

Rigorous Treatment of Metastable States in the van der Waals–Maxwell Theory

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We consider a classical system, in a ν -dimensional cube Ω , with pair potential of the form $q(r) + \gamma^\nu \phi(\gamma r)$. Dividing Ω into a network of cells $\omega_1, \omega_2, \dots$, we regard the system as in a metastable state if the mean density of particles in each cell lies in a suitable neighborhood of the overall mean density ρ , with ρ and the temperature satisfying

$$f_0(\rho) + \frac{1}{2}\alpha\rho^2 > f(\rho, 0+)$$

and

$$f_0''(\rho) + 2\alpha > 0$$

where $f(\rho, 0+)$ is the Helmholtz free energy density (HFED) in the limit $\gamma \rightarrow 0$; $\alpha = \int \phi(\mathbf{r}) d^\nu \mathbf{r}$; and $f_0(\rho)$ is the HFED for the case $\phi = 0$. It is shown rigorously that, for periodic boundary conditions, the conditional probability for a system in the grand canonical ensemble to violate the constraints at time $t > 0$, given that it satisfied them at time 0, is at most λt , where λ is a quantity going to 0 in the limit

$$|\Omega| \gg \gamma^{-\nu} \gg |\omega| \gg r_0 \ln |\Omega|$$

Here, r_0 is a length characterizing the potential q , and $x \gg y$ means $x/y \rightarrow +\infty$. For rigid walls, the same result is proved under somewhat more restrictive conditions. It is argued that a system started in the metastable state will behave (over times $\ll \lambda^{-1}$) like a uniform thermodynamic phase with HFED $f_0(\rho) + \frac{1}{2}\alpha\rho^2$, but that having once left this metastable state, the system is unlikely to return.

KEY WORDS: Fluids; metastability; phase coexistence; statistical mechanics; constraints.

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1. INTRODUCTION

In this paper, we investigate a general method for describing metastable states in statistical mechanics and we apply it rigorously to the generalized van der Waals system whose stable states we discussed in an earlier paper,⁽¹⁾ hereafter referred to as I. Our analysis will include both static and dynamic properties and goes considerably further than our preliminary results⁽²⁾ presented earlier for these systems.³

Nature provides many examples of metastable states⁽⁴⁾; they include supercooled vapors and liquids, supersaturated solutions, and ferromagnets in the part of the hysteresis loop where the magnetization and the applied magnetic field are in opposite directions. They can arise when some thermodynamic parameter of the system, such as the temperature or magnetic field, is changed from a value for which the stable equilibrium state has a single thermodynamic phase, to one for which it has at least part of the system in some new thermodynamic phase. Instead of making the appropriate phase transition, however, the system may go over continuously into a one-phase state, called a metastable state, which appears, while it lasts, to be stationary in time in the same manner as a stable equilibrium state. The properties of the metastable state are found to be reproducible; that is, they appear to be completely determined by the values of the thermodynamic parameters, in just the same way as those of a stable equilibrium state. The distinguishing feature of a metastable state is that, eventually, either through some external disturbance or a spontaneous fluctuation which nucleates the missing phase in some small part of the system, the system begins an irreversible process which leads it inexorably to the corresponding stable equilibrium state. Thermodynamically, the irreversibility of this transition corresponds to a decrease in free energy or an increase in entropy.

In this paper, we shall characterize metastable thermodynamic states by the following properties:

Only one thermodynamic phase is present (1a)

A system that starts in this state is likely to take
a long time to get out (1b)

Once the system has gotten out, it is unlikely to return (1c)

To (1), one might add the statement that thermodynamics applies to the metastable state—for example, the usual theory would apply if a substance in such a state were taken around a Carnot cycle—but beyond showing, in passing, how analogs for some of the thermodynamic functions such as the free energy can be defined for the metastable state, we shall not treat this topic in detail.

In statistical mechanics, there are several approximate theories giving metastable equilibrium states instead of, or in addition to, the stable ones. One of these is the van der Waals–Maxwell theory of the liquid–vapor transition. In this theory, an approximation which treats the system as a uniform fluid phase leads (at some suitable fixed temperature T) to a relationship between f , the Helmholtz free energy per unit volume, and ρ , the density, whose graph has the general character shown in Fig. 1.

³ For related work, see the references cited in I, as well as Refs. 3a–d.

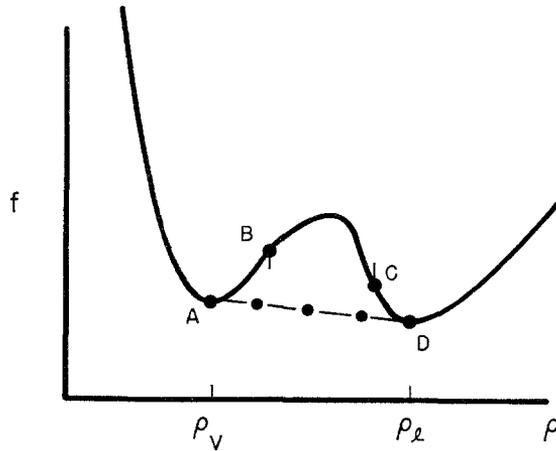


Fig. 1. Helmholtz free energy density in the van der Waals–Maxwell theory.

This figure also shows a dashed straight line touching the curve at two points A and D . The points on this line correspond to two-phase states, one phase (the vapor) having density ρ_v , the other (the liquid) having density ρ_l . Maxwell⁽⁶⁾ saw that for densities between ρ_v and ρ_l the stable equilibrium states would be the two-phase states, but thought that, by careful experimentation, it should also be possible to realize experimentally the parts of the curve labeled AB and CD ; these describe the one-phase metastable states. The part of the curve between the inflection points B and C is impossible to realize because it has $d^2f/d\rho^2 < 0$, so that the states it describes are mechanically unstable.

Although van der Waals' approximate theory gives the metastable states easily, it is more difficult to see how they could arise in an exact theory; for it follows from the general principles of statistical mechanics⁽⁶⁾ that in the thermodynamic limit the exact free energy density, calculated from the partition function, is a convex function of ρ and therefore cannot give arcs such as AB and CD , which do not lie on a convex curve. To obtain the metastable states, some extension of the usual formalism of statistical mechanics is necessary.

One possibility, suggested by the preceding example, is that the thermodynamic functions for the metastable states can be obtained by extrapolation from the nearby stable one-phase states, so that, for example, the arc AB in Fig. 1 would be obtained by extrapolation from the curve to the left of A . It is likely, however, that for real systems, for which van der Waals' theory is only an approximation, a singularity of the thermodynamic functions blocks the extrapolation⁽⁷⁾; and even when the extrapolation is possible, one still has to justify the assumption that the extrapolated thermodynamic functions really describe metastable states.

In addition to these static properties, the dynamics of the persistence and decay of the metastable state also deserve investigation. Some of the basic ideas underlying this dynamics are already contained in Maxwell's own discussion: Maxwell recognized the importance of nucleation; he saw that to set up the metastable state we must be sure that none of the new phase is present. The idea of nucleation was developed

further by Becker and Döring,^(4,8) who used quasithermodynamic arguments involving the surface tension to find the smallest “liquid droplet” in a supersaturated vapor that will “grow” to become the new liquid phase. For droplets smaller than this minimum size, the “free energy” increases with size and hence they will tend to dissipate. Using the Einstein relation between probability and free energy and some kinetic arguments about the rate of collisions between molecules and droplets which might lead to an increase in the size of the latter, the Becker–Döring theory gives an estimate for the probability of forming such a critical droplet in the homogeneous supersaturated phase. This probability is found to be extremely small (for some values of the temperature and pressure), which explains the metastability of the supercooled vapor. The basic ideas of this theory have been used with great success by many authors for a wide variety of phenomena.⁴

Despite their successes, however, these theories suffer from the lack of a precise formulation of the problem. It is never entirely clear just what, if any, exact quantity one is trying to compute approximately and the computations are of necessity approximate. That this is not purely an aesthetic defect can be seen from the recent controversy about a factor of 10^{17} in the spontaneous nucleation rate of supersaturated vapor.⁽⁹⁾ A more fundamental approach is therefore necessary.

In addition to avoiding these difficulties, a more fundamental approach could also yield information about nonthermodynamic quantities such as correlation functions, which can be measured by scattering experiments. It is our purpose here to develop such an approach, which will make precise the ideas discussed earlier and use it to carry out computations for the static and dynamic properties of metastable states of generalized van der Waals fluids.

We begin by making precise the notion, inherent in all the previous discussion, of imposing a restriction on the system which keeps its density roughly uniform. In general, such a restriction may be represented by confining the configuration of the system to a suitable region R in configuration space. In order for this region to correspond to a metastable state, the restrictions defining it should correspond to the imposition of a roughly uniform density, in accordance with the criterion (1a), and it should also have properties corresponding to the conditions (1b) and (1c) mentioned earlier: If the dynamical state is initially in R , it is unlikely to escape quickly, and once it has escaped, it is unlikely to return.

