Cluster velocity distributions in a vapor at equilibrium

Rodrigo Soto[a] and Patricio Cordero

Departamento de Física, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Santiago, Chile

We present the microscopic description of the vapor using the concept of cluster. Taking into consideration nonideal contributions, the distribution functions of every cluster species are obtained. From these distribution functions it is possible to derive kinetic ''temperatures'' associated with each cluster species and it is shown that the internal kinetic temperature and the kinetic temperature associated with the center of mass of the clusters are different from the thermodynamic temperature of the system as a whole. Molecular dynamic simulations show that the internal temperatures are smaller than the thermodynamic one, which is smaller than the kinetic temperatures for all cluster sizes. For the case of monomers more precise predictions can be made and they are in excellent agreement with our simulations. © *1998 American Institute of Physics.* [S0021-9606(98)50521-1]

I. INTRODUCTION

In a vapor at equilibrium, and not too far from the liquid-gas transition line, a large amount of clusters are present. Clusters are ensembles of molecules that can be thought of as small domains of the liquid phase. At equilibrium, the concentration of clusters with k molecules (clusters of size k) decays rapidly with size.

The properties of the vapor, both in and out of equilibrium, depend strongly on the microscopic properties of the clusters. In particular the process where the vapor condensates and transforms itself into a liquid is commonly described in terms of the concentration of clusters of different sizes. This model, the homogenous nucleation theory (HNT),[1–5] has been successful in describing the process but in some cases it fails by several orders of magnitude.[6–10]

HNT needs the equilibrium concentration of clusters and the rate of *successful reactions*, data that must come from microscopic models of the clusters. There are many articles predicting the equilibrium concentration of clusters, most of them assuming that the cluster gas mixture can be modeled as an ideal gas mixture, in which case the equilibrium concentration can be expressed in terms of the free energy of formation of a cluster.[11–20] The free energy can be calculated by means of thermodynamic models or directly from microscopic models. There have also been some works where excluded volume effects are taken into account[21–23] and detailed calculations were made in the Percus-Yevick approximation.[24] In a recent paper a new formalism based on a virial expansion that predicts the nonideal effects in the concentration of clusters is used.[25] This formalism shows good agreement with molecular dynamics simulations.

The other microscopic data necessary within the HNT is the rate of successful reactions, that is the probability per unit time that a cluster absorbs a monomer and increases its size, that can be expressed as the product of the collision rate between clusters and monomers and the *sticking coefficient*.

The latter is a measure of the fraction of collisions that are successful, namely, the reactions in which the monomer is actually absorbed by the cluster. Since this coefficient is quite difficult to estimate from a microscopic model, several phenomenological models have been put forward.[18,26] Also, some models that incorporate the internal degrees of freedom have been advanced.[27,28]

To be able to evaluate the collision rate between clusters and monomers it is necessary to have the equilibrium velocity distribution function for every species k. HNT assumes that every species k has a Maxwell distribution $f_k^{(0)}$ with the same temperature T as the system, and kinetic theory is used straightforwardly to derive the collision rates.

In this paper we first define the clusters in a dynamical way such that they are appropriate for a kinetic study of them, like HNT does. With this definition we prove that the distributions f_k associated with each cluster size are distorted Maxwellian distributions $f_k = (1 + \phi_k) f_k^{(0)}$ and the ''kinetic temperatures'' (proportional to the mean quadratic velocity) associated with these distributions depend on k and are different than the temperature of the gas as a whole.

In the following sections we define the *dynamical clusters* as a set of molecules that are energetically bound, as an improvement over the geometrical definition of clusters (set of molecules that are close together) and study some of their properties. Then we derive the equilibrium velocity distribution functions associated with the center of mass of the different species of clusters and prove some general properties for them. In particular we show that the mean quadratic velocity $\langle v^2 \rangle_k$ is different than the direct result derived from the temperature of the system. We are able to get an explicit expression for $\langle v^2 \rangle_{k=1}$ (monomers) and we compare it with the values that emerge from molecular dynamic (MD) simulations of our own, getting excellent agreement.

