Virial/Fisher models of molecular cluster populations

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The Fisher cluster model provides a phenomenological description of the populations of molecular clusters in a vapor. However, it was not designed for use at all cluster sizes, including monomers, although this is often assumed to be the case when constructing models of droplet nucleation. In order to study the accuracy of this assumption, a set of models is constructed in which, progressively, the monomer, dimer, and trimer populations are described using empirical virial coefficients, while the Fisher model accounts for higher clusters. The models are used to study the populations at the critical temperature, which is an important reference point for model parametrisation. Remarkably, the cluster populations are little changed by altering the crossover point between the virial and Fisher expressions, and furthermore, the original Fisher model provides a reasonable description even for monomers, as desired. The model is extended in one of a number of possible ways to describe cluster populations at temperatures below the critical point with less success: the Fisher model can then no longer account for the whole size distribution. © *1997 American Institute of Physics.* [S0021-9606(97)50323-0]

I. INTRODUCTION

The theory of the nucleation of a phase transition remains an unsolved problem in spite of seventy years of effort.[1,2] The classic example of the phenomenon is the nucleation of liquid droplets from a supersaturated vapor. Although the most stable thermodynamic state of the system under such circumstances is the bulk condensed phase, it is possible to prepare a supersaturated vapor in practice because it is stable with respect to small molecular clusters of the condensate. Since it is only by the nucleation and growth of these small clusters that a bulk condensate can be formed, the system is held in the metastable vapor state by a kinetic barrier. Analogous barriers impede other phase changes such as the freezing of a liquid and transformations in the solid state. For a review, see Ref. 3.

The stability of small clusters of a new phase therefore holds the key to the description of nucleation phenomena. This is traditionally studied by means of rate equations describing growth and decay amongst cluster populations. The clusters envisaged are long-lived on the timescale of molecular motions within the cluster. They are energetically bound together. On shorter timescales unbound associations of molecules might occur which do not qualify as clusters as defined in the population dynamics. This point is important since a clear idea of what constitutes a cluster is needed in order to calculate rates of growth and decay from first principles.

Cluster growth rates are determined by the collision rates between different species, assuming every collision leads to accretion. These rates can be calculated from gas kinetic theory. The key unknown quantity is the rate of decay of clusters by the emission of smaller clusters, or more usually single molecules or monomers. It is also possible, in prin-

ciple, to calculate the decay rates from first principles. Typically, this would involve atomistic modeling with varying degrees of sophistication. However, making a connection between cluster decay and the fundamental interactions between molecules is difficult, even if the cluster definition is sound, since the molecular interactions are not usually known to high enough precision. An approximate calculation is likely to be inadequate since the rate of nucleation turns out to be extremely sensitive to the cluster decay rates.

Alternatively, the decay rates can be calculated by considering a system of clusters in quasi-equilibrium with one other under the prevailing conditions. The steady state populations are taken to result from a competition between the kinetic rates of growth and decay of each cluster size. Since gas kinetic theory provides the growth rates, the quasi-equilibrium populations can be used to determine the decay rates by detailed balance, and the population dynamics equations can then be solved to calculate the rate of nucleation of large, stable clusters.[2]

These quasi-equilibrium populations have traditionally been calculated from the thermodynamics or statistical mechanics of clusters. The populations are usually expressed in terms of a free energy of cluster formation. This is related to a partition function which involves an integral over all configurations of the molecules in the system. This can be recast in terms of cluster configurations, according to some definition of a cluster, as long as care is exercised to avoid the overcounting of configurations.

However, attempts to relate this formalism to the thermodynamic properties of liquid droplets (which are known, at least for large droplets) are plagued by problems involving the correct counting of degrees of freedom. The central difficulty seems to be to choose a cluster definition in the statistical mechanics which is consistent with the concept of a physical droplet. An equivalent statement of the problem is that the degrees of freedom of a cluster in the ensemble are

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not properly represented using the traditional surface free energy term. It is not at all clear what should represent the remaining degrees of freedom, which include translation and rotation. Corrections have been suggested, which include of the so-called *replacement* free energy, but there is no consensus about the form that this should take. Discussion of this point has continued for over 30 years.[4–6] These difficulties have prevented an unambiguous theory from emerging.

An alternative line of approach has involved the construction of phenomenological models of quasi-equilibrium cluster size distributions. These are employed in the manner described above to determine the decay rates and hence the stability of the clusters. However, instead of attempting to derive the quasi-equilibrium populations from fundamental statistical mechanics, a model is used which contains fitting parameters which are chosen to reproduce a variety of known vapor properties. The free energy expression used in the model will implicitly represent the available degrees of freedom.