To compute the conditional probabilities implicit in (1b) we shall, as is usually done in statistical mechanics, use the Gibbs ensemble method. We assume that the conditional probabilities can be computed from an ensemble made up by taking an equilibrium ensemble and selecting from it at time 0 all those systems whose configurations are in R . We call this ensemble a *restricted* equilibrium ensemble. The conditional probability $p(t)$ of the configuration being outside R at time t is then equal to the fraction of the members of this subensemble that are no longer in R at time t . The question now arises, “From what kind of equilibrium ensemble should

⁴ See Ref. 4. We also have in mind the study of the decay of superconducting currents and of superfluid flows by the nucleation of vortices as well as the creation of defects in solids and other phenomena that require “activation energies.”

our restricted subensemble be chosen, e.g., should it be microcanonical, canonical, or grand-canonical?" (For the microcanonical or canonical ensembles, R would be a region in the configuration space of some given number N of particles, while for the grand canonical ensemble, R will consist of a union of regions from configuration spaces of different dimensions.) All these (and other related ensembles) are thermodynamically equivalent, i.e., they are equally suitable for computing the equilibrium thermodynamic properties of very large systems.⁽⁶⁾ This is, however, not necessarily true for properties of the metastable state obtained from the corresponding restricted ensembles. We do not attempt here to give rigorous proofs of equivalence of these different restricted ensembles. Instead we carry out our main computation (Sections 3–6) in the restricted grand canonical ensemble, where the results are easiest to prove, and then give some evidence (Sections 7–8) for expecting similar results in the canonical ensemble formalism.

The grand canonical ensemble is actually used only for setting up the restricted ensemble at time 0; it does not imply that the system is open for times >0 . The dynamics of the system are assumed to be determined entirely by its own Hamiltonian (no interaction with the outside). Hence, the probability $p(t)$ calculated using the restricted grand canonical ensemble, characterized by a certain chemical potential μ and temperature T , is a weighted average of the corresponding probabilities calculated in restricted microcanonical ensembles characterized by various energies and particle densities.

To avoid the complications arising from the walls of the container, where nucleation of the new phase may proceed at a different rate from that in the bulk liquid, we shall do our main calculations for a system with periodic boundary conditions. The escape rate we estimate will therefore be the homogeneous nucleation rate, proportional to the volume of the system. The effect of walls, which is a special case of the nucleation of a new phase at the surface of a foreign substance, will be discussed in Section 6. We shall find that perfectly elastic walls do not facilitate the formation of liquid droplets in a supercooled vapor but may play an important role in serving as loci for the formation of vapor cavities in superheated liquids. A similar effect is observed for real walls.⁽⁴⁾

This treatment of metastable states hinges on finding a suitable region R in configuration space. The ideal choice would, perhaps, be the one minimizing the escape rate—that is, the probability per unit time for the configuration of the system to move out of R . In this paper, however, we shall not attempt the difficult task of optimizing the region R . Instead, we shall make our choice on physical grounds and show that this choice leads to a very small escape rate (so that the minimum escape rate must be at least as small).

2. DESCRIPTION OF THE MODEL

Apart from the boundary conditions, the system we shall investigate is the same as in I: a classical system of identical particles, each with mass m , interacting by a pair potential $v(\mathbf{r})$ of the form

$$v(\mathbf{r}) = q(\mathbf{r}) + \gamma^r \phi(\gamma \mathbf{r}), \quad 0 \leq r < \infty \quad (2)$$

where ν is the number of space dimensions and γ is a positive quantity whose reciprocal is a measure of the range of the "Kac potential" $\gamma^\nu \phi(\gamma \mathbf{r})$.

The functions q and ϕ are assumed to satisfy the conditions

$$q(\mathbf{r}) = +\infty \quad \text{if } r < r_0 \quad (3)$$

$$|q(r)| \leq Dr^{-\nu-\epsilon} \quad \text{if } r > r_0$$

$$-Dr^{-\nu-\epsilon} \leq \phi(\mathbf{r}) \leq 0 \quad \text{for all } r \quad (4)$$

where r means $|\mathbf{r}|$, and r_0 , D , and ϵ are positive constants. Thus, we require q to have a hard core and ϕ to be nonpositive. In addition, we require the function q to be integrable for $r > r_0$, and we also require ϕ to be continuous at $r = 0$ and

$$\alpha \equiv \int \phi(\mathbf{r}) d^{\nu}\mathbf{r} \quad (5)$$

to exist as a Riemann integral. The value of this integral is nonpositive.

For the reasons stated in the introduction, we first use periodic boundary conditions, with a cubical unit cell Ω . A formal specification of these boundary conditions corresponding to their usual definition is given by Fisher and Lebowitz.⁽¹⁰⁾ Their work implies that, under the conditions (3) and (4), the thermodynamic limit of the free energy density is the same for periodic boundary conditions as for the hard-wall boundary conditions used in I. At any given temperature T , this limit for the Helmholtz free energy density [denoted here by $f(\rho, \gamma)$, though in I it was denoted by $a(\rho, \gamma)$] exists for every positive γ and every density ρ in the range $0 < \rho < \rho_{cp}$ where ρ_{cp} is the close-packing density for hard spheres of diameter r_0 . It was shown in I that this free energy is given, in the limit $\gamma \rightarrow 0$, by

$$f(\rho, 0+) \equiv \lim_{\gamma \rightarrow 0} f(\rho, \gamma) = CE[f_0(\rho) + \frac{1}{2}\alpha\rho^2] \quad (6)$$

Here, $f_0(\rho)$ denotes the free energy of the *reference system*, that is, the system whose interaction potential function is q instead of v , and the symbol CE indicates the convex envelope of the expression following it, i.e., the value of the maximal convex function whose value nowhere exceeds $f_0(\rho) + \frac{1}{2}\alpha\rho^2$. Since $\alpha \leq 0$, the function $f_0(\rho) + \frac{1}{2}\alpha\rho^2$ need not be convex even though $f_0(\rho)$ must be. In Fig. 1, the smooth curve is the graph of $f_0(\rho) + \frac{1}{2}\alpha\rho^2$, whose convex envelope is obtained by replacing the arc $ABCD$ by the corresponding double tangent AD .

The parts of the curve in Fig. 1 which Maxwell associated with metastable states are the arcs AB , CD ; these may be specified by the conditions

$$f_0(\rho) + \frac{1}{2}\alpha\rho^2 > f(\rho, 0+) \quad (7a)$$

and

$$f_0''(\rho) + \alpha > 0 \quad (7b)$$

where f_0'' denotes the second derivative of f_0 , is assumed continuous. In this paper, we shall prove a result supporting Maxwell's point of view: We shall show that a con-

figuration-space region R having the properties we have earlier used to characterize metastable equilibrium can be defined at density ρ if

$$f_0(\rho) + \frac{1}{2}\alpha\rho^2 > f(\rho, 0+) \quad (8a)$$

and

$$f_0''(\rho) + 2\alpha > 0 \quad (8b)$$

Since α is negative, this is a more restrictive condition than (7). An example is provided by the Kac–Uhlenbeck–Hemmer⁽¹¹⁾ model, which obeys van der Waals' equation of state. For this model, the criteria (8a, b) can be satisfied if $T < 0.76T_c$ for a range of densities of the form $\rho_v(T) < \rho < \rho_1(T)$, where $\rho_v(T)$ is the density of the vapor (which is $0.0647\rho_{cp}$ if $T = 0.76T_c$). Here, T_c is the critical temperature and ρ_{cp} the close-packing density (the critical density is $\frac{1}{3}\rho_{cp}$). In addition, if $T < 0.44T_c$, there is a second range of densities of the form $\rho_2(T) < \rho < \rho_l(T)$, where $\rho_l(T)$ is the density of the boiling liquid (which is $0.748\rho_{cp}$ if $T = 0.44T_c$), for which the criterion is satisfied. These two ranges of density correspond respectively to superheated vapor and supercooled liquid.

As mentioned in the introduction, we shall do our calculations using a restricted grand canonical ensemble, that is, one constructed by selecting from a grand canonical ensemble those systems whose configuration is in R . The chemical potential of this grand canonical ensemble is related to ρ by the analog of the formula $\mu = (\partial f / \partial \rho)_T$: that is, by

$$\begin{aligned} \mu &= d[f_0(\rho) + \frac{1}{2}\alpha\rho^2]/d\rho \\ &= f_0'(\rho) + \alpha\rho \end{aligned} \quad (9)$$

We shall show later (Section 7) that this choice of μ ensures that nearly all the systems in the ensemble have mean densities very close to ρ .