More specifically, in Sec. II we present the microscopic description of the vapor using the concept of cluster. In Sec. III we review the formalism developed in Ref. 25 and we display the velocity distribution function for clusters of any size. From these distribution functions f_k we derive in Sec.

[a]Electronic mail: rsoto@cec.uchile.cl

8989   © 1998 American Institute of Physics

IV expressions for a ''translational temperature'' T_k^{trans} and a ''temperature'' T_k^{int} associated with the internal degrees of freedom of every cluster species and prove that, in particular, $T_1^{\text{trans}} > T$, where T is the thermodynamic temperature of the system. These inequalities are valid irrespective of the particular molecular interaction potential. In Sec. V we describe our molecular dynamic simulations and show how the inequalities are satisfied in practice in different simulations. Also the simulations indicate that for all sizes $T_k^{\text{int}} < T < T_k^{\text{trans}}$. In Sec. VI there is a particularization to the case of monomers (clusters of size 1) and excellent agreement is shown between our simulations and our predictions. Section VII is dedicated to concluding remarks.

II. CLUSTER DEFINITION

In the following we study a gas of clusters at equilibrium considering nonideal contributions up to the first virial corrections. Microscopically, a vapor will be considered as a nonideal gas mixture where each species of clusters has a set of internal degrees of freedom. For the sake of simplicity we are going to consider a system made up of point ''molecules'' that have only translational degrees of freedom.

Even though the HNT extensively uses the concept of clusters there is no unique definition for them. The only indication is that clusters are microscopic domains of the liquid phase.[4,29] Usually a cluster is understood either as a set of molecules that are nearer to each other than a minimum distance,[23] as a set of molecules inside a spherical shell,[30] or a density fluctuation which exceeds a certain minimum.[31] These definitions have the advantage of simplifying the calculations but overestimate the number of clusters. The overestimation comes from accepting as cluster a set of particles that are coincidentally close with no further dynamical relation between them. Hence, a large number of these ''clusters by coincidence'' have a short mean life (of the order of the collision time). For example, in a collision between two particles there will be a short time in which the pair would be considered as a cluster (dimer) although the particles will not evolve together. Furthermore, for a given cluster, its size will fluctuate unphysically due to all the particles that just scatter with it.

Besides, HNT (based in the clusters dynamics) assumes the sequence of absorption and evaporation processes is Markovian. However, for geometrical clusters there is a large number of paired absorption-evaporation processes highly correlated, that correspond to the scattering processes described above. For example, if two monomers collide (absorption of one monomer by another) the instant when they dissociate (evaporation) can be calculated analytically. This implies that the two processes are highly correlated. The correlation reduces for larger clusters as the scattering time increases and the dynamics is more chaotic, making impossible the prediction of the evaporation time. Therefore, the distinction between dynamical and geometric clusters is only relevant for smaller clusters, where also the kinetic consequences to be studied are more important.

Hill[21,22] introduced the dynamical clusters in terms of ''bound'' and ''unbound'' potentials, similar to the

constraint-potential defined later in this article. The defined dimers correspond to a pair of bound particles, but for larger clusters the definition, although rigorous, does not give a clear dynamical interpretation.

We shall call cluster (*dynamical cluster*) a set of particles that in some sense are energetically bound. To define unambiguously a cluster we define first a function $C(\mathbf{r},\mathbf{v})$ that depends on the relative position and relative velocity of two particles, such that C is either 1 if the particles are energetically bound or 0 otherwise. Two particles are energetically bound if the particles are inside the potential well and with an energy lower than the maximum value of the effective potential $\varphi_{\text{eff}}(r)$ (that includes the centrifugal potential), then the precise expression for $C(\mathbf{r},\mathbf{v})$ is

$$C(\mathbf{r},\mathbf{v}) = \Theta\left(\varphi_{\text{eff}}(r_M) - \varphi(r) - \frac{mv^2}{4} \right)\Theta(r_M - r), \qquad (1)$$

where Θ is the Heaviside step function, m is mass of the particles, and r_M is the point where the effective potential reaches its maximum value.

