Nucleation and droplet growth as a stochastic process

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Abstract

A stochastic differential equation is conjectured for approximately modelling the fluctuating size changes of an individual droplet in a fluid that is metastable with respect to nucleation of a new phase, in the limit when the critical droplet size is very large. The Freidlin-Wentzell formula for this S.D.E. is used to make estimates of large-deviation type for probabilities of such events as the formation of a critical droplet at a specified time. A relation is obtained connecting these estimates to the nucleation rate predicted by the 'classical' theory of Becker and Döring.

1 Introduction

Nucleation is the initiation of a phase transition (such as the transition from gas to liquid or liquid to gas) when a significant droplet of the new phase forms. For example, when the atmospheric temperature drops in the evening, or when a stream of air cools on going up a mountainside, a phase transition becomes possible in which the water vapour mixed with the air will change from gas to liquid. At first only very small droplets of liquid water are formed. The droplets may never grow large enough to be seen; but if the atmospheric conditions are right the droplets can eventually become large enough to be seen as a mist, fog or cloud.

The growth of any individual droplet is a stochastic process: its size can either increase or decrease, as molecules attach themselves to the droplet or detach themselves from it. There is a contest between, on the one hand, the general preference of the water molecules (at a sufficiently low temperature) to be in the liquid rather than the vapour phase, which tends to increase the size of the droplet and, on the other hand, the surface tension, which tries to reduce the surface area of the droplet and, in consequence, its size. The surface tension effect is stronger for small droplets than for large ones because of the greater curvature of the surface of a small droplet. There is a critical droplet size at which the surface tension exactly balances the water's preference for being in the liquid rather than the vapour phase. Droplets of super-critical size tend to grow, while those of sub-critical size tend to shrink. At first, no super-critical droplets at all are present (except, perhaps, at places on the edge of the vapour, such as leaves on which dew may form); there is no mist, and the vapour is said to be *metastable*. If all the droplets followed the average behaviour, super-critical droplets would never form and the metastable state would last for ever. But this is a stochastic process, and the sizes of the droplets fluctuate. Eventually, as a result of these fluctutations, some droplets will reach and then surpass the critical size, and when enough of them have done so the mist will be visible.

This paper is concerned with the mathematical description of nucleation as a stochastic process. For mathematical simplicity we shall consider the limiting case of very large critical droplet size — in the physical example mentioned, this means that the temperature is only just below the dew point. The idea is to approximate the behaviour of the droplets by a stochastic differential equation, and to obtain quantitative information about the nucleation process by applying the Freidlin-Wentzell formula to this equation.

2 A mathematical description of nucleation

In 1935 R Becker and W Döring proposed a mathematical model of nucleation in which each droplet is considered to be fully described by its size, that is, by the number of molecules comprising it. The shapes and positions of the droplets are ignored. The size can be any positive integer, and by convention molecules of the vapour are treated as droplets of size 1 (usually called *monomers*). The Becker-Döring model includes two characteristic assumptions: (i) the only way the size of a droplet (other than a monomer) can change is by emitting or absorbing a monomer (ii) the probability per unit time that a given droplet will emit a monomer depends only on the size of that droplet, while the probability per unit time of absorbing a monomer depends on the size of the droplet and on the overall concentration of monomers.

Focussing attention on a particular droplet, let us denote its size (i.e. the number of molecules in it) by $N(t)$. Then, following the assumptions of Becker and Döring, we can treat $N(t)$ is a stochastic process, in which the probability per unit time for N to increase by 1 is $a_n z$ and for it to decrease by 1 is b_n, where z is a parameter representing the overall concentration of monomers (i.e. the number of monomers per unit volume). In symbols, the transition probabilities are