To define our phase-space region, we divide the unit cell Ω into cubical subcells $\omega_1, \omega_2, \dots, \omega_M$, each of volume $|\omega|$, so that the total volume $|\Omega|$ of the unit cell is equal to $M|\omega|$. For brevity, we shall also refer to these subcells as "cells." We define the dynamical variable $n_i, i = 1, \dots, M$, to be the number of particles in ω_i , and we choose two numbers ρ^- and ρ^+ such that $\rho^- < \rho < \rho^+$ and the condition

$$f_0''(x) + 2\alpha > \text{const} > 0 \quad (10)$$

holds for all $x \in [\rho^-, \rho^+]$. Such a choice must be possible, by (8a, b) and the assumed continuity of f_0'' , but the precise values of ρ^- and ρ^+ chosen are unimportant. In particular, they may be arbitrarily close to ρ . In accordance with the condition (1a), that the metastable state should correspond to a single thermodynamic phase, we now define R to be the set of all configurations compatible with the M constraints

$$\rho^- |\omega| < n_i < \rho^+ |\omega|, \quad i = 1, 2, \dots, M \quad (11)$$

In I, we evaluated the thermodynamic functions by using a triple limit process

where first $|\Omega| \rightarrow \infty$, then $\gamma \rightarrow 0$, and finally $|\omega| \rightarrow \infty$; this process can be represented by the inequalities

$$|\Omega| \gg \gamma^{-\nu} \gg |\omega| \gg r_0^\nu \quad (12)$$

where $x \gg y$ is to be interpreted as $x/y \rightarrow +\infty$.

Here, to deal with metastable states, we shall use a different limit process which can be represented by the inequalities

$$|\Omega| \gg \gamma^{-\nu} \gg |\omega| \gg r_0^\nu \ln |\Omega| \quad (13)$$

This system of inequalities looks very similar to (12), but it is very different mathematically; because of the $\ln |\Omega|$ at the right, we can no longer take the limits of very large $|\Omega|$, $\gamma^{-\nu}$, and $|\omega|$ one at a time but must instead take them all together (in such a way that $|\Omega| \gamma^\nu$, $\gamma^{-\nu}/|\omega|$, and $|\omega|/r_0^\nu \ln |\Omega|$ all become very large).

In the rest of this paper, we shall use a standard notation of analysis and denote limits of this type as follows:

$$\begin{aligned} x = o(1) & \quad \text{to mean} \quad \lim x = 0 \\ x = |\omega| o(1) & \quad \text{or} \quad x = o(|\omega|) \quad \text{to mean} \quad \lim(x/|\omega|) = 0 \end{aligned} \quad (14)$$

The main result proved in this paper is an upper bound on the rate of escape from the set of configurations defined by (11) which implies that

$$(\text{escape rate}) = o(1) \quad (15)$$

That is, by suitable choice of $|\Omega|$, γ , and $|\omega|$, we can make the escape rate as small as we please.

The importance of the condition $\gamma^{-\nu} \gg |\omega|$ here is that the restriction (11) imposes uniform density on a length scale $|\omega|^{1/\nu}$, which is small enough to prevent the formation of any droplets of the new phase with size $\geq \gamma^{-1}$. Since the range of the potential responsible for the transition is γ^{-1} , one would expect that a droplet of at least this size would be necessary to nucleate the growth of the new phase, whose density is well outside the range $[\rho^-, \rho^+]$. We therefore expect the system also to be uniform inside each cell ω_i even though this is not required by (11), which would permit the coexistence of both phases inside any cell. This expectation is supported by the fact, which we shall demonstrate in Section 7, that the Helmholtz free energy density of the metastable state as computed from ensembles confined to R (defined in Section 1) is given in the (13) limit by $f_0(\rho) + \frac{1}{2}\alpha\rho^2$. By Eq. (7a), this free energy density is greater than the stable equilibrium free energy density given in (6), which, as Fig. 1 indicates, is a weighted average of the free energy densities of two phases $f(\rho_v, 0+)$ and $f(\rho_l, 0+)$, and hence corresponds to a two-phase state.

Our interpretation of (11) as restricting the system to a single phase could be strengthened by calculating the Ursell functions for the metastable state and showing that, in the limit described by (13), they have the cluster properties which characterize a single phase.⁽⁶⁾ This can be shown, in a nonrigorous way, by calculating the metastable distribution functions using the method of Section 6 of I. For stable equilibrium,

on the other hand, this method showed in I that the pair distribution function for values of ρ satisfying (7a) is, like the free energy, a weighted average of the corresponding pair distribution functions at densities ρ_v and ρ_l and hence that the two-particle Ursell function does not have the cluster property. We shall not go further into this question here.

3. ESTIMATION OF THE ESCAPE RATE

In this section, we describe some general principles for estimating the probability of the system escaping from the region R of configuration space by a spontaneous fluctuation leading to nucleation of the new thermodynamic phase. Let us denote by $p(t)$ the conditional probability that a system that is in metastable equilibrium (defined in terms of the region R) at time 0 has escaped from it by time t , where $t \geq 0$. As explained in the introduction, we shall calculate this probability by considering a grand canonical ensemble, selecting from it all the systems that at time 0 have dynamical states in R and computing the fraction of the members of this subensemble that are no longer in R at time t .

The fraction of members of this ensemble that at time t have N particles and are in an elementary volume dX near the point X in N -particle phase space will be denoted by $\phi_t(N, X)$, so that we have (using units such that Planck's constant is 1)

$$\phi_0(N, X) = \begin{cases} \text{const} \cdot (N!)^{-1} e^{[\mu N - H(X)]/kT} & \text{for } X \in \hat{R} \\ 0 & \text{for } X \notin \hat{R} \end{cases} \quad (16)$$

where \hat{R} denotes the phase-space region comprising all phase-space points that correspond to configurations in R , and H is the Hamiltonian. The choice of μ is discussed in Section 2. Assuming that the systems in the ensemble are isolated, we can calculate the time evolution of $\phi_t(N, X)$ by Liouville's theorem, obtaining

$$\phi_t(N, X) = 0 \quad \text{or} \quad \text{const} \cdot (N!)^{-1} e^{[\mu N - H(X)]/kT} \quad (17)$$

for all phase points X , so that

$$\phi_t(N, X) \leq \phi_0(N, X) \quad \text{if } X \in \hat{R} \quad (18)$$

Let us denote by $\delta\hat{R}$ the set of all dynamical states of systems that will escape from \hat{R} during the next δt seconds: that is,

$$\delta\hat{R} = \{X : X \in \hat{R} \text{ and } U_{\delta t} X \notin \hat{R}\}$$

where U_t is the time evolution operator. The probability that the system is in R at time t and leaves it during the time interval $[t, t + \delta t]$ is

$$p(t + \delta t) - p(t) = \int_{\delta\hat{R}} \phi_t(X) dX$$

and by (18) this satisfies

$$p(t + \delta t) - p(t) \leq \int_{\delta\hat{R}} \phi_0(X) dX = p(\delta t) \quad (19)$$

[since $p(0) = 0$]. Dividing by δt and taking the limit $\delta t \rightarrow 0$, we obtain

$$dp(t)/dt \leq (dp(t)/dt)_{t=0+} \quad (\text{for } t > 0) \quad (20)$$

so that the rate of increase of $p(t)$ is a maximum when $t = 0$. We shall call this maximum the *rate of escape* from the metastable state described by R and denote it by λ .

To obtain a method of estimating λ , we use the definition (11) of R , which gives

$$\begin{aligned} p(t) &= \text{prob}_t\{n_1 \leq \rho^- | \omega | \text{ or } n_1 \geq \rho^+ | \omega | \text{ or} \\ &\quad n_2 \leq \rho^- | \omega | \text{ or } \dots \text{ or } n_M \geq \rho^+ | \omega |\} \\ &\leq \text{prob}_t\{n_1 \leq \rho^- | \omega |\} + \text{prob}_t\{n_1 \geq \rho^+ | \omega |\} + \dots + \text{prob}_t\{n_M \geq \rho^+ | \omega |\} \end{aligned} \quad (21)$$

by a standard inequality of probability theory. Here, $\text{prob}_t(A)$ means the probability of A being true at time t .

It follows that

$$\lambda = \limsup_{t \rightarrow 0} t^{-1} p(t) \leq (b^+ + b^-) M \quad (22)$$

where

$$b^\pm = \text{Max}_i \limsup_{t \rightarrow 0} t^{-1} \text{prob}_t\{n_i \geq \rho^\pm | \omega |\} \quad (23)$$

since the sum (21) has M terms of each of the two types. (With periodic boundary conditions, the probabilities in (23) are actually independent of i , but we write the formula in this way so that it can also be used for rigid-wall boundary conditions.)

We only consider here the problem of estimating b^+ , but the method for b^- is completely analogous. For very small δt , the system will leave R during the time interval $[0, \delta t]$ by breaking the restriction $n_i < \rho^+ | \omega |$ if and only if the following conditions are satisfied at time 0:

$$\text{Event (A):} \quad \rho^- | \omega | < n_j < \rho^+ | \omega |, \quad j = 1, \dots, i-1, i+1, \dots, M \quad (24a)$$

$$\text{Event (B):} \quad n_i < \rho^+ | \omega | \leq n_i + 1 \quad (24b)$$

Event (C): A particle is approaching the boundary of ω_i from outside at a distance less than δt times its component of velocity perpendicular to this boundary

(This is because, for very small δt , we can neglect possibilities such as two or more particles entering ω_i during δt , or one entering and one leaving, or the prospective entrant being deflected by a collision.) By the multiplication rule for conditional probabilities, b^+ is thus the maximum over i of the quantities

$$\limsup_{\delta t \rightarrow 0} \text{prob}(B)[\text{prob}(C | B)](\delta t)^{-1} \quad (25)$$

both probabilities being calculated in the ensemble defined by (16), so that in effect both are conditional upon the event (A) that the dynamical state of the system belongs to \hat{R} .