We assume that the molecular potential is strictly of finite range. In this case there is always a maximum in the effective potential, which we assume is unique to simplify notation but in other cases the formalism is equally valid. The case where the potential is not strictly of finite range but decays faster than r^{-2} is studied in the Appendix.

To define clusters we introduce the concept of *linked* particles as follows: (i) if $C(\mathbf{r}_{ab},\mathbf{v}_{ab}) = 1$ then by definition a and b are *linked*, (ii) if particle a is linked with b and b is linked with c then a and c are linked. Finally, (iii) *two particles belong to the same cluster if and only if they are linked*.

Using this generic definition each microscopic state has a unique decomposition in clusters.

III. STATISTICAL FORMULATION FOR A GAS OF CLUSTERS

In this article we use the formalism developed in Ref. 25, which consistently considers the nonideal contributions in a gas of clusters and predicts accurately the vapor pressure and cluster concentrations.

The system is described as a gas mixture of different cluster species (in the grand canonical ensemble), where the interactions between the different ''particles'' take into account the full interaction between all the molecules composing each cluster. But, there is another interaction between clusters that comes from the definition of clusters. Since molecules in two different clusters, of sizes k and ℓ, cannot be energetically bound, there is a restriction relating the values of the variables of the molecules in each one of the two clusters. This restriction is imposed with a *constraint-potential* $U_{k\ell}^{\text{constr}}$ that becomes infinite if such restrictions are violated and is zero otherwise, then the Boltzmann factor suppresses all the configurations where particles in different clusters are bound.

Hence, the effective Hamiltonian that describes the cluster gas mixture is the sum of the energy for each cluster H_0^k (translational and internal energy of the clusters) and the to-

tal effective interaction between clusters V_{kl} (the molecular interaction between molecules composing the clusters plus the constraint potential).

The clusters are described giving their position, momentum and internal degrees of freedom ξ of each cluster. The internal degrees of freedom take values such that the particles in the cluster are bound.

Then, the system is studied using the virial expansion based in a formal diagrammatic expansion for the case of gas of clusters.[32,33] The expansion, valid for low density vapors, is used to calculate up to first nonideal correction the velocity distribution function $f_k(\mathbf{r},\mathbf{v})$ for clusters of size k.[25]

$$f_k(\mathbf{r},\mathbf{p})=\frac{1}{k!}\lambda^k\left[\int e^{-\beta H_0^k(\mathbf{r},\mathbf{p},\xi)}d\xi+\lambda\int e^{-\beta H_0^k(\mathbf{r},\mathbf{p},\xi)}\right.$$
$$\left.\times e^{-\beta p_1^2/2m}(e^{-\beta V_{k1}(\mathbf{r},\mathbf{p},\xi;\mathbf{r}_1,\mathbf{p}_1)}-1)\ d\mathbf{r}_1\ d\mathbf{p}_1\ d\xi\right],$$
$$(2)$$

where ξ represents the internal degrees of freedom of the cluster, and $\lambda=e^{\beta\mu}$ is the small quantity used in the diagrammatic method, with μ the chemical potential. The ideal Hamiltonian of a cluster of size k, H_0^k includes the translational kinetic energy $p^2/2km$ and the internal energy $U_k(\xi)$.

The correction to the zero order distribution comes from an average of the interaction between a cluster and the monomers.