Developments of this idea have been popular in recent years. This may partly be due to the ease with which predictions of observable properties can be made, and the avoidance of the theoretical difficulties mentioned above, while retaining some element of the underlying statistical mechanics. However, perhaps the most important factor in accounting for the activity in this area was the success achieved by the model proposed by Dillmann and Meier.[7] Using nothing more than the observed vapor critical properties and the second virial coefficient, the model seemed to account for observed nucleation rates, with no adjustable parameters. This success was tempered somewhat by necessary revisions to the theory,[8] but new developments have been proposed which seem to offer successful predictions once again.[9,10]

The models are in the main based upon the Fisher cluster model[11] which was introduced in 1967 in order to explain the behavior of vapors near their critical point. A history of the use of this model for describing cluster populations and nucleation rates is given in Sec. II. An often neglected point is that the model was originally derived and intended for use only for large clusters. In spite of this, the model has been used to describe small clusters including monomers and dimers. There is some doubt as to whether this can be justified, but there is nevertheless evidence that the extrapolation is reasonably successful.

This puzzle has been the principal motivation for this work. In order to resolve it, a more acceptable description of small clusters has been introduced into the phenomenological framework to produce a set of so-called virial/Fisher models. This is described in Sec. III. The error introduced by extrapolating Fisher's expression to monomers can then be examined, particularly at the critical point, which is a common reference point for many phenomenological models. It is also possible to study the new class of models at lower temperatures, which is discussed in Sec. IV. This would be more relevant to nucleation studies. The validity of Fisher's expression for all cluster sizes is then discussed in Sec. V, and conclusions reached.

II. HISTORY OF THE FISHER MODEL

The Fisher model was originally proposed for two purposes, namely the study of vapor condensation and the description of scaling behavior near the critical point.[11] The model specifies an analytical form for the cluster size distribution. When in thermal equilibrium at a temperature T, the number of clusters per unit volume consisting of i monomers of the condensible substance is given by

$$n_i = n_s \exp(-\Delta G_i / kT), \tag{1}$$

where k is Boltzmann's constant and the exponent, which may be treated as a free energy of cluster formation, is given by

$$\Delta G_i / kT = \Theta i^\sigma + \tau \ln i - \ln\left(\frac{q_0 kT}{p_s}\right) - i \ln S_1. \tag{2}$$

In Eq. (1), n_s is the total density of clusters, including all sizes, in the saturated vapor, and p_s is the pressure of the saturated vapor; that which is in equilibrium with a plane surface of the condensate at a given temperature. It is given by $p_s = n_s kT$, if inter-cluster interactions are neglected.

The term in Eq. (2) proportional to Θ may be viewed as a surface free energy, while the other two can be associated with entropic contributions, including the introduction of a replacement free energy. The parameters q_0, Θ, σ and τ are in the first instance unknown, but the proposed strategy is to choose them to ensure that the model correctly reproduces known properties of clusters and vapors. This is what makes the theory phenomenological.

S_1 is the supersaturation in the monomer density and is given by $S_1 = n_1 / n_1^s$, with n_1^s the monomer population when the vapor is saturated at the given temperature. At low temperatures S_1 is equal to the usual vapor supersaturation $S = p/p_s$, where p is the actual vapor pressure, but at high temperatures, particularly close to the critical point, the difference between S and S_1 is important, as was noted recently.[12]

Fisher used his model to prove the existence of a singularity at the coexistence point on the model isotherm, which signals the onset of the condensation phase transition without reference to a Maxwell construction across a van der Waals-type loop. This picture was later revised slightly when additional effects were taken into account.[13]

However, the focus of Fisher's attention was scaling near the critical point. In this region of the phase diagram a number of physical phenomena are controlled by the populations of large clusters, in particular the manner in which various quantities such as the specific heat diverge. Large clusters assume an important role near the critical point since their relative proportion in the mixture rises due to a reduction in the surface free energy with temperature. Fisher showed that critical scaling was brought about by the temperature dependence of the Θ term, which vanishes linearly as T approaches the critical temperature T_c, and that the terms in Eq. (2) were the minimum required to account for the behavior of the vapor pressure, density, and specific heat. He showed that observed scaling exponents could be repro-

duced by using $\sigma \approx 2/3$ and $\tau \approx 2.2$ (in three dimensions). The phenomenological character of the model is reflected by the fitting of these parameters to experiment.

However, the form proposed by Fisher for n_i in Eqs. (1) and (2) is justified theoretically only for large values of i.[11] This was ideal for the purpose of studying critical divergences, but it is rarely emphasized that the Fisher model has no clear foundation for application at low values of i. Unfortunately, the theory of homogeneous nucleation typically requires a detailed knowledge of the populations of clusters of only a few tens of monomers, a range where the validity of the Fisher model is suspect.