$$\begin{aligned}\mathbf{Pr}(N(t+\delta t)=n+1\,|N(t)=n) &= a_n z\delta t+O(\delta t)^2 \quad (n=1,2,\ldots)\\ \mathbf{Pr}(N(t+\delta t)=n-1\,|N(t)=n) &= b_n\delta t+O(\delta t)^2 \quad (n=2,3,\ldots)\\ \mathbf{Pr}(|N(t+\delta t)-N(t)|\geq 2\ |N(t)=n) &= O(\delta t)^2 \qquad (1)\end{aligned}$$

where the constants $a_1, a_2, \ldots, b_2, b_3, \ldots$ depend on the physical situation. Here we shall assume them to be given by the following approximate formulas, for which there is some physical justification (Lifshits and Slyozov 1961, Wagner 1961, Penrose and Buhagiar 1983, Penrose 1997)[1]:

$$\begin{array}{rclr} a_n & = & n^\gamma & (n = 1, 2, \ldots) \\ b_n & = & n^\gamma(1 + \mu n^{-1/3}) & (n = 2, 3, \ldots) \end{array} \qquad (2)$$

where μ is a positive constant proportional to the surface tension at the surface of a droplet and γ is a constant satisfying $\gamma \geq \frac{1}{3}$. Later in this paper we shall specialize to the case $\gamma = \frac{1}{3}$. The significance of the exponents $\frac{1}{3}$ and $-\frac{1}{3}$ is that the radius of a droplet is proportional to the cube root of its size. From the formulas (2) it can be seen that $a_n z < b_n$ if $n^{1/3}(z-1) < \mu$, but $a_n z > b_n$ if $n^{1/3}(z-1) > \mu$; so provided that $z > 1$ there is a critical droplet size $n_c := [\mu/(z-1)]^3$ such that any droplet whose size exceeds this is more likely to grow than to shrink.

To finish specifying the model we need to say how z depends on time. In this paper, following the original paper of Becker and Döring (1935), we shall assume that z is a constant. Physically, z is the concentration of monomers, and is related to $\mathbf{Pr}\{N(t) = 1\}$, the probability that a randomly chosen droplet will be a monomer, by the formula

$$z = c\mathbf{Pr}\{N(t) = 1\} \qquad (3)$$

where c is the total number of molecules per unit volume. Thus the assumption of constant z can be arrived at physically by assuming that c is a constant and that nearly all the droplets are monomers, so that $\mathbf{Pr}\{N(t) = 1\} \approx 1$ and $z \approx c = \text{const}$. Alternatively one may assume that $\mathbf{Pr}\{N(t) = 1\}$ does change with time but that c changes in such a way that z remains constant: this will happen, for example if the process takes place at constant pressure. The case where c is constant but both z and $\mathbf{Pr}\{N(t) = 1\}$ change with time has many interesting features (see for example Lifshitz and Slyozov (1961), Ball *et al.* (1986)) but is not our concern here

There are two ways to obtain information about metastability and nucleation from this stochastic model. The one devised by Becker and Döring was to study the average behaviour of the entire collection of droplets, described by the probability distribution

$$p_n(t) := \mathbf{P}\{N(t) = n\} \qquad (4)$$

They found a steady-state distribution in which, for each droplet size n, the rate of occurrence of events which increase the droplet size from n to $n+1$ slightly exceeds the rate for events which decrease the size from $n+1$ to n. The excess, which is independent of n, can be interpreted as at the rate at which droplets

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[1] The formulas in eqn (2) are often presented in a more general form such as $a_n = an^\gamma, b_n = an^\gamma z_s(1+\mu n^{-1/d})$ where a and z_s are positive constants, d is the number of space dimensions (at least 3), and γ satisfies $\gamma \geq 1/d$. The version used in (2) can, however, be obtained from the more general version by setting $d = 3$ and making a suitable choice of time and length units

surpass the critical size; it is called the nucleation rate. This approach, now known as ‘classical nucleation theory’, is summarized in section 5.

In 1984 Cassandro *et al* introduced an alternative way of obtaining information about metastability and nucleation in stochastic models. In this method, the ‘pathwise approach’, we focus not on averages but on the stochastic behaviour of a single droplet. The pathwise approach has been used to study metastability in a variety of statistical mechanics models. A very thorough account of this body of work and the related theory is given in the book by Olivieri and Vares (2006); for a shorter account see den Hollander (2004).