The estimation of $\text{prob}(B)$ will be tackled in the next section. All we need to note here is that it does not depend on δt . The event (C) , on the other hand, does depend on δt , and its probability (neglecting terms of order smaller than δt) may be written, using the Maxwellian velocity distribution and taking a coordinate system with the first of its ν axes perpendicular to the relevant boundary of ω_i ,

$$(2\pi mkT)^{-\nu/2} \int_{-\infty}^0 dv_1 \int_{-\infty}^{\infty} dv_2 \cdots \int_{-\infty}^{\infty} dv_\nu \exp(-|v|^2/2mkT) \times \int_{\partial\omega_i} d^{\nu-1}\mathbf{r} [(v_1 \delta t) \rho_i^+(\mathbf{r})] \tag{26}$$

where v_1, \dots, v_ν are the components of velocity, $\partial\omega_i$ represents the boundary of ω_i , and $\rho_i^+(\mathbf{r})$ represents the mean number density, conditional on the events (A) and (B) , just outside the cell ω_i , at the point \mathbf{r} on $\partial\omega_i$. It follows from (26) that

$$\lim_{\delta t \rightarrow 0} (\delta t)^{-1} p(C | B) = (kT/2\pi m)^{1/2} \int_{\partial\omega_i} d^{\nu-1} \mathbf{r} \rho_i^+(\mathbf{r}) \leq (kT/2\pi m) 2\nu |\omega|^{1-1/\nu} \rho_{\max} \tag{27}$$

where

$$\rho_{\max} = \sup_{\mathbf{r}} \rho(\mathbf{r}) \tag{28}$$

Combining (27) with (25), we obtain

$$b^+ \leq (kT/2\pi m)^{1/2} 2\nu |\omega|^{1-1/\nu} \rho_{\max} \{\text{Max}_i \text{prob}(n_i < \rho^+ | |\omega| \leq n_i + 1)\} \tag{29}$$

A similar calculation holds for b^- and so, by (22), we conclude that

$$\lambda \leq M(kT/2\pi m)^{1/2} 2\nu |\omega|^{1-1/\nu} \rho_{\max} \{\text{Max}_i \text{prob}(n_i = n^+ \text{ or } n^-)\} \tag{30}$$

where n^+ and n^- are the integer solutions of

$$\begin{aligned} n^+ &< \rho^+ |\omega| \leq n^+ + 1 \\ n^- &> \rho^- |\omega| \geq n^- - 1 \end{aligned} \tag{31}$$

An important feature of the estimate (30) of the escape rate is that it contains the factor M , which is proportional to the size of the system. This corresponds to the physical fact, noted in the introduction, that the homogeneous rate of nucleation is proportional to the volume of the system. For this reason, we cannot hope to show that λ is small in the thermodynamic limit. We shall, however, show that it is vanishingly small in the special limit defined in (13), where $|\Omega|$, $\gamma^{-\nu}$, and $|\omega|$ all tend to infinity together. The main technical problem is to obtain an upper bound on $\text{prob}(n_i = n^+ \text{ or } n^-)$. For our periodic system, where $\text{prob}(n_i = n^+ \text{ or } n^-)$ is independent of i , a suitable bound will be obtained in the next section. For systems confined by rigid walls, $\text{prob}(n_i = n^+ \text{ or } n^-)$ will have the same small bounds for ω_i in the ‘interior’ of the system but may be large for cells near the walls, and if so, our treatment based on (22) has to be modified. This is done in Section 6.

4. THE PROBABILITY OF BEING AT THE EDGE OF R

To complete our estimate of the escape rate λ , we now estimate the last factor in the upper bound (30), representing the probability that the i th cell contains exactly n^+ or n^- particles at $t = 0$. Because of the periodicity, all cells are equivalent; we have therefore worded our discussion for a cell ω_i far from the surface of Ω . In this section, we concentrate on estimating the probability of finding n^+ particles in ω_i ; the estimate for n^- is analogous.

Let $p_i(n)$ denote the probability of finding exactly n particles in the i th cell. Then, the quantity we wish to estimate is $p_i(n^+)$. Let Γ_i be the complement of ω_i in Ω ,

$$\Gamma_i = \Omega - \omega_i \quad (32)$$

and let η denote any configuration of Γ_i and $p_i(n | \eta)$ the conditional probability that exactly n particles are in ω_i , given that the configuration of Γ_i is η , i.e., η stands for the set of coordinates $(\mathbf{r}_1, \dots, \mathbf{r}_N)$, $\mathbf{r}_j \in \Gamma_i$, and $N \in \{0, 1, \dots\}$. We then have

$$p_i(n^+) = \sum_N \int p_i(n^+ | \eta) q_N(\eta) d\eta \quad (33)$$

where $q_N(\eta) d\eta$ is the probability that the configuration η of Γ_i consists of N points located in the element $d\eta$ of the N -particle configuration space and the integration is carried out over Γ . The probability is obtained from the ensemble defined in Section 3. A convenient way to estimate $p_i(n^+)$ is to compare it with the probability $p_i(\bar{n})$ for some suitably chosen integer \bar{n} in the range $[n^-, n^+]$. This gives

$$\begin{aligned} p_i(n^+) &= \sum_N \int [p_i(n^+ | \eta)/p_i(\bar{n} | \eta)] p_i(\bar{n} | \eta) q_N(\eta) d\eta \\ &\leq \sum_N \int p_i(\bar{n} | \eta) q_N(\eta) d\eta \sup_{\eta} [p_i(n^+ | \eta)/p_i(\bar{n} | \eta)] \\ &= p_i(\bar{n}) \sup_{\eta} [p_i(n^+ | \eta)/p_i(\bar{n} | \eta)] \leq \sup_{\eta} [p_i(n^+ | \eta)/p_i(\bar{n} | \eta)] \\ &= \sup_{\eta} [Q_i(n^+ | \eta)/Q_i(\bar{n} | \eta)] \end{aligned} \quad (34)$$

where

$$Q_i(n | \eta) \equiv (e^{un/kT}/n!) \Lambda^{-vn} \int_{\omega_i} \dots \int_{\omega_i} d^v \mathbf{r}_1 \dots d^v \mathbf{r}_n e^{-V/kT} \quad (35)$$

where $\Lambda \equiv (2\pi mkT)^{-1/2}$ is a factor arising from the momentum integrations, and V is the potential energy of the configuration $\{\mathbf{r}_1, \dots, \mathbf{r}_n, \eta\}$.

Writing ξ for $\mathbf{r}_1, \dots, \mathbf{r}_n$, the configuration ω_i , we can split the potential energy V in (35) into various parts

$$V = V(\xi) + V(\eta) + V(\xi, \eta) \quad (36)$$

where $V(\xi)$ is the interaction of the particles in ω_i with each other, $V(\xi, \eta)$ is that of the particles in ω_i with those in Γ_i , and so on. (The extra interactions coming from the periodic boundary conditions are also included in each of these terms.)

Using (36) in the definition (35) of $Q_i(n, \eta)$, we can write

$$Q_i(n | \eta) = e^{\mu n/kT} Z_i(n | \eta) \quad (37)$$

where

$$Z_i(n | \eta) = (A^{-\nu n}/n!) \int_{\omega_i} \cdots \int_{\omega_i} d\xi e^{-[V(\xi) + V(\xi, \eta)]/kT} \quad (38)$$

is the partition function for n particles confined to the cell ω_i and moving in an external field whose potential at \mathbf{r} is

$$\sum_{\mathbf{r}' \in \eta} v(\mathbf{r}, \mathbf{r}') \quad (39)$$

Substituting (37) into the right side of (34), we obtain

$$Q_i(n^+ | \eta)/Q_i(n^- | \eta) = [Z_i(n^+ | \eta)/Z_i(n^- | \eta)] \exp[\mu(n^+ - n^-)/kT] \quad (40)$$

To estimate $Z_i(n | \eta)$, we use some of the results from I. We deal separately with the long-range and short-range contributions to the external potential (39). The long-range contribution is given approximately by

$$n_i \sum_{\substack{j \\ \omega_j \in \Gamma_i}} n_j w(\mathbf{k}_{ij}) \quad (41)$$

where $w(r) \equiv \gamma^\nu \phi(\gamma r)$ and \mathbf{k}_{ij} is the vector from the center of ω_i to that of ω_j . The error in this approximation is at most

$$n_i \sum_j n_{\max} | \text{Max } w(\mathbf{r} - \mathbf{r}') - \text{Min } w(\mathbf{r} - \mathbf{r}') |, \quad \mathbf{r} \in \omega_i, \quad \mathbf{r}' \in \omega_j \quad (42)$$

where n_{\max} is the largest possible number of particles in a cell. The methods used in I to estimate sums like (41), based on the Riemann-integrability of ϕ , show that the coefficient of n_i in this error bound approaches zero as $\gamma \rightarrow 0$, and hence that the error itself is $o(|\omega|)$.