The extension of the model down to small clusters is comparable to the capillarity approximation of classical nucleation theory, according to which small clusters are considered to be liquid spheres with densities and surface energies equal to those of the bulk condensate. This approximation is quite rightly viewed as unsatisfactory. However, the use of the Fisher model for monomers and dimers is even more dangerous since these populations have an important effect on the parametrization of the model, and hence the nucleation rate predictions.

In spite of this lack of a firm foundation, models have been constructed involving such an extrapolation of the Fisher model down to monomers. One of the earliest, due to Kiang,[14] proposed that Eqs. (1) and (2) are valid for all i, so that the vapor pressure is given by

$$p = \sum_{i=1}^{\infty} n_i kT, \tag{3}$$

and the number of molecules per unit volume is

$$\rho = \sum_{i=1}^{\infty} i n_i, \tag{4}$$

with n_i given by Eqs. (1) and (2). Note that it is assumed that the clusters are noninteracting, so that each population makes a contribution towards the vapor pressure according to Dalton's law. Kiang then showed that the observed compressibility factors at the critical point $Z_c = p_c / (\rho_c k T_c)$ (where the suffix denotes critical properties) were, for a wide range of substances, consistent with the form

$$Z_c = \sum_{i=1}^{\infty} i^{-\tau} \Big/ \sum_{i=1}^{\infty} i^{-(\tau-1)} = \zeta(\tau)/\zeta(\tau-1), \tag{5}$$

using the value $\tau \approx 2.2$ obtained from scaling properties. $\zeta(\tau)$ is the Riemann zeta function. Equation (5) is obtained from Eqs. (1)–(4) by setting $\Theta = 0$, which is the defining characteristic of the critical point, and p_c, ρ_c, and T_c are the pressure, molecular density, and temperature of the vapor, respectively, at the critical point. Although Kiang expressed some doubt that the Fisher model was really valid at such low i, the agreement between experimental values of Z_c and the model predictions was a powerful inducement to accept the hypothesis. [More precisely, Kiang used the experimental

Z_c to fit the value of τ using Eq. (5) and showed that it was close to the value required by Fisher's analysis of critical exponents.]

The next step was to use the model to study nucleation phenomena away from the critical point. This was carried out by Kiang et al.[15] and later by Hamill et al.[16] In these treatments, the parameter Θ was chosen such that the low temperature imperfect properties of the vapor were reproduced. This was equivalent to introducing a size independent microscopic surface energy and relating it to the low temperature second virial coefficient of the vapor. The parameter q_0 was obtained from a critical point parameter such as the molecular density:

$$\rho_c = q_0 \zeta(\tau - 1). \tag{6}$$

Another development was to use the extrapolated Fisher model to represent the equation of state of vapor for the full range of temperatures between the triple point and the critical point.[17]

The step taken by Dillmann and Meier,[7] which reignited interest in the Fisher cluster model, was to extend the theory further, once again imposing upon the model a consistency with observed cluster properties. For large cluster sizes, and for temperatures well below the critical temperature, the free energy of formation should tend towards that of a macroscopic liquid drop. That is, for large i, Θ should approach $A_1 \gamma_\infty / (kT)$, where $A_1 i^{2/3}$ is the surface area of a spherical droplet containing i monomers at the bulk liquid density, and γ_∞ is the surface tension of a planar interface. In order that this should be consistent with the Θ chosen by Kiang et al.[15] and Hamill et al.,[16] i.e., with the low temperature equation of state, Θ has to be size dependent. Dillmann and Meier wrote

$$\Theta_i = \kappa_i A_1 \gamma_\infty / (kT), \tag{7}$$

where κ_i is a set of unknown correction factors. Again assuming that the Fisher model can be applied to all cluster sizes, the lowest few κ_i can be related to terms in a virial expansion in order to reproduce the low temperature imperfect vapor behavior. To describe higher κ_i, Dillmann and Meier suggested the ansatz:

$$\kappa_i = 1 + \alpha_1 i^{-1/3} + \alpha_2 i^{-2/3}. \tag{8}$$

The coefficients α_1 and α_2 can be found in terms of κ_1 and κ_2 and hence virial coefficients. The form of this ansatz was motivated by demanding that the model should be consistent with another cluster property: the curvature dependence of the bulk surface tension as derived in classical thermodynamics by Tolman.[18]

Actually, it is another gross assumption that the Tolman form (in fact a truncated expansion of the Tolman expression) should apply for all cluster sizes including monomers. Perhaps it is better to consider the Dillmann–Meier free energy to be a general expansion in $i^{1/3}$. Nevertheless, the Dillmann–Meier model was found to provide excellent fits to experimental data, with all the model parameters determined by measured experimental information. Interest in Fisher-based phenomenological models was thus kindled.

