i^{1/3}k.$$

We then expand (4.4) to first order in $(T_i - T)$ to obtain

$$\begin{aligned} c_i^{\mathrm{ss}}(T_i - T) &= \frac{\bar{\beta}_{i-1}(T)c_{i-1}^{\mathrm{ss}} - \hat{\alpha}_i(T)c_i^{\mathrm{ss}} - J}{\mathrm{d}\hat{\alpha}_i(T)/\mathrm{d}T} \\ &= \frac{-Tc_i^{\mathrm{eq}}}{K'/T - \frac{1}{2}}\left(\frac{\mathrm{d}}{\mathrm{d}i}\left(\frac{c_i^{\mathrm{ss}}}{c_i^{\mathrm{eq}}}\right) + \frac{J}{\hat{\alpha}_i(T)c_i^{\mathrm{eq}}}\right) \end{aligned} \tag{4.9}$$

where the final form follows from using (4.8) and taking the continuum limit (i.e. replacing $f(i) - f(i-1)$ by $\mathrm{d}f/\mathrm{d}i$. We similarly expand the energy differences in (4.7) to first order (i.e. $\bar{E}_i(T_{i+1}) - \bar{E}_i(T_i) = ic_{\mathrm{vc}}(T_{i+1} - T_i)$, etc). Then, using (4.4), (4.8) and (4.9) in (4.7) and again taking the continuum limit we obtain,

$$\begin{aligned} J\left[k(K'/T + \tfrac{1}{2}) + (c_{\mathrm{vc}} + \tfrac{1}{2}k - c_{\mathrm{bv}})(T_i - T)/T + \frac{\hat{\alpha}_i(T)c_{\mathrm{bv}} + \bar{\beta}_{ig}\lambda c_{\mathrm{bg}}}{(K'/T - \frac{1}{2})\hat{\alpha}_i(T)}\right] \\ &= -\left(\frac{\hat{\alpha}_i(T_i)c_{\mathrm{bv}} + \bar{\beta}_{ig}\lambda c_{\mathrm{bg}}}{K'/T - \frac{1}{2}}\right) c_i^{\mathrm{eq}} \frac{\mathrm{d}}{\mathrm{d}i}\left(\frac{c_i^{\mathrm{ss}}}{c_i^{\mathrm{eq}}}\right) \\ &\quad + \frac{c_{\mathrm{vc}}}{K'/T - \frac{1}{2}} \frac{\mathrm{d}}{\mathrm{d}i}\left(i\bar{\beta}_i c_i^{\mathrm{eq}} \frac{\mathrm{d}}{\mathrm{d}i}\left[\frac{\mathrm{d}}{\mathrm{d}i}\left(\frac{c_i^{\mathrm{ss}}}{c_i^{\mathrm{eq}}}\right) + \frac{J}{\hat{\alpha}_i(T)c_i^{\mathrm{eq}}}\right]\right). \end{aligned} \tag{4.10}$$

To a very good approximation, we can ignore the term involving $(T_i - T)$ on the left-hand side. An approximate solution can be found by also ignoring the last term on the right and integrating, using the fact that c_i^{eq} has a deep narrow minimum at $i = i^*$ where $(\hat{\alpha}_{i^*} = \bar{\beta}_{i^*})$ to obtain

$$J = \frac{J_{\text{ISO}}}{1 + ((K'/T)^2 - \frac{1}{4}) \Big/ \left(\tilde{c}_{\text{bv}} + \lambda \tilde{c}_{\text{bg}} \dfrac{P_{\text{g}}}{SP_{\text{ve}}(T)} \left(\dfrac{m_{\text{v}}}{m_{\text{g}}} \right)^{1/2} \right)} \tag{4.11}$$

where $S = p_{\text{v}}/p_{\text{ve}}(T)$ is the saturation and $J_{\text{ISO}} = (\int_1^\infty \mathrm{d}i/(\beta_i c_i^{\text{eq}}))^{-1}$ is the usual isothermal flux ignoring any difference between the equilibrium and steady-state energy distributions. Equation (4.11) is very similar to that derived by Feder *et al* [13], if we use the asymptotic form for K' given after (4.8). The principal difference is that Feder *et al* have $[K'/T - \frac{1}{2}]^2$ in place of our factor $[(K'/T)^2 - \frac{1}{4}]$.