To estimate the short-range contribution to (39), we consider the upper and lower bounds separately, just as we did in I. For an upper bound on this potential, we can follow the method used to prove (2.9) of I and show that if the points $\mathbf{r}_1, \dots, \mathbf{r}_n$ are all confined to a cell ω_i' , concentric with ω_i but smaller, then their short-range interaction energy with the rest of the system is at most

$$D n_i n_{\max} J_\nu t^{-\nu-\epsilon} \quad (43)$$

where J_ν is the constant defined in (2.10) of I and t is defined by (see Fig. 2)

$$t = |\omega|^{1/\nu} - |\omega'|^{1/\nu} \quad (44)$$

If, in taking the (13) limit, we relate t to $|\omega|$ in such a way that $|\omega| t^{-\nu-\epsilon} \rightarrow 0$, then the upper bound (43) is $o(|\omega|)$. This upper bound gives us a lower bound on the cell partition function $Z_i(n | \eta)$; it is, by (38), (41), and (43),

$$Z_i(n | \eta) \geq \exp[-F_0(n, \omega') - n \sum_j n_j w(\mathbf{k}_{ij}) + o(|\omega|)]/kT \quad (45)$$

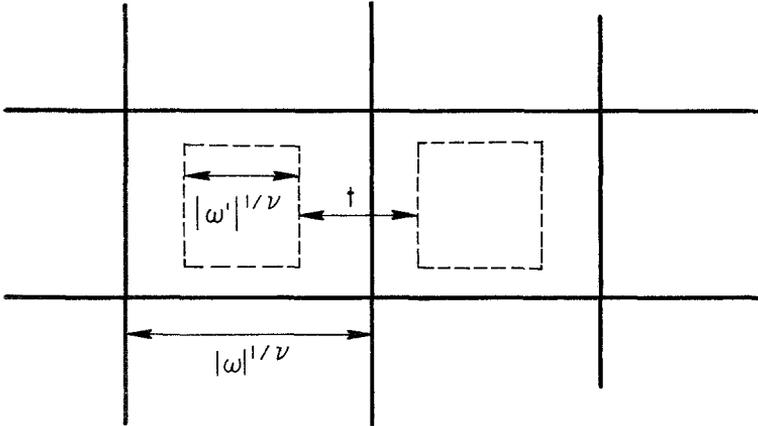


Fig. 2. Specification of cells ω and ω' .

where

$$F_0(n, \omega') = -kT \ln \left\{ \frac{\Lambda^{-n}}{n!} \int_{\omega'_i} \dots \int_{\omega'_i} d\xi e^{-V(\xi)/kT} \right\} \tag{46}$$

is the free energy of n particles confined to the inner cell ω'_i .

For a lower bound on the short-range contribution to $V(\xi, \eta)$, we use the method that led in I to (4.8) and (4.9), obtaining the bound

$$-Dn_i n_{\max} J_y t^{-\nu-\epsilon} - n_{\text{corr}} \Phi \tag{47}$$

where n_{corr} is the maximum number of particles in a ‘‘corridor’’ $\omega''_i - \omega'_i$, with ω''_i a cube of side $|\omega|^{1/\nu} + t$ concentric with ω_i , and $-\Phi$ is the lower bound on the short-range interaction of any particle with all its neighbors, whose existence is a consequence of (3). By the method that gives (4.14) of I, it follows that the lower bound (47) is $o(|\omega|)$, just like the other corrections we have considered. Using this lower bound, together with the corresponding result for the long-range component in (38) we obtain an upper bound on $Z_i(n | \eta)$:

$$Z_i(n | \eta) \leq \exp[-F_0(n, \omega) - n \sum_j n_j w(\mathbf{k}_{ij}) + o(|\omega|)]/kT \tag{48}$$

with $F_0(n, \omega)$ defined analogously to (46).

Our estimate for $p_i(n^+)$ is obtained by substituting (45) and (48) into (40) and the result into (34):

$$\begin{aligned} p_i(n^+) &\leq \exp\{[\mu(n^+ - n^-) - F_0(n^+, \omega) + F_0(n^-, \omega') \\ &\quad - (n^+ - n^-) \sum_j n_j w(\mathbf{k}_{ij}) + o(|\omega|)]\}/kT \end{aligned} \tag{49}$$

This can be further simplified by using the definition of the thermodynamic free energy density f_0 of the reference system, which implies

$$\begin{aligned} F_0(n, \omega) &= |\omega| f_0(n/|\omega|) + o(|\omega|) \\ F_0(n, \omega') &= |\omega'| f_0(n/|\omega'|) + o(|\omega'|) \\ &= |\omega| f_0(n/|\omega|) + o(|\omega|) \end{aligned} \tag{50}$$

where in the last line we have assumed that the (13) limit is taken in such a way that $|\omega'|/|\omega| \rightarrow 1$ and also used the continuity of the function f_0 . The compatibility of the condition $|\omega'|/|\omega| \rightarrow 1$ with our earlier condition $|\omega| t^{-\nu-\epsilon} \rightarrow 0$ is proved in (2.22) and (2.23) of I. To use (50), we note that $n^+/|\omega| \rightarrow \rho^+$ in the (13) limit, and we now make our choice of n^- , choosing it so that $n^-/|\omega| \rightarrow \rho$. Equation (49) then becomes

$$p_i(n^+) \leq \exp \left\{ (|\omega|/kT) \left[\mu(\rho^+ - \rho) - f_0(\rho^+) + f_0(\rho) - (\rho^+ - \rho) \sum_j n_j w(\mathbf{k}_{ij}) + o(1) \right] \right\} \tag{51}$$

The exponent in (51) can be further simplified. By Taylor’s theorem and the condition (10) defining ρ^- and ρ^+ , we have

$$f_0(\rho^+) \geq f_0(\rho) + (\rho^+ - \rho) f_0'(\rho) + \frac{1}{2}(\rho^+ - \rho)^2 (kTC - 2\alpha) \tag{52}$$

where

$$C \equiv \inf_{x \in [\rho^-, \rho^+]} \{f_0''(x) + 2\alpha\}/kT \tag{53}$$

which is positive, by (10). Also, since $n_j \leq n^+$ for all j , and w is nonpositive by (4), we have

$$\begin{aligned} \sum_j n_j w(\mathbf{k}_{ij}) &\geq n^+ \sum_j w(\mathbf{k}_{ij}) \\ &= \rho^+ [\alpha + o(1)] \end{aligned} \tag{54}$$

where the last line follows from (5) and I(2.20). Using the estimates (52) and (54) in (51) and making use of the condition $\mu = f_0'(\rho) + \alpha\rho$ [Eq. (9)], we find

$$p_i(n^+) \leq \exp \left\{ -\frac{1}{2} |\omega| [C(\rho^+ - \rho)^2 + o(1)] \right\} \tag{55}$$

To obtain an upper bound on $p_i(n^-)$, the analysis (in the case of periodic boundary conditions) proceeds entirely as before. The analog of (54) is

$$\sum_j n_j w(\mathbf{k}_{ij}) \leq n^- \sum_j w(\mathbf{k}_{ij}) = (n^-/|\omega|) [\alpha + o(1)] \tag{56}$$

where the inequality obtains because $n_j \geq n^-$ for all j , and so the analog of (55) is

$$p_i(n^-) \leq \exp \left\{ -\frac{1}{2} |\omega| [C(\rho^- - \rho)^2 + o(1)] \right\} \tag{57}$$

Thus, if $|\omega|$ is large, the probability, calculated using the restricted grand canonical ensemble with $\mu = f_0'(\rho) + \alpha\rho$, of having either n^+ or n^- particles in the cell ω_i is

extremely small. Consequently, the corresponding factor $\text{Max}_i \text{prob}(n_i = n^+ \text{ or } n^-)$ in the upper bound (30) for the escape rate λ is extremely small if $|\omega|$ is at all large, and in fact approaches 0 rapidly in the (13) limit.