Some revisions of the Dillmann–Meier theory were necessary to overcome an internal inconsistency,[8] and the revised predictions agreed less well with the experiment. However, there have been further developments of the model which have restored a fair degree of agreement, including the introduction[9] of a temperature dependent exponent σ to make sure that both the critical and low temperature surface area scaling behavior are reproduced. Another approach was to make τ a free parameter at temperatures away from the critical point.[19] A further development by Kalikmanov and van Dongen[10] is to set $\alpha_2 = 0$ (this term can be absorbed into q_0 anyway) but to choose α_1 such that the saturated vapor pressure p_s at *any* temperature is reproduced by the model. The Dillmann–Meier model reproduced only the low temperature vapor pressure (by fitting to the first two virial coefficients): a fit to p_s is an attempt to match all the virial coefficients, at vapor-liquid coexistence. In this sense, the Kalikmanov–van Dongen theory should approach the (revised) Dillmann–Meier theory at low temperature, but ought to provide a better description at higher T.

All these models are based on the assumption that a single analytic expression can model the cluster populations for all sizes. At the critical point, the models are identical to those studied by Fisher[11] and Kiang,[14] since $\Theta = 0$. Therefore, a study of the validity of the Fisher model at the critical point is relevant to the whole class of models. This is the main purpose of the present article, which will be developed in Sec. III.

III. VIRIAL/FISHER MODELS AT THE CRITICAL POINT

The pattern which emerges from the history given above is one of progressive extension of the Fisher model of noninteracting clusters to take account of an increasing range of experimentally determined vapor and cluster properties. Throughout, however, the assumption is made that the model applies for all cluster sizes. This extrapolation is supported by indications[5,20] that a complete statistical mechanical description of the cluster free energy of formation should include logarithmic and constant terms similar to those in Eq. (2), although there is wide variation in the coefficients of such terms between models. More decisively, there is evidence that the model is successful in predicting both nucleation rates and vapor properties. A powerful demonstration of the success and limitations of the original Fisher model was provided by Binder and Stauffer[21] in the context of cluster populations in a kinetic Ising model. Cluster distributions in saturated and supersaturated states were described well by the model, but significantly, there were deviations for small i, as might be expected.

The description of monomer and dimer populations within the Fisher model is clearly a matter for concern. In this work we examine the consequences of using a virial expansion to describe the small cluster populations, while retaining the Fisher expression for larger sizes. Hence the models are referred to as virial/Fisher models. We shall examine how well the two branches of the model (virial for small i, Fisher for large i) join together, and how sensitive

the predictions are to the choice of when to switch between descriptions.

A. Virial branch

First, we refer to Saltz[12] who showed how a cluster model could be related to a virial expansion. It is important to note here that a direct relation between populations of real, physical clusters and virial coefficients is valid only if we assume the intermolecular interaction to be strong and short range. In other words, we assume the clusters considered in the model do not interact with each other. As noted earlier, this is an implicit assumption of all the Fisher models: each cluster population is assumed to contribute an independent partial pressure to the total vapor pressure [see Eqs. (3) and (4)] without interactions between them being taken into account. Therefore consistency within the model *requires* us to make the connection between measured virial coefficients and the cluster populations.

We write the cluster populations in the general form:

$$n_i = n_s \beta_i S_1^i, \tag{9}$$

so that β_i is the fraction of i-clusters in the vapour at coexistence, as a proportion of all the clusters present. The essence of the virial/Fisher approach is summed up in the following normalization condition:

$$1 = \sum_{i=1}^{\infty} \beta_i = \sum_{i=1}^{N} \beta_i^{\text{virial}} + \sum_{i=N+1}^{\infty} \beta_i^{\text{Fisher}}, \tag{10}$$

indicating that different models are used to describe the cluster fractions in the small and large size regimes, with a crossover size defined at $i = N$.

Beginning with the virial branch of the model, we write the virial expansion in the form

$$\frac{p}{\rho} = kT + \sum_{i=2}^{\infty} B_i p^{i-1}, \tag{11}$$

where B_i is the ith virial coefficient. We follow Saltz[12] who showed that within a noninteracting cluster model, the following relationships hold between the lowest few cluster fractions (at coexistence) and the first few virial coefficients:

$$\beta_2^{\text{virial}} = -\bar{B}_2 \beta_1^2, \tag{12}$$

$$\beta_3^{\text{virial}} = \tfrac{1}{2}(3\bar{B}_2^2 - \bar{B}_3)\beta_1^3, \tag{13}$$

where the dimensionless virial coefficients $\bar{B}_i = p_s^{i-1} B_i/(kT)$ have been introduced. It is therefore apparent that as long as the virial coefficients are known (which is often only true for B_2 and no further) the virial branch of the model contains one undetermined parameter, namely β_1, the monomer fraction in the mixture.