It remains to estimate the magnitude of the final term in (4.10) which we ignored in deriving (4.11). This can be done by substituting the solution for c_i^{ss} of (4.10) without this term, into this term and comparing it with the terms on the left-hand side. It appears that this term is small at normal gas pressures by may become significant at very low gas pressures. However, the term is always positive, as we would expect on physical grounds (there are more cold clusters growing from $(i^* - 1)$ to i^* than hot clusters evaporating from $(i^* + 1)$ to i^*). Therefore it always leads to an increase in J above the value given by (4.11). In other words, (4.11) represents the greatest possible reduction in flux from its isothermal value within the approximation taken in assuming C_i^{ss} is given by (4.3). Numerical solution of (4.4) and (4.7) by integrating the time dependent equations to steady state confirm that the flux is slightly greater than that given by (4.11).

4.2. *Numerical solution*

To solve (4.1) numerically with gain and loss rates given by our liquid drop model in section 3, we assume that $C_i^{\text{ss}}(E)$ can be expressed as a polynomial in energy multiplied by the equilibrium distribution, that is

$$\begin{aligned} C_i^{\text{ss}}(E)\,\mathrm{d}E &= c_i^{\text{eq}}(E) \sum_{j=0}^{m-1} \mu_j^{(i)} \left(\frac{E - U_i}{kT} \right)^j \mathrm{d}E \\ &= c_i^{\text{eq}} \frac{x^{\tilde{c}_{\text{vv}} - 1}}{\Gamma(i\tilde{c}_{\text{vv}})} \mathrm{e}^{-x} \sum_{j=0}^{m} \mu_j^{(i)} x^j \,\mathrm{d}x = \tilde{C}_i^{\text{ss}}(x)\,\mathrm{d}x \end{aligned} \tag{4.12}$$

where $x = (E - U_i)/kT$. We assume that clusters of size $i \leqslant i_{min}$ are in equilibrium and that clusters larger than $i_{\max}$ are removed from the system. We therefore have $(m+1) \times (i_{\max} - i_{\min})$ unknowns $\mu_j^{(i)}$ which can be found by substituting (4.12) in the $(i_{\max} - i_{\min})$ equations (4.1) (for $i_{\min} < i \leqslant i_{\max}$), multiplying each equation by x^n, for $n = 0, 1, 2, \ldots, m$, and integrating over x. The resulting linear equations can be solved by standard methods and the flux can then be found using (4.2). More details of the solution method appear in the appendix.

We have performed calculations with parameters characteristic of n-nonane in argon at 0 °C ($c_{\text{vv}} = 3k$, $c_{\text{vg}} = 1.5k$, $a = 20.1kT$, $b = 14.0kT$) and of water in air at 20 °C ($c_{\text{vv}} = 3k$, $c_{\text{vg}} = 2.5k$, $a = 18.1kT$, $b = 8.4kT$). Although we refer to these systems as n-nonane/argon and water/air below, it should be noted that our model is too crude to reproduce all experimentally measured characteristics of these systems. In particular it predicts the equilibrium vapour pressure incorrectly so our predictions of absolute values of nucleation rates as a function of vapour pressure are likely to be in error.

However, here we present ratios of nucleation rates at given saturations, which are insensitive to the absolute values of the vapour pressure and J. These ratios are also insensitive to the value of δ.

In the limit of high gas pressure, collisional energy transfers dominate and the energy distributions are close to thermal equilibrium characterized by the gas temperature T. The $j = 0$ term then dominates in the expression for the C_i^{ss} in (4.12). The system may therefore be considered to be isothermal, which is assumed in most developments of nucleation theory, with the result that no gas pressure dependence appears. For finite gas pressures, however, the steady-state cluster energy distributions deviate from thermal equilibrium and a pressure dependence of the nucleation rate emerges. Figures 4 and 5 illustrate the effect for *n*-nonane nucleation in argon, and water nucleation in air, for particular conditions, over a range of system pressures.