5. THE KINETIC FACTOR

The probability we have just been estimating is only one of the factors in our original upper bound (30) on λ , the rate of escape from the configuration-space region R . To complete our estimation of λ , we now consider the remaining factors in this upper bound which, when combined with (57) and (59), takes the form

$$\lambda \leq M(kT/2\pi m)^{1/2} 2\nu |\omega|^{1-1/\nu} \rho_{\max} \exp[o(|\omega|)] \\ \times [\exp\{-\frac{1}{2} |\omega| C(\rho^+ - \rho)^2\} + \exp\{-\frac{1}{2} |\omega| C(\rho - \rho^-)^2\}] \quad (58)$$

The only factor remaining to be estimated is ρ_{\max} , and we can deal with this by the method of Lieb.^(13,14) The formula for the local number density at a point \mathbf{r}_1 , for the ensemble we are using, is

$$\rho(\mathbf{r}_1) = \sum_{N=1}^{\infty} N(z^N/N!) \int_{\Omega} \cdots \int_{\Omega} h_R(\xi) e^{-V(\xi)/kT} d^{\nu}\mathbf{r}_2 \cdots d^{\nu}\mathbf{r}_N / \mathcal{E}_R(\mu, \Omega) \quad (59)$$

where $\xi = \{r_1, \dots, r_N\}$, now representing a configuration for all N particles,

$$z = e^{\mu/kT} \Lambda^{-\nu} \quad (60)$$

$$h_R(\xi) = \begin{cases} 1 & \text{if } \xi \in R \\ 0 & \text{otherwise} \end{cases} \quad (61)$$

and

$$\mathcal{E}_R(\mu, \Omega) = \sum_{N=0}^{\infty} (z^N/N!) \int_{\Omega} \cdots \int_{\Omega} h_R(\xi) e^{-V(\xi)/kT} d\xi \quad (62)$$

This formula for ρ implies the upper bound

$$\rho(\mathbf{r}_1) \leq z e^{\Phi/kT} \sum_{N'=0}^{\infty} (z^{N'}/N'!) \int_{\Omega} \cdots \int_{\Omega} d\xi' h_{R1}(\xi') \{\exp[-V(\xi')/kT]\} / \mathcal{E}_R \quad (63)$$

where Φ is the upper bound on $\sum_{j=2}^N v(\mathbf{r} - \mathbf{r}_j)$ used in (49), N' means $N - 1$, ξ' means $\{r_2, r_3, \dots, r_N\}$, and

$$h_{R1}(\xi') \equiv \begin{cases} 1 & \text{if } n^- \leq n_i' + \delta_i(\mathbf{r}_1) \leq n^+, \quad i = 1, 2, \dots, N \\ 0 & \text{otherwise} \end{cases} \quad (64)$$

with

$$\delta_i(\mathbf{r}_1) \equiv \begin{cases} 1 & \text{if } r_1 \in \omega_i \\ 0 & \text{otherwise} \end{cases} \quad (65)$$

and n_i' the number of points of ξ' within ω_i . The sum in (63) therefore exceeds the one in (62) by

$$\sum_{N=0}^{\infty} (z^N/N!) \int_{\Omega} \cdots \int_{\Omega} d\xi [h_{R1}(\xi) - h_R(\xi)] e^{-V(\xi)/kT} \tag{66}$$

For an upper bound, we restrict the integration to configurations for which $h_{R1}(\xi) > h_R(\xi)$; that is, for which

$$n_1 = n^- - 1 \quad \text{and} \quad n^- \leq n_i \leq n^+, \quad i = 2, \dots, M \tag{67}$$

where we have allotted the label 1 to the cell containing \mathbf{r}_1 . The upper bound so obtained, when divided by Ξ_R , gives an expression analogous in structure to the one defining $p_1(n^-)$, the only difference being that we now have $p(n^- - 1)$ in place of $p(n^-)$. It can therefore be estimated by the same method that we used in Section 4 for $p_i(n^-)$, and the result, corresponding to (57), is

$$\text{Eq. (66)}/\Xi_R \leq \exp\{-\frac{1}{2} |\omega| [C(\rho^- - \rho)^2 + o(1)]\} \tag{68}$$

since $(n^- - 1)/|\omega| \rightarrow \rho^-$ in the limit specified in (13). Combined with (63), the estimate (68) gives us

$$\rho(\mathbf{r}_1) \leq ze^{\phi/kT} (1 + \exp\{-\frac{1}{2} |\omega| [C(\rho^- - \rho)^2 + o(1)]\}) \tag{69}$$

so that $\rho(\mathbf{r})$ is uniformly bounded in the (13) limit.

We can now complete our estimation of the escape rate λ . Using (69) and the relation $|\Omega| = M|\omega|$ in (58), we obtain

$$\begin{aligned} \lambda &\leq \text{const} \cdot |\Omega| |\omega|^{-1/\nu} \exp(o|\omega|) \\ &\quad \times \{\exp[-\frac{1}{2} |\omega| C(\rho^+ - \rho)^2] + \exp[-\frac{1}{2} |\omega| C(\rho - \rho^-)^2]\} \end{aligned} \tag{70}$$

Combining this with the last inequality in the condition

$$|\Omega| \gg \gamma^{-\nu} \gg |\omega| \gg r_0^\nu \ln |\Omega| \tag{71}$$

[which is the same as (13)], we conclude that

$$\lambda = o(1) \tag{72}$$

Thus, by choosing suitable values of $|\Omega|$, γ , and $|\omega|$, we can make the rate of escape from the metastable state as small as we please. One should remember, however, that the condition (71) above implies $\gamma \rightarrow 0$, so that very small escape rates can only be achieved with Kac potentials of very long range. The machine computations by Andrews^(3c) and by Griffith et al.^(3b) provide some corroboration of our main result (72).

6. RIGID-WALL BOUNDARY CONDITIONS

In this section, we indicate how our previous analysis for periodic boundary conditions can be generalized to the more realistic case of rigid-wall boundary

conditions. If the system is enclosed in a container with rigid walls at the boundary of Ω , there may be a small proportion of cells near the walls in which the rate of nucleation per cell is much higher than in the interior. To allow for these, we generalize the derivation of the upper bound (30) by allowing for each cell separately, to obtain

$$\lambda \leq (kT/2\pi m)^{1/2} 2\nu |\omega|^{1-1/\nu} \rho_{\max} \sum_{i=1}^M \text{prob}(n_i = n^+ \text{ or } n^-) \quad (73)$$

For a preliminary discussion, it is convenient to assume that the Kac potential has a cutoff, which, with γ and ϕ suitably scaled, can be expressed as a condition $\phi(\gamma r) = 0$ for $r > \gamma^{-1}$. We distinguish two types of cell: "interior" cells, whose distance from the boundary of Ω is at least γ^{-1} , and "surface" cells, for which it is not. Then, we can use (73) by putting it in the form

$$\lambda \leq (kT/2\pi m)^{1/2} 2\nu |\omega|^{1-1/\nu} \rho_{\max} [M_1 P_1 + M_2 P_2] \quad (74)$$

where M_1 is the number of interior cells, M_2 the number of surface cells, P_1 an upper bound on $\text{prob}(n_i = n^+ \text{ or } n^-)$ for interior cells ω_i , and P_2 an upper bound for surface cells.

To find a suitable P_1 , we can use the analysis given in Section 4 without modification, obtaining

$$P_1 \leq \exp\{-\frac{1}{2} |\omega| [C(\rho^+ - \rho)^2 + o(1)]\} + \exp\{-\frac{1}{2} |\omega| [C(\rho^- - \rho)^2 + o(1)]\} \quad (75)$$

The simplest possibility for P_2 is $P_2 = 1$. If we use this in (74), we obtain⁵

$$\lambda/|\Omega| \leq \text{const} \cdot [M_1 \cdot o(1) + M_2]/|\Omega| \quad (76)$$

and since $M_2/|\Omega|$ approaches 0 when $|\Omega| \rightarrow \infty$, we have, by (32) or (33),

$$\lambda/|\Omega| = o(1) \quad (77)$$

showing that the escape rate per unit volume can be made arbitrarily small, but it is not possible to prove λ itself small by this method.

To prove that $\lambda = o(1)$, we would like to find a P_2 that is exponentially small for large $|\omega|$, just as P_1 is. We can adapt the analysis given in Section 4 to this case too. Even if ω_i is a surface cell, this analysis still applies for $p_i(n^+)$ provided the equality in (54) is replaced by the inequality

$$n^+ \sum_j w(\mathbf{k}_{ij}) \geq (n^+/|\omega|)[\alpha + o(1)] \quad (78)$$

which is valid since the terms in the sum are nonpositive, and there are fewer of them if ω_i is a surface cell. For $p_i(n^-)$, on the other hand, the analysis in Section 4 breaks down in general because (56) must now be replaced by

$$n^- \sum_j w(\mathbf{k}_{ij}) \leq (n^-/|\omega|)[\alpha' + o(1)] \quad (79)$$

⁵ We are assuming that ρ_{\max} also stays bounded for surface cells.

where

$$\begin{aligned} \alpha' &= \text{limit of } \text{Mjn } |\omega| \sum_j w(\mathbf{k}_{ij}) \\ &= 2^{-\nu} \alpha \end{aligned} \tag{80}$$

since for a cubical container Ω the minimum is achieved with ω_i at the corner of Ω . Equations (78) and (79) do not depend on our earlier assumption that ϕ has a cutoff; the only special assumption now is that ϕ is spherically symmetric [for (80)].

There are two ways of using (79). One is to take $\rho^- = 0$ so that $n^- = 0$, and then it does not matter that we have α' rather than α on the right-hand side. This can be done provided the condition (8b) is replaced by

$$f_0''(x) + 2\alpha > 0, \quad x \in [0, \rho^+] \tag{81}$$

so that (10b) will hold with $\rho^- = 0$. For the Kac–Uhlenbeck–Hemmer model, the conditions (8a) and (81) can be satisfied at all temperatures below the temperature $0.76T_0$ mentioned in Section 2. Whatever model we consider, however, the condition cannot be satisfied for any ρ greater than the one at B in Fig. 1, and therefore we cannot describe superheated liquid by this method. This asymmetry between liquid and vapor arises in our model because the effect of the attractive Kac potential is to reduce the density of the system near a hard wall, thus tending to nucleate the vapor phase near the wall in a metastable liquid, but to inhibit nucleation near the wall in the vapor phase. A similar asymmetry is observed experimentally: it is more difficult to superheat a liquid than to supercool a vapor, because bubbles form easily at the interface between a liquid and its container.⁽⁴⁾ (The homogeneous nucleation rates are small in both cases.)