IV. KINETIC TEMPERATURES

Some interesting properties can be derived from the generic expression (2). The limit of zero density (zero order approximation) of f_k is directly a Maxwell-Boltzmann distribution. But when the interaction with monomers is included it becomes distorted. Changing the integration variables of the monomer to those in the reference frame of the cluster, the distribution function can be written as

$$f_k(\mathbf{r},\mathbf{v})=f_k^{(0)}(\mathbf{r},\mathbf{v})\left[1+m^d\lambda\int F(\mathbf{r}_0,\mathbf{v}_0)\right.$$
$$\left.\times e^{-m(\mathbf{v}_0+\mathbf{v})^2/2T}d\mathbf{r}_0\ d\mathbf{v}_0\right],\qquad(3)$$

where

$$f_k^{(0)}(\mathbf{r},\mathbf{v})=(mk)^d\lambda^k q_k e^{-\beta mkv^2/2},\qquad(4)$$

$$F(\mathbf{r}_0,\mathbf{v}_0)=\left.\frac{\int e^{-\beta U_k(\xi)}(e^{-\beta V_{k1}}-1)d\xi}{\int e^{-\beta U_k(\xi)}d\xi}\right|_{\mathbf{r}=0,\mathbf{v}=0},\qquad(5)$$

$$q_k=\frac{1}{k!}\int e^{-\beta U_k(\xi)}d\xi,\qquad(6)$$

namely, the distribution function is the Maxwell-Boltzmann distribution $f_k^{(0)}$ corrected by the monomer-cluster interaction, integrated over all the possible configurations of the cluster and all the possible positions and velocities of the monomer (velocities measured in the reference frame of the cluster). The function F depends on velocities because the

constraint potential, which is part of the effective potential V_{k1}, depends on the relative velocity between the monomer and the cluster.

Before modeling the form in which the monomer interacts with the cluster we will derive an interesting general property. Let us calculate the mean quadratic velocity of a cluster of size k. Expanding the result to first order in λ yields

$$\frac{mk}{2}\langle v^2\rangle_k=\frac{d}{2}T\left[1+\lambda\frac{m^d}{k+1}\int d\mathbf{r}_0\ d\mathbf{u}\right.$$
$$\left.\times F\left(\mathbf{r}_0,\sqrt{\frac{2T(k+1)}{mk}}\mathbf{u}\right)\left(\frac{2}{d}u^2-1\right)e^{-u^2}\right],$$
$$(7)$$

where $\langle\cdots\rangle_k$ means an average evaluated using f_k.

Since for energetically defined clusters, the function F depends nontrivially on velocities, the above integral is generally not zero. Hence,

$$\frac{mk}{2}\langle v^2\rangle_k\neq\frac{d}{2}T.\qquad(8)$$

That is, the translational kinetic energy is not equal to the value obtained in simple statistical mechanics. The difference comes from the existence of the constraint potential that depends on velocities.

We will define the kinetic or *translational temperature* of a cluster as

$$T_k^{\text{trans}}=\frac{mk}{d}\langle v^2\rangle_k\qquad(9)$$

and the *internal temperature*

$$T_k^{\text{int}}=\frac{2K_k^{\text{int}}}{(k-1)d},\qquad(10)$$

where K_k^{int} is the internal kinetic energy divided by $(k-1)d/2$, because d degrees of freedom must be subtracted in the center-of-mass reference frame. T_k^{trans} plays an important role in the kinetic properties of the clusters.

The three "temperatures" that we are using are then the thermodynamic temperature T of the system and the translational and internal temperatures T_k^{trans}, T_k^{int} of the clusters k, and they turn out to be different. Only T, of course, is a true temperature.

It can be argued, and proved for the case of monomers, that the three temperatures satisfy,

$$T_k^{\text{int}}<T<T_k^{\text{trans}}.\qquad(11)$$

The restriction that the particles inside a cluster have to be energetically bound puts an upper limit on the relative velocities of the particles, and therefore the total internal kinetic energy per degree of freedom is less than $T/2$, giving $T_k^{\text{int}}<T$. From the equipartition theorem, the total kinetic energy should be equal to $T/2$ for each degree of freedom, then to compensate the energy deficit in the internal degrees of freedom, the translational ones must have more than $T/2$, giving $T<T_k^{\text{trans}}$.