It is the purpose of this article to apply a variant of the pathwise approach to the Becker-Döring model. The idea is to concentrate on a particular droplet and represent its size as a stochastic process. We can treat such questions as how likely it is that the size of a given droplet will reach or pass the critical size, and if it does so how long that is likely to take.

3 The proposed SDE

One can think of the process (1) as a biassed random walk along the positive integer axis – or as a birth-and-death process. The expected rate of increase in the droplet size N is given by

$$\mathbf{E}(N(t+\delta t)-N(t)|N(t)=n)=(a_n z-b_n)\delta t+O(\delta t)^2 \tag{5}$$

Thus there is a drift in the expected size of $N(t)$; the rate of drift is

$$a_n z-b_n=n^{\gamma}((z-1)-\mu n^{-1/3}) \tag{6}$$

The rate of increase in the variance of n per unit time may be estimated as

$$\lim_{\delta t\to 0}\frac{1}{\delta t}\mathbf{E}((N(t+\delta t)-N(t))^2|N(t)=n)=a_n z+b_n \tag{7}$$

The idea of the present work is to approximate this stochastic process by one in which the unit-size jumps are replaced by jumps with a Gaussian distribution having the same mean and variance. This approximating process corresponds to the stochastic differential equation

$$dN \quad = \quad (a_n z-b_n)dt+\sqrt{a_n z+b_n}\,dW(t) \tag{8}$$

where $W(t)$ is a Wiener process.

Although such an SDE would not be a good approximation for the individual jumps, it may be a good one if we look at the process on a different scale where the jumps look very small and there are a large number of them. There is an analogy with Khinchin’s method of deriving the Central Limit Theorem[2], which involves re-scaling the time and space variables in a similar way, although in their case the re-scaled equation is deterministic (the heat equation) rather

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[2] There is a description of this method on page 10 of Ito and McKean 1996

than stochastic. Our re-scaling will use, in place of N, a new random variable X proportional to N/n_c. The jumps in X will then be proportional to $1/n_c$, so they will be small if we consider a limit in which n_c is large. As we have seen, n_c is proportional to $(z-1)^{-3}$ so z is close to 1 in this limit; we shall write

$$\begin{aligned} z &:= 1+\epsilon \\ X &:= \epsilon^3 N \end{aligned} \tag{9}$$

and consider the limit $\epsilon \to 0$.

In addition to re-scaling the size of the jumps, it is useful to re-scale the time, so that X is regarded as a function of a re-scaled time variable τ rather than of the original time variable t. The advantage of re-scaling the time is that the drift velocities of the two processes, each with respect to its own time scale, can be made comparable. According to eqn (5), the drift velocity of the random walk variable N is

$$\begin{aligned} D_t N(t) &:= \lim_{\delta t \searrow 0} \mathbf{E}\left\{ \frac{N(t+\delta t)-N(t)}{\delta t} \middle| N(t) \right\} \\ &= a_{N(t)} z - b_{N(t)} = N(t)^\gamma (z-1-\mu N(t)^{-1/3}) \end{aligned} \tag{10}$$

Consequently the drift velocity of X, with respect to the re-scaled time variable τ, is

$$\begin{aligned} D_\tau X(\tau) &:= \lim_{\delta \tau \searrow 0} \mathbf{E}\left\{ \frac{X(\tau+\delta\tau)-X(\tau)}{\delta\tau} \middle| X(\tau) \right\} \\ &= \epsilon^3 \frac{dt}{d\tau} n^\gamma (z-1-\mu n^{-1/3}) \quad \text{where} \quad n = \epsilon^{-3} X(\tau) \\ &= \epsilon^3 \frac{dt}{d\tau} (\epsilon^{-3} X(\tau))^\gamma (\epsilon - \mu(\epsilon^{-3} X(\tau))^{-1/3}) \\ &= \epsilon^{4-3\gamma} \frac{dt}{d\tau} X(\tau)^\gamma (1-\mu/X(\tau)^{1/3}) \end{aligned} \tag{11}$$

On making the choice

$$\tau := t\epsilon^{4-3\gamma} \tag{12}$$

this simplifies to

$$D_\tau X(\tau) = X(\tau)^\gamma (1-\mu/X(\tau)^{1/3}) \tag{13}$$

Comparison with (10) shows that the drift velocities of the two processes, each relative to its own time scale, are given by the same differential equation.