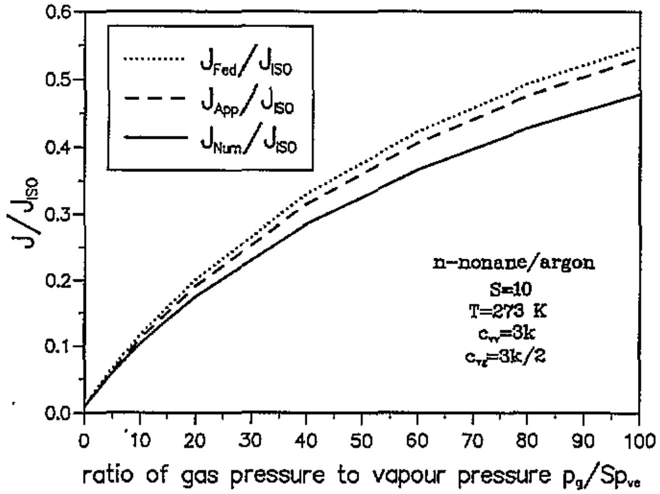

Figure 4. Nucleation rate dependence on carrier gas pressure, comparing our numerical results to an analytical approximation. J_{ISO} is the pressure independent isothermal prediction.

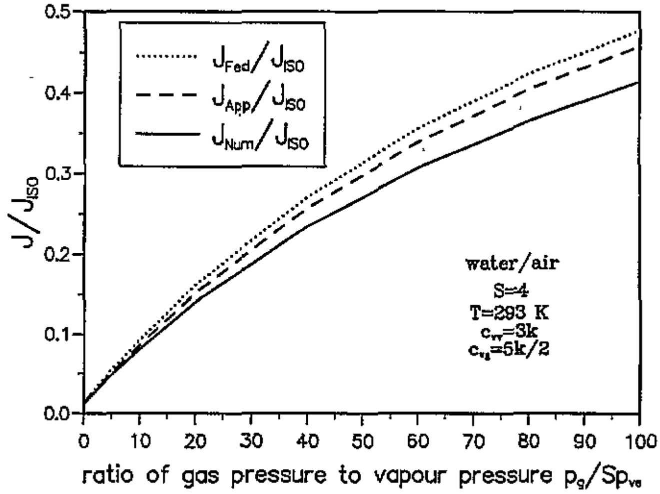

Figure 5. As for figure 4 but for water droplet nucleation in air.

The nucleation rate rises with pressure, saturating at the isothermal rate for large pressures. The numerical predictions of the 2D model, denoted J_{Num} are compared with the analytical approximation J_{App}, equation (4.11), and also the formula of Feder *et al* [13]. For our liquid drop model, $kK' = a - b(i^{*2/3} - (i^* - 1)^{2/3})$. The similarity of the predictions implies that it is a reasonable approximation to describe the cluster energy fluctuations using equilibrium distributions characterized by a size and pressure dependent temperature, the line of development pursued in subsection 4.1. However, note that numerical values are smaller than those given by (4.11), which gives the minimum possible flux in the approximation used in section 4.1. Hence the differences are due to the non-equilibrium energy distribution rather than the approximations involved in deriving (4.11).

In figure 6 this concept is illustrated by defining an effective cluster temperature τ_i in the numerical calculations, related to the mean energy $\bar{E}_i$ according to $ic_{\mathrm{vv}}\tau_i = \bar{E}_i - U_i$. τ_i rises above the gas temperature T as the cluster size increases, corresponding to the heating effect of latent heat release.