To estimate the translational temperature for the case of large clusters it is necessary to model how a cluster interacts with a monomer. We will work the case when the temperature is low enough so that we can assume that the cluster is spherical and compact in the sense that the energy of the monomer inside the cluster would be infinite. Therefore,

$$F(\mathbf{r}_0, \mathbf{v}_0) = \begin{cases} -1 & r_0 \in \text{Volume} \\ G(\mathbf{r}_0, \mathbf{v}_0) & r_0 \in \text{Surface} \\ 0 & r_0 \in \text{External zone} \end{cases}. \tag{12}$$

Replacing this expression back in (3) implies that the mean quadratic velocity of the cluster is

$$\frac{mk}{2}\langle v^2 \rangle_k = \frac{d}{2} T \left[1 + \lambda \frac{m^d}{k+1} A_{cl} \Delta \frac{1}{\Delta} \int_\Delta dr_0 \, d\mathbf{u} \right.$$
$$\left. \times G\left(r_0 \hat{\mathbf{r}}, \sqrt{\frac{2T(k+1)}{mk}} \mathbf{u} \right) \left(\frac{2}{d} u^2 - 1 \right) e^{-u^2} \right], \tag{13}$$

where A_{cl} is the surface of the cluster, Δ the width of the interface and the integration is only over the radial component since the approximation $\Delta \ll R$ has been made.

From (13) it is seen that only the surface term contributes since the volumetric term, which corresponds to the -1 in F, vanishes when it is integrated. The contribution is of the order of the volume of the interface. For large k the correction goes to zero as,

$$\frac{T_k^{\text{trans}} - T}{T} = \mathcal{O}\left(\frac{A_{cl}\Delta}{k} \right)$$
$$= \begin{cases} \mathcal{O}(k^{-1/4}) & d=2 \\ \mathcal{O}(k^{-1/3}\sqrt{\log(k)}) & d=3 \end{cases}, \tag{14}$$

where we have used that $A_{cl} = \mathcal{O}(k^{(d-1)/d})$ and that the width of the interface is given by

$$\Delta = \begin{cases} \mathcal{O}(k^{1/4}) & \text{if } d=2 \\ \mathcal{O}(\sqrt{\log(k)}) & \text{if } d=3 \end{cases}, \tag{15}$$

as in Ref. 34. This result shows that in both two and three dimensions the correction to the translational temperature is more important for small clusters, where the distinction between the geometric and energetic clusters is important to the dynamics. The size dependence of the nonideal correction to the translational temperature should be compared to the nonideal correction to the cluster free energy,[25] which increases linearly with cluster size.

A. Monomers

In the case of monomers, it can be shown that the correction is always positive. In fact, in this case the cluster (monomer) does not have internal degrees of freedom, then the function F is reduced to,

$$F(\mathbf{r}_0, \mathbf{v}_0) = e^{-\beta V_{11}(\mathbf{r}_0, \mathbf{v}_0)} - 1. \tag{16}$$

The integration over velocities of the second term in F vanishes. Then the mean quadratic velocities for monomers is

$$\frac{m}{2}\langle v^2 \rangle_1 = \frac{d}{2} T \left[1 + \lambda \frac{m^d}{2} \int d\mathbf{r}_0 \, d\mathbf{u} \right.$$
$$\left. \times e^{-\beta V_{11}^{\text{constr}}(\mathbf{r}_0, \mathbf{v}_0)} e^{-\beta\varphi(r_0)}\left(\frac{2}{d} u^2 - 1 \right) e^{-u^2} \right]. \tag{17}$$

But the exponential of the constraint potential between two monomers vanishes if the two monomers are bound, which happens when the relative velocity u is small. Then this exponential acts as a lower limit in the integration in $u = |\mathbf{u}|$, where this lower limit depends on the position r_0, the relative orientation between $\mathbf{r}_0$ and $\mathbf{u}$, and the molecular potential. Moreover the integration in u,

$$\int_a^\infty du \, u^{d-1}\left(\frac{2}{d} u^2 - 1 \right) e^{-u^2}, \tag{18}$$

is always positive. Hence the correction in the mean quadratic velocities of monomers is always positive.