We can do a similar calculation for the variance of $X(\tau)$, using the formula (7):

$$\begin{aligned} \frac{\mathbf{E}\left\{ [X(\tau+\delta\tau)-X(\tau)]^2 \middle| X(\tau) \right\}}{\delta\tau} &= \frac{\epsilon^6 \mathbf{E}\left\{ [N(t+\delta t)-N(t)]^2 \middle| N(t) = \epsilon^{-3} X(\tau) \right\}}{\delta\tau} \\ &= \epsilon^6 [\epsilon^{-3} X(\tau)]^\gamma (2+\epsilon+\mu(\epsilon^{-3} X(\tau))^{-1/3}) \epsilon^{3\gamma-4} + O(\delta\tau) \\ &= 2\epsilon^2 X(\tau)^\gamma + O(\epsilon) + O(\delta\tau) \end{aligned} \tag{14}$$

This is the same rate of change of variance as for a Brownian motion multiplied by $\sqrt{2}\epsilon X(\tau)^{\gamma/2}$. Adding together this Brownian motion and the drift given by (13), we may conjecture that in the limit of small ϵ the random variable X will obey the stochastic differential equation

$$dX(\tau) = X(\tau)^\gamma(1 - \mu/X(\tau)^{1/3})d\tau + \sqrt{2}\epsilon X(\tau)^{\gamma/2}dw(\tau) \tag{15}$$

where $w(\tau)$ is a Brownian motion.

4 Applying the Freidlin-Wentzell formula

4.1 A formula for the action

In this section we shall use ideas from the Freidlin-Wentzell theory (Freidlin & Wentzell 1998, Olivieri and Vares 2006) to estimate the probabilities for different ways in which the size of a droplet can change over time. The Freidlin-Wentzell theory applies to SDEs of the form

$$dX(\tau) = v(X(\tau))d\tau + \epsilon\sigma(X(\tau))dW(\tau) \tag{16}$$

The fundamental object in this theory is the 'action' or rate function. For an arbitrary trajectory $x(\tau)$ the action is defined to be

$$S(\tau_1, \tau_2) := \tfrac{1}{2}\int_{\tau_1}^{\tau_2} \left(\frac{\dot{x}(\tau) - v(x(\tau))}{\sigma(x(\tau))}\right)^2 d\tau \tag{17}$$

where $\dot{x}(\tau) := dx/d\tau$. The main property of the action is that, in the limit of small ϵ, the probability of executing the path $x(\tau)$, or one very similar to it, between times τ_1 and τ_2, conditional on starting at the given point $x(\tau_1)$ at time τ_1, is $\exp\{-\epsilon^{-2}\, S(\tau_1, \tau_2) + o(\epsilon^{-2}\}$.

The conjectural SDE (15) is of the Freidlin-Wentzell form, with

$$v(x) = x^\gamma(1 - \mu x^{-1/3}), \quad \sigma(x) = \sqrt{2}\, x^{\gamma/2} \tag{18}$$

and so the action for eqn (15) is

$$\begin{aligned} S(\tau_1, \tau_2) \quad &:= \quad \tfrac{1}{2}\int_{\tau_1}^{\tau_2} \frac{[\dot{x}(\tau) - x(\tau)^\gamma(1 - \mu x(\tau)^{-1/3})]^2}{2x(\tau)^\gamma} d\tau \\ &= \quad \tfrac{1}{2}\int_{\tau_1}^{\tau_2} \frac{[\dot{x}(\tau) + x(\tau)^\gamma U'(x(\tau))]^2}{2x(\tau)^\gamma} d\tau \end{aligned} \tag{19}$$

where

$$U(x) := \tfrac{3}{2}\mu x^{2/3} - x \tag{20}$$

and the prime denotes a derivative, so that $U'(x) = \mu x^{-1/3} - 1$.