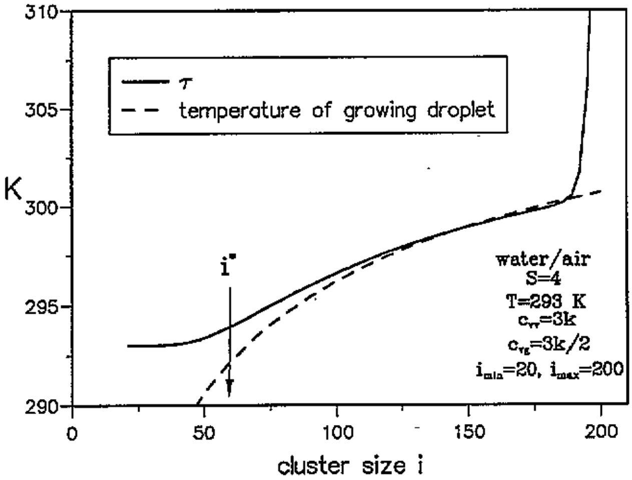

Figure 6. Mean cluster energy, parametrized as τ, during steady-state nucleation, compared with temperature of growing droplet, calculated from kinetic heat and mass transfer relations.

For higher gas pressures, the rise in τ_i is smaller. At quite low values of i, τ_i approaches a temperature characteristic of a growing physical droplet. This temperature is based on kinetic relations for heat and mass transfer to a droplet, such that heat loss balances heat gained by condensation [21]. The implication is that the concept of a droplet with a well-defined temperature applies for clusters of molecules only a little larger than the critical size.

5. Discussion and conclusions

In this work we have studied the influence of the carrier gas upon the energy distribution of nucleating clusters, which can alter the rate of droplet formation. The motivation is the strong pressure effect seen in some experiments, which seems to depend on the substances and conditions used. The problem requires a two-dimensional set of evolution equations for the cluster populations: transitions being allowed in cluster energy and cluster size. These include the gain and loss of vapour monomers by condensation and evaporation, and the gain and loss of energy by non-sticking gas and vapour molecule collisions with clusters, as well as latent heat transfers. In this study, detailed balance, together with a model of cluster interactions corresponding to the liquid drop concept, provide the rate coefficients for transitions. The numerical solution of the equations for the steady-state situation with appropriate boundary conditions yields the nucleation rate. The effect of changes in the gas pressure can then be studied. Alternatively, approximate analytical results may be obtained by assuming cluster energy distributions which are in thermal equilibrium characterized by a cluster temperature τ_i. It is worth underlining here that clusters can only be discussed in terms of temperature if they assume equilibrium energy distributions. In general, a cluster energy description is necessary. A confusion between cluster energy and cluster temperature has appeared in the literature [13–16]. This is one reason why previous treatments of this problem have been inadequate.

The original analysis by Feder *et al* [13] used detailed balance in thermal equilibrium to obtain the rate coefficients, but assumed a Gaussian cluster energy distribution with mean and standard deviation based on continuum thermodynamics. Consequently, the cluster decay rate used depended, erroneously, on the temperature of the surroundings. However, the resulting non-isothermal nucleation rate is similar to our approximate analytic result, equation (4.11), with the implication that as long as detailed balance is invoked, the form assumed for the energy distribution is not vital.

Ford and Clement [14, 15] also used a Gaussian distribution similar to (2.3) to describe energy fluctuations. However, detailed balance in an equilibrium situation was not invoked to obtain the decay coefficients, but rather the Kelvin form, equation (3.19) was used, motivated by large droplet considerations. The decay rate correctly depended only on cluster properties and not on those of the environment. However, it has been shown here that this form is only appropriate for large cluster sizes and that an exact expression for all cluster sizes can be derived, again dependent only on cluster properties, based on detailed balance and a cluster energy distribution which goes beyond the Gaussian approximation. Results based on these developments are similar to those of Feder *et al* and do not show the suppression effects proposed in [14]. Clearly, these effects arise from the use of the inappropriate decay rate at small cluster size, coupled with the Gaussian distribution. The key to the new approach, and that of Feder *et al*, is the use of detailed balance in a reference thermal equilibrium situation.