The conclusion is that *for any intermolecular interaction potential the monomers move (on average) faster than the thermal velocity associated with the temperature T of the system.*

V. MOLECULAR DYNAMIC SIMULATIONS

We have made molecular dynamic simulations of a two-dimensional system of particles interacting with a pair potential given by

$$\varphi(r) = \begin{cases} \infty & r < \sigma \\ -\varepsilon & \sigma < r < \alpha \, \sigma \\ 0 & r > \alpha \, \sigma \end{cases}, \tag{19}$$

where we have chosen units so that $m=1$, $\varepsilon=1$, $\sigma=1$ and we have set $\alpha=1.5$.

Our system has $N=10^4$ particles at temperatures and number densities n corresponding to the pure, homogeneous gas phase but with the presence of clusters. The boundary conditions are chosen to be periodic to avoid heterogeneous condensation. Systems like this one are known to relax to a state totally independent of the details of the initial condition. Given any microscopic state it is possible to identify the clusters present in it and from here to determine the instantaneous value of their properties.

For the case of the potential (19) the value of r_M in (1) is always $r_M = \alpha\sigma$. Then the function $C(\mathbf{r}, \mathbf{v})$ is,

$$C(\mathbf{r}, \mathbf{v}) = \Theta(\alpha\sigma - r)\Theta\left(\varepsilon + \frac{l^2}{m(\alpha\sigma)^2} - \frac{mv^2}{4} \right), \tag{20}$$

where l is the angular momentum.

In each simulation the system was relaxed until it reached equilibrium (at least constant temperature and constant number of clusters of each size). After relaxation the velocity distribution of the center of mass and the internal kinetic energy for the different cluster sizes k were measured. These measurements were made taking periodic snapshots of the system. Each snapshot was taken at regular intervals of about two collisions per particle. From the center-

TABLE I. Global density n and temperature T used in the molecular dynamics simulations.

	n	T
Simulation 1	0.02	0.602
Simulation 2	0.05	0.802
Simulation 3	0.05	0.987

TABLE II. Mean value of the fourth cumulant of the velocity distributions for different cluster sizes. The simulations are those of Table I.

Cluster size	Sim 1	Sim 2	Sim 3
1	0.001	−0.005	−0.010
2	0.004	0.000	−0.002
3	0.000	0.002	−0.001
4	−0.002	0.000	0.000
5	−0.008	0.004	0.004
6	0.003	0.003	0.004
7	−0.002	0.000	0.001
8	0.007	0.004	0.000
9	0.012	−0.009	0.000
10	−0.040	0.015	0.004

of-mass velocity distribution different moments of it were calculated, thus allowing the determination of the translational temperatures.

We have made simulations for different global conditions (density and temperature) which are shown in Table I.

In Fig. 1 one can see the translational and internal temperatures observed in the simulations described in Table I. For larger clusters the statistical error increases due to decreasing number of clusters as the size increases. All the simulations give results clearly satisfying our predictions. Also it seems that, within the error range, the translational temperature is always (not just for monomers) higher than the thermodynamic temperature.

Also, the fourth cumulant of the distributions, k_4, was measured to see how close to a Maxwellian about T_k^{trans} were the observed velocity distributions. The fourth cumulant is a standard way to measure the departure from a Maxwellian distribution. For an isotropic two-dimensional distribution, the adimensional fourth cumulant $\widehat{k_4}$ is defined by the following combination of the second and fourth moments:

$$\widehat{k_4} = \frac{8}{3} \frac{k_4}{\langle v^4 \rangle} = \left(1 - \frac{2\langle v^2 \rangle^2}{\langle v^4 \rangle} \right). \tag{21}$$

The results are shown in Table II. It can be seen that for all our simulations and for all the observed cluster sizes the fourth cumulant is quite small. Therefore it is justified to approximate the distribution to a Maxwellian not at T but rather *at the translational temperature* associated with each size.