4.2 The minimization problem

Let (x_1, τ_1) and (x_2, τ_2) be given inital and final states of the re-scaled process. The most probable path connecting them can be found by minimizing the action $S(\tau_1, \tau_2)$ subject to the constraints $x(\tau_1) = x_1, x(\tau_2) = x_2$, using the calculus of variations. To carry out the minimization we first multiply out the integrand in (19), obtaining

$$\begin{aligned} 2S(\tau_1, \tau_2) &= \tfrac{1}{2} \int_{\tau_1}^{\tau_2} x(\tau)^{-\gamma} \dot{x}(\tau)^2 d\tau + \int_{\tau_1}^{\tau_2} U'(x(\tau)) \dot{x}(\tau) d\tau + \\ &\quad + \tfrac{1}{2} \int_{\tau_1}^{\tau_2} x(\tau)^{\gamma} U'(x(\tau))^2 d\tau \\ &= \int_{\tau_1}^{\tau_2} L(\dot{x}(\tau), x(\tau)))\, d\tau + U(x_2) - U(x_1) \end{aligned} \tag{21}$$

where L is a ‘Lagrangian’ defined by

$$L(\dot{x}, x) := \tfrac{1}{2} x^{-\gamma} \dot{x}^2 + \tfrac{1}{2} x^{\gamma} U'(x)^2 \tag{22}$$

The minimizer satisfies the Euler-Lagrange equation

$$\frac{d}{d\tau} \frac{\partial L}{\partial \dot{x}} = \frac{\partial L}{\partial x} \tag{23}$$

The following procedure gives a first integral of this equation, enabling its solution to be reduced to a quadrature. We define a ‘momentum’ p by[3]

$$p := \frac{\partial L}{\partial \dot{x}} = x^{-\gamma} \dot{x} \tag{24}$$

and a ‘Hamiltonian’ H by

$$H := p\dot{x} - L(\dot{x}, x) = \tfrac{1}{2} x^{\gamma} p^2 - \tfrac{1}{2} x^{\gamma} U'(x)^2 \tag{25}$$

These definitions imply $dH = \dot{x} dp + p d\dot{x} - (\partial L / \partial \dot{x}) d\dot{x} - (\partial L / \partial x) dx = \dot{x} dp - (\partial L / \partial x) dx$. Consequently, looking on H as a function of p and x and using (23), we find that Hamilton's equations

$$\frac{\partial H(p, x)}{\partial p} = \frac{dx}{d\tau}, \quad \frac{\partial H(p, x)}{\partial x} = -\frac{dp}{d\tau} \tag{26}$$

are satisfied on the minimizer. It follows that $dH/d\tau = 0$, so that H is a constant along the minimizer. The value of this constant, which is analogous to the energy in mechanics, will be denoted by E.

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[3] This use of the symbol p is traditional in Hamiltonian dynamics. It is hoped that there will be no confusion with the use of the same symbol for probability in other parts of this paper.

4.3 Paths for which $E = 0$

The calculation of the action is particularly simple in the case $E = 0$. Setting $H = 0$ in eqn (25) yields $p = \pm U'(x)$ and then, from (24), $\dot{x} = \pm x^\gamma U'(x)$, so that the equation of the minimizer is

$$\frac{dx}{d\tau} = \pm x^\gamma (\mu x^{-1/3} - 1) \tag{27}$$

With the minus sign, this is the equation of the 'average' path which, according to equation (15) the droplet size would follow if there were no noise at all. For that path the value of S is zero (by eqn (19)) and so the the probability of the 'average' path, or one very similar to it, is $\exp\{-o(\epsilon^{-2})\}$.