B. Fisher branch

Turning to the Fisher branch of the model, we find by examining Eq. (2) that

$$\beta_i^{\text{Fisher}} = \left(\frac{q_0 kT}{p_s}\right) \exp(-\tau \ln i - \Theta i^\sigma) \tag{14}$$

and at the critical point, the second term in the exponent vanishes since $\Theta = 0$. Since accordance with critical exponents requires $\tau = 2.2076$,[22] there remains a single parameter determining the Fisher branch of the model, namely q_0.

We can now write the normalization condition, Eq. (10), in a variety of forms, depending on where we switch over from a virial to a Fisher description of the population fractions:

$$1 = \beta_1 + \sum_{i=2}^{\infty} \beta_i^{\text{Fisher}} \tag{15}$$

$$= \beta_1 - \bar{B}_2 \beta_1^2 + \sum_{i=3}^{\infty} \beta_i^{\text{Fisher}} \tag{16}$$

$$= \beta_1 - \bar{B}_2 \beta_1^2 + \frac{1}{2}(3\bar{B}_2^2 - \bar{B}_3)\beta_1^3 + \sum_{i=4}^{\infty} \beta_i^{\text{Fisher}}, \tag{17}$$

where the choice of right hand sides corresponds to $N = 1, 2,$ and 3, respectively.

A similar series of expressions can be written for the mean cluster size, $\sum_{i=1}^{\infty} i n_i / n_s$, which is equal to the ratio of the molecular density to the total cluster density at coexistence:

$$\frac{\rho_s}{n_s} = \frac{\sum_{i=1}^{\infty} i n_i}{\sum_{i=1}^{\infty} n_i} = \beta_1 + \sum_{i=2}^{\infty} i \beta_i^{\text{Fisher}} \tag{18}$$

$$= \beta_1 - 2\bar{B}_2 \beta_1^2 + \sum_{i=3}^{\infty} i \beta_i^{\text{Fisher}} \tag{19}$$

$$= \beta_1 - 2\bar{B}_2 \beta_1^2 + \frac{3}{2}(3\bar{B}_2^2 - \bar{B}_3)\beta_1^3$$
$$+ \sum_{i=4}^{\infty} i \beta_i^{\text{Fisher}}. \tag{20}$$

The suffix s denotes the value at saturation, or coexistence.

Equations (15)–(17) and (18)–(20) provide the two conditions which fix the two unknown parameters in the model β_1 and q_0. The ratio ρ_s / n_s is simply equal to $1/Z_s$, the inverse of the compressibility factor $Z = p/(\rho kT)$ evaluated at vapor saturation. In order to parametrize the model at a given temperature, one needs information regarding this quantity. It can be obtained from experimental data or empirical equations of state.[12] We shall briefly examine the simplest possible virial/Fisher model for temperatures below the critical temperature in the next section. However, for now we concentrate on the critical point, since as described in Sec. II, the surface term Θi^σ has been treated in different ways within different models, and would introduce too many options for theoretical development. This would confuse the issue we wish to address, namely whether the Fisher model is appropriate for small clusters. At the critical point, all the

TABLE I. Parameters and first few cluster fractions β_i for various virial/Fisher models of molecular clusters at the critical point (with N the highest cluster size represented by the virial branch) compared with those of the original Fisher model.

Model	q_0/ρ_c	β_1	β_2	β_3
Original Fisher ($N=0$)	0.1512	0.6610	0.1473	0.0612
Virial/Fisher $N=1$	0.1965	0.5832	0.1858	0.0759
$N=2$	0.1996	0.6300	0.1352	0.0771
$N=3$	0.2017	0.6416	0.1402	0.0590

Fisher-based models reduce to the same form since $\Theta = 0$ by definition. The conclusions reached under these conditions are more general.

Having now derived a class of mixed virial/Fisher models which can be used to represent vapor properties, we now consider the sensitivity of the model to the cluster size at which the Fisher representation takes over from the virial description.

C. Application

At the critical point, we attach a suffix c to various substance properties instead of the suffix s used at other temperatures. We consider water as the prime example, since its third virial coefficient is fairly well known, at least compared to other materials. For water we have $Z_c = 0.229$,[7] together with dimensionless virial coefficients $\bar{B}_2 = -0.341$ and $\bar{B}_3 = -0.0988$ at the critical point. These virial coefficients are based on measured values tabulated in Ref. 23. The deduced parametrization of various virial/Fisher models is shown in Table I. The original Fisher model [$N = 0$, or equivalently β_i given by Eq. (14) with $\Theta = 0$ for all i] is parametrized using $\tau = 2.166$ [based on a fit to Z_c (Ref. 7)] since β_1 is then determined by q_0 and is not a free parameter in the model. For the other models, the value $\tau = 2.2076$ is used based on critical scaling behavior.