VI. MONOMERS

Studying the case of monomers (free molecules) it is possible to get quantitative comparisons between our predictions and our simulations since in this case the different integrals of the distribution function can be reduced considerably. In fact, if we consider the intermolecular potential (19) in two dimensions we get from (3),

$$n_1 = n \, \exp\left[-n \, e^{\beta\varepsilon} \left(\pi(\alpha^2 - 1) \right. \right.$$
$$\left. \left. - \frac{1}{2} \int_1^{\alpha^2} dy \int_0^{2\pi} d\phi \, e^{-R} \right) \right], \tag{22}$$

$$\frac{m}{2} \langle v^2 \rangle = T \left[1 + \frac{n}{4} e^{\beta\varepsilon} \int_1^{\alpha^2} dy \int_0^{2\pi} d\phi \, R e^{-R} \right], \tag{23}$$

$$k_4 = \frac{3nT^2}{16} e^{\beta\varepsilon} \int_1^{\alpha^2} dy \int_0^{2\pi} d\phi \, R(R-2) e^{-R}, \tag{24}$$

with

$$R = \frac{\beta\varepsilon}{1 - y \, \sin^2\phi/\alpha^2}, \tag{25}$$

where n_1 is the density of monomers, and k_4 is the fourth cumulant of the distribution.

The density of monomers has been written in the form of an exponential to be able to compare it with the classic form given in the HNT where the exponent is basically the free energy associated with the formation of a cluster. When non-ideal contributions are considered, the free energy necessary to have a monomer is not zero because the particles in the neighborhood have to have an energy above a certain value to avoid being bound with the monomer.
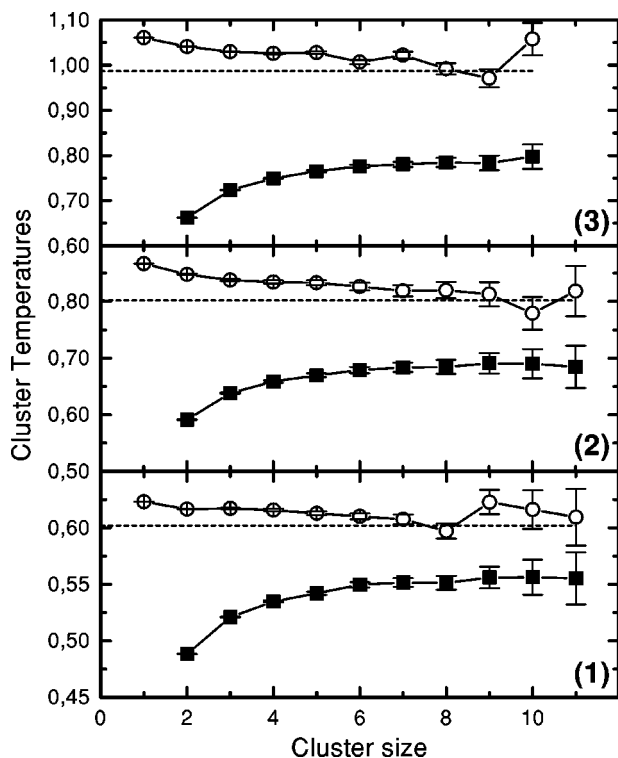

FIG. 1. Cluster temperatures as a function of cluster size. The open circles correspond to the translational temperature and the solid square to the internal temperature for different cluster sizes. The dashed straight lines show the values of the thermodynamic temperature. The simulations are those of Table I.

TABLE III. Comparison of the predicted and simulational properties for the monomers for the simulations under different conditions. The simulations are those of Table I.

	Sim 1		Sim 2		Sim 3	
	Theo	Sim	Theo	Sim	Theo	Sim
N_1	6858	6918	5591	5826	6497	6642
T_1^{trans}	0.625	0.623	0.868	0.867	1.06	1.06

In the simulations cited above we have measured these quantities getting excellent agreement with our predictions. In Table III there is a comparison between predictions and the results of our simulations.