The pressure dependence arising from non-isothermal effects, however, does not explain the behaviour of nucleation rates reported experimentally. The fall in rate with an increase in pressure for *n*-nonane in argon using a diffusion chamber [7] is contrary to the effect described here. The rise in rate with pressure for dibutylphthalate (DBP) in CO_2 in a flow diffusion chamber [12] is stronger than would be predicted here, as is illustrated in figure 7.

In conclusion, therefore, it has been shown that a simple cluster model can be used to study non-isothermal effects in homogeneous nucleation theory, avoiding the deficiencies of previous approaches. However, the resulting pressure dependence of the nucleation rate is weak and cannot explain the pressure effects seen in recent nucleation experiments. An explanation of these effects will probably require alternative

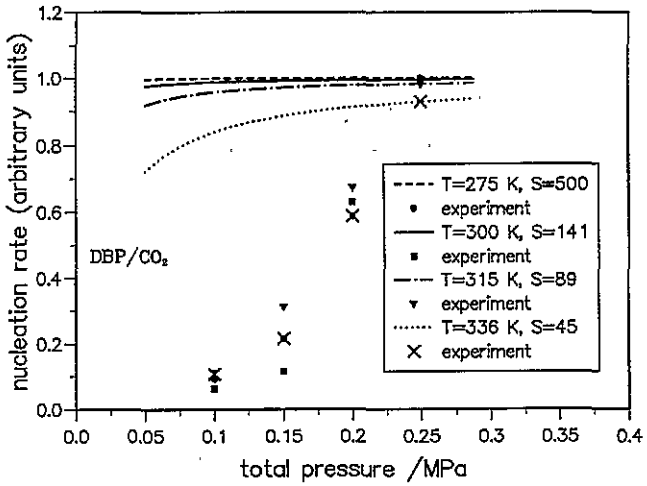

Figure 7. Pressure dependence of the nucleation rate for DBP. Curves are the non-isothermal correction factors according to Feder *et al*, and the points are data from Anisimov and Vershinin, normalized to the curves at 0.25 MPa.

mechanisms. The importance of this in the nuclear context is the wide range of pressures relevant to the nucleation of fission product aerosols in pressurized reactors.

Acknowledgment

This work was supported by the UK Department of Energy within the General Nuclear Safety Research programme.

Appendix

Dividing (4.1) by $A_1 p_{\mathrm{ve}}(T)/\sqrt{2\pi m_{\mathrm{v}} kT}$ and using (3.12), (3.13), (3.16) and (3.17), the equations of C_i^{ss} can be written

$$\begin{aligned}
&\frac{S(i-1)^{2/3}}{\Gamma(\tilde{c}_{\mathrm{bv}})} \int \mathrm{d}x_1\, x_1^{\tilde{c}_{\mathrm{bv}}-1}\, \mathrm{e}^{-x_1} \tilde{C}_{i-1}^{\mathrm{ss}}(x-x_1-h_i) \\
&\quad + \int \mathrm{d}x_1 \frac{kTi^{2/3}}{v_0 p_{\mathrm{ve}}(T)\Gamma(\tilde{c}_{\mathrm{bv}})} \left(\frac{i}{i+1}\right)^{i+2-\delta} \frac{\Gamma(y+\tilde{c}_{\mathrm{vv}})}{\Gamma(y)}\, x_1^{\tilde{c}_{\mathrm{bv}}-1} \\
&\quad \times \frac{x^{y-1}}{(x+x_1+h_{i+1})^{y+\tilde{c}_{\mathrm{vv}}-1}}\, \tilde{C}_{i+1}^{\mathrm{ss}}(x+x_1+h_{i+1}) \\
&\quad - \left(Si^{2/3} + (i-1)^{2/3} \left(\frac{i-1}{i}\right)^{i+1-\delta} \frac{\Gamma(y)}{\Gamma(y+\frac{1}{2})} \frac{(x-h_i)^{y-1/2} kT}{x^{y-1} v_0 p_{\mathrm{ve}}(T)} \right) \tilde{C}_i^{\mathrm{ss}}(x) \\
&\quad + \sqrt{\frac{m_{\mathrm{v}}}{m_{\mathrm{g}}}}\, \frac{p_{\mathrm{g}} i^{2/3}}{p_{\mathrm{ve}}(T)} \left[\int P(x' \to x) \tilde{C}_i^{\mathrm{ss}}(x')\, \mathrm{d}x' - \tilde{C}_i^{\mathrm{ss}}(x) \right] = 0 \qquad \text{(A.1)}
\end{aligned}$$