The cluster fractions up to size $i = 6$ are shown in Fig. 1. With the choice of axes made in the figure, the curves for the larger clusters are straight lines with a constant gradient equal to $-\tau$. They differ only to the extent that q_0 changes from model to model. The relatively small changes in q_0 shown in Table I, in spite of larger changes in β_{1-3}, lead to small differences in cluster fractions in the larger size classes as the junction between the virial and Fisher branches of the model is varied.

Although the lack of information on higher virial coefficients has not allowed an examination of crossovers between descriptions beyond $N = 3$, it is not unreasonable to suggest that if the crossover point is moved to larger N, similar pictures will emerge.

A similar analysis has been performed for the substance n-nonane. The input data are $Z_c = 0.256$ and $\bar{B}_2 = -0.3904$.[7] The second virial coefficient is obtained from the correlation given in Ref. 7. In this case, the third virial coefficient is not well enough known and so we shall limit ourselves only to the first two virial/Fisher models given by Eqs. (15) and (16) and (18) and (19), together with
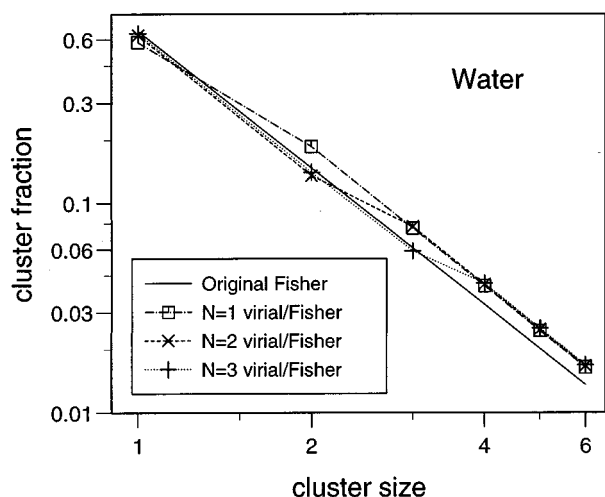
FIG. 1. Molecular cluster population fractions for water at its critical point according to various virial/Fisher models and the original Fisher model. The virial/Fisher models shown differ according to the size at which the description changes from an expression based on a virial series to an expression based on the Fisher model. The legend indicates the cluster size at which the virial description ends. Note that the Fisher prediction is a good approximation to the entire size range.

the predictions of the original Fisher model ($N=0$) which is now characterized by $\tau=2.190$.[7] The cluster fractions at the critical point for this substance are shown in Fig. 2. The insensitivity to the crossover point is even more pronounced than was the case for water.

Cluster fractions at the critical point for the substances methanol, ethanol, n-propanol and n-butanol are shown in Fig. 3 for the $N=2$ virial/Fisher model. As with n-nonane, physical data are taken from Ref. 7. The input data and the derived fitting parameters for this model are given in Table II. The size distributions are all fairly smooth at the junction between the two branches of the theory. Note that as the
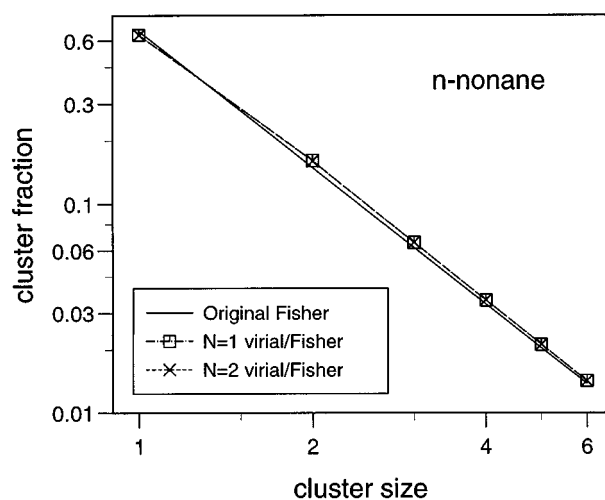

FIG. 2. Cluster fractions for n-nonane at its critical point according to the first two virial/Fisher models and the original Fisher model, using data from Table II and Ref. 7.
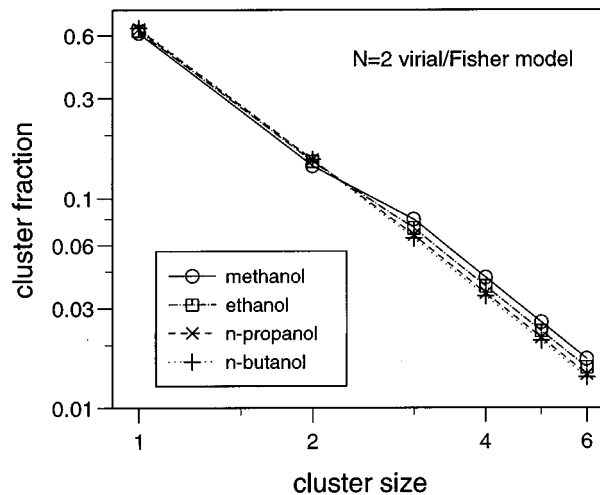

FIG. 3. Cluster fractions for the $N=2$ virial/Fisher model for a number of substances, using data given in Table II and Ref. 7.

values in the virial branch decrease from substance to substance, the values in the Fisher branch increase to achieve the correct normalization.