A second way of using (79), which does not require $\rho^- = 0$, is to replace (10) by the stronger requirement

$$\begin{aligned} f_0''(x) + 2\alpha &> [2\rho^-(\rho - \rho^-)](|\alpha| - |\alpha'|), & x \in [\rho^-, \rho] \\ &> 0, & x \in [\rho, \rho^+] \end{aligned} \tag{82}$$

If this is satisfied, then even (79) is sufficient to give a satisfactory upper bound on $p_i(n^-)$: this upper bound is once again of the form (57).

7. STATIC PROPERTIES OF THE RESTRICTED ENSEMBLES

In this section, we indicate how to calculate analogs for thermodynamic functions, applying to the metastable state. We also prove a result relevant to the problem of the equivalence of ensembles, showing that in the restricted grand canonical ensemble with chemical potential $f_0'(\rho) + \alpha\rho$, most of the systems have mean densities very close to ρ .

We first consider the restricted canonical ensemble. The analog of the free energy F is defined by

$$e^{-F_R(N)/kT} = (A^{-\nu N}/N!) \int_{\Omega} \dots \int_{\Omega} d\xi e^{-V(\xi)/kT} h_R(\xi) \tag{83}$$

where

$$\xi = \{\mathbf{r}_1, \dots, \mathbf{r}_N\}$$

and

$$h_R(\xi) = \begin{cases} 1 & \text{if } \xi \in R \\ 0 & \text{otherwise} \end{cases}$$

The free energy density in the limit defined in (13),

$$f_R(\rho) = \lim [F_R(N) / |\Omega|], \quad N / |\Omega| \rightarrow \rho \tag{84}$$

can be evaluated by a modification of the method used in I. The modification is, in equations such as (4.19) of I, to replace $F_0(n_i, \omega_i)$, the free energy of n_i particles in the cell ω_i , by $F_0(n_i, \omega_i) + G(n_i, \omega_i)$, where $G = 0$ if $\rho^- |\omega| < n_i < \rho^+ |\omega|$ and $= +\infty$ if not. This gives

$$f_R(\rho) = CE\{f_0(\rho) + g(\rho) + \frac{1}{2}\alpha\rho^2\} \tag{85}$$

where

$$g(x) = \begin{cases} 0 & \text{if } \rho^- < x < \rho^+ \\ +\infty & \text{otherwise} \end{cases} \tag{86}$$

By (10), the expression in braces in (85) is a convex function of ρ , and since $g(\rho) = 0$, we obtain^(2,15)

$$f_R(\rho) = f_0(\rho) + \frac{1}{2}\alpha\rho^2, \quad \rho \in [\rho^-, \rho^+] \tag{87}$$

We have already referred to this result in the discussion at the end of Section 2.

A similar calculation is possible for the restricted grand canonical ensemble. The analog of the grand canonical pressure is $P_R(\mu)$, defined by

$$e^{P_R(\mu)|\Omega|/kT} = \sum_{N=0}^{\infty} e^{[\mu N - F_R(N)]/kT} \tag{88}$$

It can be evaluated rigorously in the (13) limit, using the corresponding modification of the method of Gates and Penrose⁽¹⁶⁾; the result is

$$\lim P_R(\mu)/kT = \max_{\rho} [\mu\rho - f_R(\rho)] \equiv \pi_R(\mu) \tag{89}$$

Thus, the restricted grand canonical pressure and the restricted free energy are related in just the same way as the corresponding unrestricted quantities. The mean density of particles in the restricted grand canonical ensemble is given by

$$\begin{aligned} \langle N \rangle_R / |\Omega| &= [\exp(-P_R(\mu)|\Omega|/kT)] \sum_{N=0}^{\infty} N \exp \left\{ \sum [\mu N - F_R(N)]/kT \right\} \\ &= \partial P_R(\mu) / \partial \mu = \partial \pi_R(\mu) / \partial \mu + o(1) \end{aligned} \tag{90}$$

To see this, we merely note that $P_R(\mu)$ is a convex function of μ whose limit $\pi_R(\mu)$ is differentiable at the values of μ given in (9) with ρ satisfying (8). Hence, the interchange

of the limit and the differentiation is justified.⁽¹⁾ In a similar way, we can relate the mean energy density in the restricted ensemble to the derivative of $(kT)^{-1} f_R$ with respect to $(kT)^{-1}$.

Results such as (87), (89), and (90), showing that thermodynamic functions can be defined and calculated for the metastable state by methods analogous to the usual methods of equilibrium statistical mechanics, provide a partial demonstration that our definition of metastable states satisfies the condition mentioned after the three listed under (1)—that thermodynamics should apply to the metastable state.

Related to this question of defining thermodynamic functions is the question of the equivalence of ensembles. In particular, we should like to show that the restricted grand canonical, canonical, and microcanonical ensembles give the same result not only for thermodynamic properties but also for the rate of escape from the metastable state. As a step toward demonstrating this, we shall prove that the restricted grand canonical ensemble with chemical potential given, as before, by $\mu = f'_0(\rho) + \alpha\rho$ has, for any positive number δ , the property

$$\text{prob}\{|N/|\Omega| - \rho| > \delta\} = o(1) \tag{91}$$

indicating that almost all the systems in this ensemble have densities very close to ρ .

In the restricted grand canonical ensemble, the probability that the system contains N particles is given, for any $N_1 \in (\rho^-|\Omega|, \rho^+|\Omega|)$, by

$$\text{prob}(N) = \exp\{[N\mu - F_R(N) - P_R(\mu)|\Omega|]/kT\} \tag{92}$$

Writing \bar{N} for the integer closest to $\rho|\Omega|$, we deduce that

$$\begin{aligned} \text{prob}(N_1) &\leq \text{prob}(N_1)/\text{prob}(\bar{N}) \\ &= \exp\{[(N_1 - \bar{N})\mu - F_R(N_1) + F_R(\bar{N})]/kT\} \\ &= \exp\{|\Omega|[(\rho_1 - \rho)\mu - f_R(\rho_1) + f_R(\rho) + o(1)]/kT\} \end{aligned} \tag{93}$$

where $\rho_1 = N_1/|\Omega|$. Using the formulas (9) for μ and (87) for f_R in (93) and (52) for the $f_0(\rho_1)$ in the result, we obtain

$$\text{prob}(N_1) \leq \exp\{-|\Omega|[C(\rho_1 - \rho)^2/2 + o(1)]\} \tag{94}$$

To estimate the probability in (91), we consider the two events $N/|\Omega| - \rho > \delta$ and $N/|\Omega| - \rho < -\delta$ separately. For the first of these, we have

$$\text{prob}(N/|\Omega| - \rho > \delta) = \sum_{N_1} \text{prob}(N_1), \quad N_1 > (\rho + \delta)|\Omega| \tag{95}$$

Since

$$\sum_{N_1=N}^{\infty} \phi(N_1) \leq \int_{N-1}^{\infty} \phi(N_1) dN_1$$

if ϕ is a decreasing function, and

$$\int_A^{\infty} \exp(-Bt^2) dt < \int_A^{\infty} (t/A) \exp(-Bt^2) dt = [\exp(-BA^2)]/2AB$$

the right side of (95) has, by (94), the upper bound

$$\begin{aligned}
 & \int_{(\rho+\delta)|\Omega|-1}^{\infty} \exp\{-|\Omega|[C(\rho_1 - \rho)^2/2 + o(1)]\} d(\rho_1 | \Omega) \\
 & < \frac{2|\Omega| \exp\{-C(\delta|\Omega|-1)^2/2|\Omega| + o(|\Omega|)\}}{\{(\rho + \delta)|\Omega| - 1\} C} \quad (96) \\
 & = [\text{const} + o(1)] \exp\{-|\Omega|[C\delta^2/2 + o(1)]\} \\
 & = o(1)
 \end{aligned}$$

In just the same way, we can show that $\text{prob}(N|\Omega | -\rho < \delta) = o(1)$, and the result (91) follows.