where $y = i\tilde{c}_{vv}$, $h_i = (U_{i-1} - U_i)/kT$, $x_1 = E_1/kT$ and $P(x' \to x)$ is the suitably non-dimensionalized form of (3.10). We introduce the approximation (4.12) for $\tilde{C}_i^{ss}(x)$, divide through by $i^{2/3}c_i^{eq}$ and perform the integrations over x_1 to obtain

$$\begin{aligned}
&\left(\frac{i-1}{i}\right)^{\frac{5}{3}-\delta} e^{a/kT} \frac{e^{-x}}{\Gamma(y-\tilde{c}_{vv})} \sum_{j=0}^{m-1} \mu_j^{(i-1)} \frac{\Gamma(y-\tilde{c}_{vv}+j)}{\Gamma(y+\frac{1}{2}+j)} (x-h_i)^{y-\frac{1}{2}+j} \\
&\qquad + Sx^{y-1} e^{-x} \frac{1}{\Gamma(y)\Gamma(\tilde{c}_{bv})} \sum_{j=0}^{m-1} \mu_j^{(i+1)} \left(\sum_{r=0}^{j} \binom{j}{r} (x+h_{i+1})^r \Gamma(\tilde{c}_{bv}+j-r) \right) \\
&\qquad - \left(\frac{Sx^{y-1}}{\Gamma(y)} + \left(\frac{i-1}{i}\right)^{\frac{5}{3}-\delta} e^{a/kT} \frac{(x-h_i)^{y-\frac{1}{2}}}{\Gamma(y+\frac{1}{2})} \right) e^{-x} \sum_{j=0}^{m-1} \mu_j^{(i)} x^j \\
&\qquad + \sqrt{\frac{m_g}{m_v}} \frac{p_g}{p_{ve}(T)} \left[\int dx'\, P(x' \to x) \frac{x'^{y-1}}{\Gamma(y)} e^{-x'} \sum_{j=0}^{m-1} \mu_j^{(i)} x'^j \right. \\
&\qquad \left. - \frac{x^{y-1}}{\Gamma(y)} e^{-x} \sum_{j=0}^{m-1} \mu_j^{(i)} x^j \right] = 0 \qquad \text{(A.2)}
\end{aligned}$$

where

$$\binom{j}{r} = j!/[r!(j-r)!]$$

are the binomial coefficients and we have used (from (2.4) and (2.7))

$$\frac{c_{i-1}^{eq}}{c_i^{eq}} = \frac{kT}{Sp_{ve}(T)v_0} \left(\frac{i-1}{i}\right)^{i+1-\delta} e^{-h_i} \simeq \frac{e^{a/kT}}{S} \left(\frac{i-1}{i}\right)^{1-\delta} e^{-h_i} \qquad \text{(A.3)}$$

the final form following from the vapour pressure for this model, $p_{ve}(T) = (kT/ev_0)\, e^{-a/kT}$, with the approximation $(1-1/i)^i = e^{-1}$. Note that terms involving $(x-h_i)$ in (A.2) are only present for $x \geqslant h_i$. To evaluate the terms in square brackets in (A.2) we use the detailed balance condition (3.9) to write