The insensitivity of the cluster fractions to the substance studied is a consequence of the relatively small variation in the experimental values of the compressibility factor and the dimensionless virial coefficients at the critical point from substance to substance. This is, of course, a reflection of the success of laws of corresponding states. For example, the Van der Waals model predicts the critical values $Z_c=0.375$, $\bar{B}_2=-0.297$, and $\bar{B}_3=0.0725$. The Dieterici imperfect gas model suggests the values $Z_c=0.2706$, $\bar{B}_2=-0.406$, and $\bar{B}_3=0.0730$, respectively.[24] These values are universal to the extent that each law of corresponding states is obeyed, and are not too dissimilar to the values used above for the various substances.

Furthermore, it has been found that variations in the virial coefficients which are presented to the model do not lead to large variations in fitted parameters, so the models are not overly sensitive to experimental errors in the virial coefficients.

The major implication of these calculations is that the original Fisher model provides a description of small cluster populations which is numerically consistent with a more elaborate description based partly on a virial series, at least at the critical point.

TABLE II. Compressibility factor and dimensionless second virial coefficient at the critical point for various substances, used in calculating the cluster fractions shown in Fig. 3, together with fitted parameters β_1 and q_0.

Substance	Z_c	$\bar{B}_2$	β_1	q_0/ρ_c
methanol	0.224	−0.3742	0.6164	0.200
ethanol	0.240	−0.3740	0.6316	0.195
n-propanol	0.253	−0.3665	0.6444	0.191
n-butanol	0.259	−0.3610	0.6505	0.189

TABLE III. Compressibility factor[a] and dimensionless virial coefficients of water at various sub-critical temperatures.[b]

Temperature/K	Z_s	$\bar{B}_2$	$\bar{B}_3$
373	0.9836	−0.0147	$−2.17×10^{-4}$
473	0.9051	−0.0824	−0.011

[a]See Ref. 25.
[b]Derived from Reference 23.

IV. VIRIAL/FISHER MODELS AT LOW TEMPERATURES

Finally, we shall construct virial/Fisher models for temperatures below the critical temperature. This proceeds in exactly the same way as before, using input data for the required temperature, except that the Fisher branch cluster fractions are now given by Eq. (14) with $\Theta \neq 0$. We choose the exponent of the surface term to be 2/3, so that the new term is proportional to the droplet surface area, i.e.,

$$\beta_i^{\text{Fisher}} = \left(\frac{q_0 kT}{p_s}\right) \exp(-\tau \ln i - \Theta i^{2/3}). \tag{21}$$

There are a number of options for fixing the parameter Θ, but we choose the simplest prescription, as used in the original Fisher cluster model:

$$\Theta = \gamma_\infty A_1/(kT). \tag{22}$$

This is the Dillmann–Meier prescription, Eq. (7), without the correction factors κ_i. The model is once again illustrated for water. Thermodynamic data are taken from Ref. 7. The compressibility factor for saturated vapor Z_s is calculated using a simple empirical equation of state due to Keyes.[25] The virial coefficients are taken from Ref. 23, and are shown in Table III. The $N=0$ (original Fisher) model once again uses $\tau=2.166$ instead of the value based on scaling behavior. The cluster fractions at various temperatures as a function of the crossover point between branches of the theory are shown in Fig. 4.

In this case, we find that q_0, and therefore the cluster fractions along the Fisher branch, depend on the crossover point between descriptions. For the limited number of crossover sizes examined, there does not seem to be convergence to a crossover-independent solution. Consequently, the original Fisher model does not account for the entire size distribution of clusters with particular success at temperatures away from the critical point. The original Fisher model would not make a successful nucleation theory.

Virial/Fisher models might make better nucleation theories, but only if the predictions were independent of the crossover size. The simple surface energy term in Eq. (22) does not achieve this, and so more complicated expressions would be needed. The drawback is then that insufficient experimental data may be available to fix its form.