With the plus sign, the path is the time inverse of an 'average' path. Since the right side is zero at the critical cluster size $x = \mu^3$ and varies approximately linearly nearby, with a negative derivative, the value of $x(\tau)$ for this path approaches the critical size asymptotically as $\tau \to \infty$. For a path of this type the action is, using first (19) and then the fact that $\dot{x} = x^\gamma U'(x)$ on this path,

$$\begin{aligned} S(\tau_1, \tau_2) \quad &:= \quad \tfrac{1}{2} \int_{\tau_1}^{\tau_2} \frac{[\dot{x}(\tau) + x(\tau)^\gamma U'(x(\tau))]^2}{2x(\tau)^\gamma} d\tau \\ &= \quad \tfrac{1}{2} \int_{\tau_1}^{\tau_2} \frac{[2x(\tau)^\gamma U'(x(\tau))][2\dot{x}(\tau)]}{2x(\tau)^\gamma} d\tau \\ &= \quad \int_{\tau_1}^{\tau_2} U'(x(\tau))\dot{x}(\tau) d\tau = U(x_2) - U(x_1) \end{aligned} \tag{28}$$

In particular, if the initial scaled droplet size is small and the final size is close to the scaled critical size, which is μ^3, the action is $U(\mu^3) - U(0) = \frac{1}{2}\mu^3$, so that the probability of the droplet's reaching the critical size by a path close to the $E = 0$ path is $\exp\left\{-\frac{1}{2}\epsilon^{-2}\mu^3 + o(\epsilon^{-2})\right\}$

4.4 General values of E

Putting $H = E$ in eqn (25), solving for p and then using (24) we get

$$\begin{array}{rcccl} x^{-\gamma}\dot{x} & = & p & = & \pm\sqrt{2Ex^{-\gamma} + (\mu x^{-1/3} - 1)^2} \\ \text{i.e.} \qquad \dot{x} & = & x^\gamma p & = & \pm\sqrt{2Ex^\gamma + (\mu x^{\gamma - 1/3} - x^\gamma)^2} \end{array} \tag{29}$$

The qualitative features of the solution depend on the value of E. They can be worked out by studying how the radicand (the expression under the radical sign) depends on x. We give below the analysis for the important case $\gamma = \frac{1}{3}$, in which eqn (29) simplifies to

$$\dot{x} \quad = \quad \pm\sqrt{\mu^2 + 2(E - \mu)x^{1/3} + x^{2/3}} \tag{30}$$

1. if $E < 0$ the radicand (now a polynomial in $x^{1/3}$) is zero for two positive values of x, whose geometric mean is μ^3. The solution can have a minimum at the root lying between $x = 0$ and $x = \mu^3$, or a maximum at the root above μ^3, or it can oscillate between these two roots.

2. if $E = 0$ the radicand has a double zero $x = \mu$. The formula (30) simplifies to

$$\dot{x} = \pm(\mu - x^{1/3}) \quad \text{whence} \quad \tau = \text{const} \pm \int (\mu - x^{1/3})^{-1} dx \tag{31}$$

   The solutions are monotonic and have an asymptote $x = \mu^3$. The most probable path through any given point (x_0, τ_0) is of this type (with the negative sign chosen if $0 < x_0 < \alpha^3$). For the calculation of the action in this case, see eqn (28).

3. if $0 < E < 2\mu$ the radicand is positive for all x. The solutions go monotonically from $-\infty$ to $+\infty$ or vice versa

4. if $E = 2\mu$ the radicand has a double zero at $x = -\mu^3$. The formula (30) simplifies to

$$\dot{x} = \pm(\mu + x^{1/3}) \quad \text{whence} \quad \tau = \text{const} \pm \int (\mu + x^{1/3})^{-1} dx \tag{32}$$

   The solutions are monotonic and have an (unphysical) asymptote $x = -\mu^3$.