$$\begin{aligned}
[\;] &= \frac{x^{y-1}}{\Gamma(y)} e^{-x} \sum_{j=0}^{m-1} \mu_j^{(i)} \left(\frac{\Gamma(y+\tilde{c}_{bg})}{\Gamma(\tilde{c}_{bg})^2 \Gamma(y)} \int dx_1 \int dx_2 \int dx' \right. \\
&\qquad \left. \times \frac{(x_1 x_2)^{\tilde{c}_{bg}-1} e^{-x_1} x'^{y+j-1}}{(x+x_1)^{y+\tilde{c}_{bg}-1}} \delta(x+x_1-x'-x_2) - x^j \right) \\
&= \frac{x^{y-1} e^{-x}}{\Gamma(y)} \sum_{j=0}^{m-1} \mu_j^{(i)} \left(\frac{\Gamma(y+\tilde{c}_{bg})\Gamma(y+j)}{\Gamma(y)\Gamma(y+j+\tilde{c}_{bg})} \sum_{r=0}^{j} \binom{j}{r} x^r \frac{\Gamma(\tilde{c}_{bg}+j-r)}{\Gamma(\tilde{c}_{bg})} - x^j \right).
\end{aligned}$$

We now multiply (A.2) by x^n and integrate over x to obtain the following expressions for the coefficients of the μ_j:

coefficient of $\mu_j^{(i-1)}$: $M(I-m+n+1, I-m+j+1)$

$$= \left(\frac{i-1}{i}\right)^{\frac{5}{3}-\delta} e^{a/kT-h_i} \frac{\Gamma(y-\tilde{c}_{vv}+j)}{\Gamma(y-\tilde{c}_{vv})} \sum_{r=0}^{n} \binom{n}{r} \frac{\Gamma(y+\frac{1}{2}+j+r)}{\Gamma(y+\frac{1}{2}+j)} h_i^{n-r}$$

coefficient of $\mu_j^{(i+1)}$: $M(I+m+n+1, I+m+j+1)$

$$= S \sum_{r=0}^{j} \binom{j}{r} \frac{\Gamma(\tilde{c}_{\mathrm{bv}}+j-r)}{\Gamma(\tilde{c}_{\mathrm{bv}})} \sum_{t=0}^{r} \binom{r}{t} \frac{\Gamma(y+n+t)}{\Gamma(y)} h_{i+1}^{r-t}$$

coefficient of $\mu_j^{(i)}$: $M(I+n+1, I+j+1)$

$$= -S\frac{\Gamma(y+n+j)}{\Gamma(y)} - \left(\frac{i-1}{i}\right)^{\frac{5}{3}-\delta} \mathrm{e}^{a/kT-h_i} \sum_{r=0}^{n+j} \binom{n+j}{r} \frac{\Gamma(y+\frac{1}{2}+r)}{\Gamma(y+\frac{1}{2})} h_i^{n+j-r}$$
$$+ \sqrt{\frac{m_{\mathrm{v}}}{m_{\mathrm{g}}}} \frac{p_{\mathrm{g}}}{p_{\mathrm{ve}}(T)} \left[\frac{\Gamma(y+j)}{\Gamma(y)} \frac{\Gamma(y+\tilde{c}_{\mathrm{bg}})}{\Gamma(y+j+\tilde{c}_{\mathrm{bg}})} \sum_{r=0}^{j} \binom{j}{r} \right.$$
$$\left. \times \frac{\Gamma(\tilde{c}_{\mathrm{bg}}+j-r)}{\Gamma(\tilde{c}_{\mathrm{bg}})} \frac{\Gamma(y+r+n)}{\Gamma(y)} - \frac{\Gamma(y+j+n)}{\Gamma(y)} \right]$$

where $I=(i-i_{\min})m$. Note that the ratios of gamma functions in these formulae can be generated recursively using $\Gamma(z+1)=z\Gamma(z)$.