V. CONCLUSIONS

We have constructed models of quasi-equilibrium populations of noninteracting molecular clusters using a virial ex-
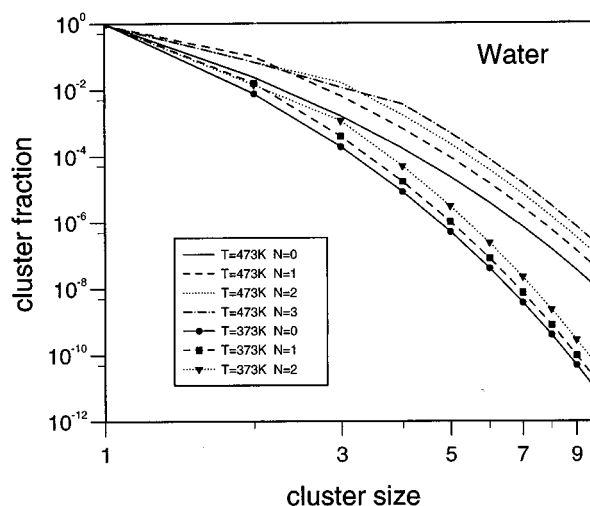

FIG. 4. Cluster populations for water at two sub-critical temperatures, with the surface term coefficient Θ given by Eq. (22), and for a range of virial/Fisher crossover points.

pansion for small clusters and a Fisher model for larger sizes. It has been possible to examine the sensitivity of the model predictions to the choice of when to swap from one description to the other.

It turns out that at the critical temperature, the model is not sensitive to the junction position, and furthermore that the original Fisher model then provides a good description of the entire size distribution, even monomers and dimers. In Fig. 1 the solid line is the original Fisher model for water and the others are various virial/Fisher model predictions, with the crossover point between descriptions varying from $N=1$ to 3. Similar calculations for various other substances repeat this behavior.

The implication is that at the critical point, the more elaborate virial/Fisher models proposed here are well approximated by the simpler Fisher model based on a single expression for the cluster populations at all sizes. This is a surprise, not only because the Fisher model was derived for large cluster sizes, as discussed earlier, but also because the algebraic structures of the two branches of the theory are quite different. The virial branch is a power series in β_1, with the density of i clusters given by $n_i \propto \beta_1^i$; whereas for the Fisher branch (at the critical point) the functional form is $n_i \propto i^{-\tau}$. Yet the two branches in Figs. 1–3 have a similar slope and axis intercept, when the parameters associated with each are adjusted to satisfy experimental data. This need not have been the case.

Because the Fisher model is (accidentally?) so successful at the critical point, it is no surprise that Kiang's analysis of critical compressibilities using this model gave encouraging agreement with the experiment.[14] It is then difficult not to suppose that a smooth curve can be used to describe quasi-equilibrium cluster populations at all temperatures, which is a fundamental assumption of the phenomenological approaches. Extended phenomenological models of the Fisher type, parametrized such that low temperature imperfect gas

behavior is reproduced,[7,9,10] have been used with some success, which is additional support for this view.

On the other hand, since the success of the Fisher model at the critical point seems to be coincidental to some extent, it may be unwise to assume that the model and its derivatives provide a good description of cluster fractions away from the critical point.

These concerns have been investigated by constructing a virial/Fisher model for low temperatures. This can be done if accurate compressibility factor data are available in order to fix the parameters. In addition, it is also necessary to decide how to treat the surface energy term: in the style of Kiang *et al.*,[15] Dillmann and Meier,[7] Delale and Meier,[9] or Kalikmanov and van Dongen.[10] Some of these approaches introduce additional unknown parameters. To illustrate the possibilities, the simplest surface energy term,[15] given in Eq. (22), has been used to produce such a model. For water at two subcritical temperatures, the predicted cluster fractions retain a dependence on the choice of crossover point between branches of the model, at least for the points investigated. Such behavior is not acceptable in the model. Surface terms which introduce a more complicated size dependence than Eq. (22) might improve matters, but introduce additional parameters which need to be fixed. The success of the Dillmann–Meier class of models may well lie in the fact that the functional form of the surface term chosen is such that a virial/Fisher model based upon it is insensitive to the crossover point.

At the critical point the model is much more straightforward since the Fisher expression is simpler ($\Theta=0$). Although critical conditions are far removed from those encountered in typical nucleation experiments, the behavior of the model at the critical point is an important test of the validity of the entire class of Fisher-derived models, and also a point of reference for the parametrization of such models.

In summary, the main motivation for this work was to resolve concerns that the Fisher model has been wrongly employed to describe all molecular cluster sizes. A more careful approach, taking into account known information about small clusters in the form of virial coefficients, leads to a model which is numerically quite similar to the original Fisher model, at least at the critical point, which is unexpected. Equivalently, the model predicts virial coefficients for these conditions with surprising success. For lower temperatures, the agreement is a function of the choice made for the surface term in the model. This underlines the relative success of the various derivatives of the basic Fisher model in nucleation theory.

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