5. if $E > 2\mu$ the radicand is zero for two different values of x, both negative, whose geometric mean is $-\mu^3$. The solutions oscillate between these two values. (These solutions are irrelevant to the problem under consideration, for which x cannot be negative.)

4.5 The probability of a given droplet's becoming critical in a given time

To get a path which increases from a subcritical value ($x_1 < \mu^3$) to a supercritical one ($x_2 > \mu^3$) we need the positive sign in the formula (29) and we also need $E > 0$. The time to get from x_1 to x_2 along such a path is, by (29),

$$\tau_2 - \tau_1 = \int_{x_1}^{x_2} \frac{dx}{\dot{x}} = \int_{x_1}^{x_2} \frac{dx}{x^\gamma \sqrt{2Ex^{-\gamma} + (\mu x^{-1/3} - 1)^2}} \tag{33}$$

If we assume $x_1 < \mu^3 \leq x_2$ and $\tau_1 < \tau_2$, then, as E increases from 0 to $+\infty$, the value of the integral decreases (at fixed x_1, x_2) from $+\infty$ to zero, and so the given values of x_1, x_2, τ_1, τ_2 determine a unique positive value of E.

The action along this path is, by (19) and (29)

$$\begin{aligned} S &= \tfrac{1}{4} \int_{\tau_1}^{\tau_2} x^{-\gamma} [\dot{x} + x^\gamma U'(x)]^2 \frac{dx}{\dot{x}} = \tfrac{1}{4} \int_{\tau_1}^{\tau_2} x^\gamma [x^{-\gamma}\dot{x} + U'(x)]^2 \frac{dx}{\dot{x}} \\ &= \tfrac{1}{4} \int_{\tau_1}^{\tau_2} \frac{\{\sqrt{2Ex^{-\gamma} + (\mu x^{-1/3} - 1)^2} + \mu x^{-1/3} - 1\}^2 dx}{\sqrt{2Ex^{-\gamma} + (\mu x^{-1/3} - 1)^2}} \end{aligned} \tag{34}$$

4.6 Exact solutions for the case $\gamma = 1/3$

In the physically important case $\gamma = 1/3$, the integrals in (33) and (34) simplify to

$$\tau_2 - \tau_1 = \int_{x_1}^{x_2} \frac{dx}{\sqrt{2Ex^{1/3} + (\mu - x^{1/3})^2}} \tag{35}$$

$$S(\tau_1, \tau_2) = \frac{1}{4} \int_{x_1}^{x_2} \frac{[\sqrt{2Ex^{1/3} + (\mu - x^{1/3})^2} + \mu - x^{1/3}]^2 \, dx}{x^{1/3}\sqrt{2Ex^{1/3} + (\mu - x^{1/3})^2}} \tag{36}$$

Both integrals can be done analytically.

Of particular interest is the case where $x_1 = 0$, $x_2 = \mu^3$, in which the droplet starts out very small and ends up at the critical size. Fig. 1 shows a graph of S as a function T for this case, obtained by eliminating E between eqns (35) and (36). The interpretation of the graph is that the probability for a very small droplet to reach the critical size after a time T is $\exp\{-\epsilon^{-2}S + o(\epsilon^{-2})\}$.

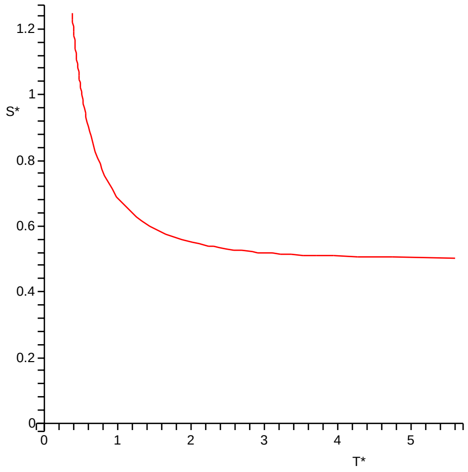

Figure 1: The action (approximately ϵ^2 times the negative logarithm of the probability) of the most probable path taking a small cluster to one of critical size in a given time, plotted as a function of that given time. The abscissa, labelled T^*, is μ^{-2} times the integral in eqn (35), which in turn is ϵ^3 times the physical time for the droplet to grow. The ordinate, labelled S^*, is μ^{-3} times the action $S(\tau_1, \tau_2)$ as given by eqn (36). At large times, S^* approaches the limit $\frac{1}{2}$, in agreement with eqn (41).