We can use this result to relate the escape rate we have calculated to escape rates calculated in a canonical ensemble. If $\lambda(N)$ denotes the escape rate calculated in a canonical ensemble with N particles, and I the interval $[(\rho - \delta)|\Omega|, (\rho + \delta)|\Omega|]$, then we have

$$\begin{aligned}
 \lambda &= \sum_{N_1} \text{prob}(N_1) \lambda(N_1) \\
 &> \sum_{N_1 \in I} \text{prob}(N_1) \lambda(N_1) \quad (97) \\
 &> \min_{N_1 \in I} \lambda(N_1) \cdot \text{prob}(N_1 \in I)
 \end{aligned}$$

so that for at least one value of N in the interval I we have

$$\lambda(N) < \lambda / [\text{prob}(N_1 \in I)] = \lambda + o(1) \quad (98)$$

8. THE PROBABILITY OF RETURN

To complete our justification for claiming that R describes a metastable state, we shall now argue that it has the third property of metastable states listed in (1): once the system has escaped from R , it is unlikely to return. To estimate the probability of such a return, we shall use the standard methods of (stable) equilibrium statistical mechanics. That is, to represent the final equilibrium reached by the system after it has left the metastable state, we shall use one of the equilibrium ensembles of statistical mechanics, and as our estimate of the probability of returning to the metastable state, we shall use the fraction of members of this ensemble that have configurations in R . This amounts to assuming that a system whose dynamical state has just left R is no more likely to return to it than one whose dynamical state was never anywhere near R . The validity of this assumption, at least in the short run, is dubious, but at least it provides us with some indication of what to expect.

If an ensemble of isolated systems starts in the metastable set R and eventually comes to stable equilibrium, then, since energy and particle number are constants of the motion, the final equilibrium ensemble will be characterized by the fact that its mean energy and particle number are the same as for the initial ensemble. Thus, the

natural way of calculating the probability of a return to R is from the formula of the microcanonical ensemble

$$\text{prob}(\text{return}) = \int_{\bar{R}} \Delta(E - H(X)) dX / \int \Delta(E - H(X)) dX \quad (99)$$

where X is a variable over the phase space of an N -dimensional system, E and N are the initial energy and particle number, and Δ is defined by

$$\Delta(x) = \begin{cases} 1 & \text{if } 0 \leq x < \Delta E \\ 0 & \text{otherwise} \end{cases}$$

with ΔE a positive number, representing the tolerance in energy measurements, and satisfying $\Delta E/E = o(1)$.

If, on the other hand, the systems after leaving the metastable state are not isolated but interact with a heat bath at temperature T equal to the temperature of the original restricted ensemble, then it is natural to use the canonical ensemble formula

$$\text{prob}(\text{return}) = \int_{\bar{R}} e^{-H(X)/kT} dX / \int e^{-H(X)/kT} dX \quad (100)$$

In this second case, the probability of return is easily shown to be very small; the standard formula (46) for free energy gives

$$\begin{aligned} \text{prob}(\text{return}) &= \exp\{[F - F_R]/kT\} \\ &= \exp\{|\Omega| [f(\rho, 0+) - f_0(\rho) - \frac{1}{2}\alpha\rho^2 + o(1)]/kT\} \end{aligned} \quad (101)$$

by (87) and the definition of $f(\rho, 0+)$; then the condition (8a) shows that the quantity in square brackets tends to a negative value in the (13) limit, so that

$$\text{prob}(\text{return}) = o(1) \quad (102)$$

Moreover, the probability of return is many orders of magnitude smaller than the probability of escape, since the former has a factor $|\Omega|$ in the exponent, whereas the latter has only $|\omega|$.

A difficulty with this calculation based on (99) is that the device of connecting the system to a reservoir is not really consistent with our method of calculating escape rates, where the system was taken to be isolated. Accordingly, we also give a calculation for isolated systems, based on the microcanonical ensemble formula (98). This formula can be written

$$\text{prob}(\text{return}) = e^{[S_R - S]/kT} \quad (103)$$

where the entropies S_R and S are defined by making $e^{S_R/k}$ and $e^{S/k}$ equal to $A^{-\nu N}/N!$ times the numerator and denominator of (98). Just as in the calculation shown in (101), the probability in (103) will approach 0 in the triple limit if

$$s(\epsilon) > s_R(\epsilon) \quad (104)$$

where $s(\epsilon)$ and $s_R(\epsilon)$ are entropy densities defined by

$$s(\epsilon) = \lim S/|\Omega|, \text{ etc.} \quad (105)$$

where S is the entropy of a system of N particles with energy E , and $N/|\Omega| \rightarrow \rho$ and $E/|\Omega| \rightarrow \epsilon$ in the triple limit.

Our demonstration of (104) is based on the thermodynamic formula

$$s(\epsilon) = \min_T \{[\epsilon - f(T)]/T\} \quad (106)$$

where $f(T)$ is the Helmholtz free energy density calculated at the same particle density as $s(\epsilon)$. Equation (106) is a consequence of the facts that $s(\epsilon) = [\epsilon - f(T_\epsilon)]/T$ holds when T_ϵ is the temperature at which the energy density $d(f/T)/d(1/T)$ is equal to ϵ , and that $-f(T)/T$ is a convex function of $1/T$ (its second derivative being T^2 times the specific heat). We shall assume without proof that (106) also holds for the "metastable" thermodynamic functions s_R and f_R .

We distinguish two cases, according to whether the temperature T_ϵ defined above, which we call the final temperature, is equal to the corresponding temperature for s_R and f_R at the same energy, which we call the initial temperature.

Case I. Initial and final temperatures equal. Here, using first (106), then (8), and finally the metastable version of (106), we obtain

$$s(\epsilon) = [\epsilon - f(T_\epsilon)]/T_\epsilon > [\epsilon - f_R(T_\epsilon)]/T_\epsilon = s_R(\epsilon) \quad (107)$$

since the temperature at which (8) applies is the one we have called the initial temperature.

Case II. Initial and final temperatures different. Here, using first (106), then the fact that the convex envelope construction used in (6) implies $f_R(T) \geq f(T)$ for all T , and finally the metastable version of (106) remembering that T_ϵ is now different from the temperature at which $[\epsilon - f_R(T)]/T$ is minimized, we obtain

$$s(\epsilon) = [\epsilon - f(T_\epsilon)]/T_\epsilon \geq [\epsilon - f_R(T_\epsilon)]/T_\epsilon > s_R(\epsilon)$$

Thus, in both cases, (104) holds, and the rest of the argument proceeds as from (101).

9. DISCUSSION

In this paper, we have shown that for a system with a long-range Kac potential it is possible to give a precise meaning to the statement that a system is in a metastable state. We have done this by finding a region R in configuration space which has, on the one hand, a small probability in one of the equilibrium ensembles and, on the other hand, a small escape rate λ . This was made possible by the fact that, in the limit we are considering, the range γ^{-1} of the Kac potential becomes very large compared

with the other physical lengths, r_0 and $\rho^{-1/\nu}$. This permits a clean separation of the effects of the Kac potential from those of the short-range potential q . This separation is accomplished by introducing an artificial new length $|\omega|^{1/\nu}$ satisfying the two conditions [both coming from (13)]

$$|\omega|^{1/\nu} \gg \rho^{-1/\nu} \ln |\Omega|, \quad |\omega|^{1/\nu} \ll \gamma^{-1} \quad (108)$$

and defining R through constraints [Eq. (11)] on density variations over the length scale $|\omega|^{1/\nu}$.

The first condition in (108) ensures that there are enough particles in each cell to make a fluctuation, from the average occupation number assumed in the metastable state, violating the “constraints,” an unlikely event in the restricted equilibrium ensemble, and hence enables us to prove that the escape rate is small. The second condition ensures that any phase transition due to the Kac potential is completely suppressed by the constraints, and hence makes the state defined by these constraints a very unlikely one in the full equilibrium ensemble, if this ensemble predicts such a phase transition. (On the other hand, the constraints have no effect on any phase transition that may be produced by the short-range part of the potential. If a phase transition occurs in the absence of the constraints and of the Kac potential, at the mean density ρ , then it also occurs in their presence: because of the first condition in (108), each cell ω_j will contain the two phases side by side.)

Since both parts of (108) are crucial to our treatment of metastability, the result that λ can be made as small as we please does not apply to real physical systems, for which there is no $\gamma \rightarrow 0$ limit. For a realistic potential, it may well be impossible to find regions R which have both arbitrarily small escape rates and arbitrarily small equilibrium probabilities—particularly in view of the apparent impossibility of analytically continuing the equilibrium free energies and correlation functions for such potentials into the domain of metastability.⁽⁷⁾ In principle, however, it should still be possible to obtain some information from the theory in these cases. A realistic potential such as the Lennard-Jones potential could be arbitrarily separated into two parts according to the formula (2), with $\gamma = 1$, and then the method of estimation we have used here could be used to calculate an upper bound on λ , which, though positive, might be small at suitable temperatures and densities, if the separation of the potential and the choice of $|\omega|$ had been done skillfully. The difficulty with such a calculation is that all the quantities we have disposed of in this paper by writing $O(1)$ or $O(|\omega|)$ would now have to be estimated explicitly; since γ would now be fixed, it would no longer be enough to know only the behavior of these quantities in the limit $\gamma \rightarrow 0$.

The form of our upper bound on λ is roughly $|\Omega| e^{-\Delta/kT}$, with Δ a positive “activation energy” proportional to $|\omega|$. Similar formulas for escape rates occur in other theories; for example, the Arrhenius formula for chemical reaction rates has this form, and so do the ones of Griffith *et al.*^(3b) and van Kampen.^(3a) The main difference between these formulas and ours is that they are intended to be approximations to the true escape rate, whereas ours is a rigorous upper bound, but not necessarily a good approximation.

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