The equations can then be written in matrix form

$$\boldsymbol{M}\boldsymbol{\mu} = \boldsymbol{d} \tag{A.4}$$

where the column vector μ is the transpose of $(\mu_0^{(i_{\min}+1)}, \mu_1^{(i_{\min}+1)}, \ldots, \mu_{m-1}^{(i_{\min}+1)}, \mu_0^{(i_{\min}+2)}, \ldots, \mu_0^{(i_{\max})}, \ldots, \mu_{m-1}^{(i_{\max})})$ and the only non-zero elements of $\boldsymbol{d}$ are the first m which are minus the appropriate moments of the equilibrium distribution at size $i_{\min}$ (i.e. $-M(1-m, -m)$, $-M(2-m, -m)$, etc). Although the dimension of $\boldsymbol{M}$ may be very large, the matrix is banded (with bandwidth $4m-1$) and efficient subroutines are available for solving (A.4). Once the μs are known, the flux can be found from (using (4.11) in (4.2))

$$J = \frac{A_1 i^{2/3} p_{\mathrm{ve}}(T)}{\sqrt{2\pi m_{\mathrm{v}} kT}} c_i^{\mathrm{eq}} \left(\frac{i-1}{i}\right)^{\frac{5}{3}-\delta} \mathrm{e}^{a/kT-h_i}$$
$$\times \left[\sum_{j=0}^{m-1} \mu_j^{(i-1)} \frac{\Gamma(y-\tilde{c}_{\mathrm{vv}}+j)}{\Gamma(y-\tilde{c}_{\mathrm{vv}})} - \mu_j^{(i)} \sum_{r=0}^{j} \binom{j}{r} h^{j-r} \frac{\Gamma(y+\frac{1}{2}+r)}{\Gamma(y+\frac{1}{2})} \right]. \tag{A.5}$$

References

[1] Wagner P E and Strey R 1984 *J. Chem. Phys.* **80** 5266
[2] Adams G W, Schmitt J L and Zalabsky R A 1984 *J. Chem. Phys.* **81** 5074
[3] Hung C-H, Krasnopoler M J and Katz J L 1989 *J. Chem. Phys.* **90** 1856
[4] Wagner P E and Strey R 1981 *J. Phys. Chem.* **85** 2694
[5] Strey R, Wagner P E and Schmeling T 1986 *J. Chem. Phys.* **84** 2325
[6] Schmitt J L, Zalabsky R A and Adams G W 1983 *J. Chem. Phys.* **79** 4496
[7] Katz J L, Hung C-H and Krasnopoler M 1988 *Atmospheric Aerosols and Nucleation* ed P E Wagner and G Vali (Berlin: Springer) p 356
[8] Becker R and Döring W 1935 *Ann. Phys., Lpz.* **24** 719
[9] Lothe J and Pound G M 1963 *Condensation and Evaporation* (New York: Pergamon) p 31
[10] Reiss H, Katz J L and Cohen E R 1968 *J. Chem. Phys.* **48** 5553
[11] Steinwandel J and Buchholz T 1984 *Aerosols, Proc. First Int. Aerosols Conf. (Minneapolis, Sept. 1984)* ed B Y H Liu, D Y H Pui and H J Fissan (New York: Elsevier) pp 877–80
[12] Anisimov M P and Vershinin S N 1990 *J. Aerosol Sci.* **21** Suppl. 1 S11, S15
[13] Feder J, Russell K C, Lothe J and Pound G M 1966 *Adv. Phys.* **15** 111

[14] Ford I J and Clement C F 1989 *J. Phys. A: Math. Gen.* **22** 4007
[15] Clement C F and Ford I J 1989 *J. Aerosol Sci.* **20** 1015
[16] *Grinin A P and Kuni F M* 1989 *Teor. Mat. Fiz.* **80** 418
[17] Ford I J, Barrett J C and Lazaridis M 1992 Uncertainties in cluster energies in homogeneous nucleation theory *J. Aerosol Sci.* submitted
[18] Nishioka K 1987 *Phys. Rev.* A **36** 4845
[19] Reiss H, Tabazadeh A and Talbot *J 1990 J. Chem. Phys. 92 1266*
[20] Blatt J M and Weisskopf V F 1952 *Theoretical Nuclear Physics* (New York: Wiley)
[21] Barrett J C and Clement C F 1988 *J. Aerosol Sci.* **19** 223
[22] Abraham F F 1974 *Homogeneous Nucleation Theory* (New York: Academic) p 3
[23] Kantrowitz A 1951 *J. Chem. Phys.* **19** 1097