5 Relation of the results of section 4 to the 'classical' Becker-Döring nucleation theory

The method used by Becker and Döring to estimate nucleation rates was based on the time evolution equations for the probability $p_n(t)$ that the size of the droplet at time t is n, i.e. $p_n(t) = \mathbf{Pr}(N(t) = n)$, as in eqn (4). The evolution equations for $p_2(t), p_3(t), \ldots$ can be written

$$\begin{aligned} dp_n/dt &= J_{n-1} - J_n \quad (n = 2, 3, \ldots) \\ J_n &= a_n z p_n - b_{n+1} p_{n+1} \quad (n = 1, 2, 3, \ldots) \end{aligned} \tag{37}$$

Becker and Döring looked for a solution which was stationary, in the sense that $p_2, p_3, ..$ are independent of time, and p_1 (whose evolution equation they did not discuss) varies only very slowly. For a solution that is stationary in this sense, J_n must be independent of n. The common value of J_n is interpreted as the rate of nucleation. Denoting this common value by J, we can solve the equations (37) successively to get

$$\begin{aligned} p_1 &= \frac{J + b_2 p_2}{a_1 z} = \frac{J}{a_1 z} + \frac{b_2}{a_1 z}\left(\frac{J + b_3 p_3}{a_2 z}\right) = \frac{J}{a_1 z} + \frac{b_2 J}{a_1 a_2 z^2} + \frac{b_2 b_3}{a_1 a_2 z^2}\left(\frac{J + b_4 p_4}{a_3 z}\right) \\ &= J\left(\frac{1}{a_1 z} + \frac{b_2}{a_1 a_2 z^2} + \frac{b_2 b_3}{a_1 a_2 a_3 z^3} + \ldots\right) \\ &= J \sum_{n=1}^{\infty} \frac{Q_1}{Q_n a_n z^n} \end{aligned} \tag{38}$$

where

$$Q_1 := 1, \quad Q_n := \frac{a_1 a_2 \ldots a_{n-1}}{b_2 \ldots b_n} \sim \text{const.} \exp(-\tfrac{3}{2}\mu n^{2/3}) \quad (n = 1, 2, \ldots) \tag{39}$$

The series in (38) converges for $z > 1$ and its largest term occurs at the value of n satisfying $a_n z = b_n$, i.e. the critical droplet size. Under the approximations used earlier, this size is $(\mu/\epsilon)^3$ and the size of the corresponding term in the series is

$$\frac{Q_1}{Q_n a_n z^n} \approx \text{const.} \exp\left(\tfrac{3}{2}\mu\left(\frac{\mu}{\epsilon}\right)^2 - \left(\frac{\mu}{\epsilon}\right)^3 \log z\right) \approx \text{const.} \exp\left(\frac{\mu^3}{2\epsilon^2}\right) \tag{40}$$

since $\log z \approx \epsilon$. The rate of nucleation J, calculated from (38) is therefore equal to the reciprocal of this expression, multiplied by a factor whose logarithm is $o(1)$, so that $J = \exp\left(-\mu^3/2\epsilon^2 + o(1)\right)$. This formula agrees with the large-deviation estimate obtained in Section 4 for the probability that a given droplet will escape, which (after division by the time needed for the escape to take place) can also be thought of as a rate of nucleation. For large times, this probability, according to (28) with $U(x)$ given by (20), is

$$\exp(-\epsilon^{-2}\{U(\mu^3) - U(0)\}) = \exp(-\mu^3/2\epsilon^2) \tag{41}$$

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