VII. CONCLUSION

We have made a definition of clusters that allows a kinetic study of them. The clusters are defined using an energetic criterion instead as the usual distance criterion. With this definition we have studied a vapor at equilibrium, and it has been verified that when nonideal contributions are included to describe the vapor as a gas of clusters, the translational temperature of each cluster size is larger than the global temperature of the system. The extra energy comes from the internal degrees of freedom of the clusters which are colder because the clusters are energetically bound.

The predicted inequalities between the different temperatures have been corroborated qualitatively in several cases by means of MD simulations. For the predictions concerning different moments of the velocity distribution for monomers, an agreement within 4% was obtained.

ACKNOWLEDGMENTS

APPENDIX: CLUSTER DEFINITION FOR NONSTRICTLY FINITE RANGE POTENTIALS

If the interaction potential is not strictly of finite range, the definition (1) would count as clusters a pair of particles that are far away but their relative velocity is, by coincidence, small. To avoid this problem we should take a critical distance r_c such that particles whose separation is greater than r_c will not be taken as linked. But since in an isolated cluster energy is conserved, it is possible to have elongated orbits that cross this distance, making the size of the cluster to fluctuate unphysically. Then, if r_M (the point where the effective potential is maximum) is larger than r_c, the effective potential at r_c is evaluated $\varphi_c = \varphi(r_c)$, and two particles will be taken as linked if in their center of momentum frame, their total energy is lower than φ_c.

Then, the final expression for the function $C(\mathbf{r}, \mathbf{v})$ that we use is,

$$C(\mathbf{r}, \mathbf{v}) = \Theta\left(\varphi_{\text{eff}}(r_0) - \varphi(r) - \frac{mv^2}{4} \right)\Theta(r_0 - r), \quad (A1)$$

where

$$r_0 = \min\{r_M, r_c\}. \quad (A2)$$

The function defined above is strictly short range.

[1] R. Beker and W. Döring, Ann. Phys. (Paris) **24**, 719 (1935).
[2] Y. B. Zeldovich, Acta Physicochim. URSS **18**, 1 (1943).
[3] F. F. Abraham, *Homogeneous Nucleation Theory* (Academic, New York, 1974).
[4] J. D. Gunton, M. San Miguel, and P. S. Sanhi, in *Phase Transitions and Critical Phenomena,* edited by D. Domb and J. L. Lebowitz (Academic, London, 1983), Vol. 8, pp. 267–466.
[5] D. W. Oxtoby, J. Phys.: Condens. Matter **4**, 7627 (1992).
[6] V. I. Kalikmanov and M. E. H. van Dongen, Phys. Rev. E **47**, 3532 (1993).
[7] G. W. Adams, J. L. Schmitt, and R. A. Zalabsky, J. Chem. Phys. **81**, 5074 (1984).
[8] R. Strey, P. E. Wagner, and T. Schmeling, J. Chem. Phys. **84**, 2325 (1986).
[9] A. Kacker and R. H. Heist, J. Chem. Phys. **82**, 2734 (1985).
[10] C. Hung, M. Krasnopoler, and J. L. Katz, J. Chem. Phys. **92**, 7722 (1990).
[11] J. Lothe and G. M. Pound, in *Nucleation*, edited by A. C. Zettlemoyer (Marcel Dekker, New York, 1969).
[12] M. Blander and J. L. Katz, J. Stat. Phys. **4**, 55 (1972).
[13] A. Dillmann and G. E. A. Meier, Chem. Phys. Lett. **160**, 71 (1989).
[14] A. Dillmann and G. E. A. Meier, J. Chem. Phys. **94**, 3872 (1991).
[15] R. A. LaViolette and L. R. Pratt, Phys. Rev. A **28**, 2482 (1983).
[16] S. L. Girshick and Chia-Pin Chiu, J. Chem. Phys. **93**, 1273 (1990).
[17] J. Barrett, J. Phys. A **27**, 5053 (1994).
[18] P. Demo and Z. Kožíšek, Phys. Rev. B **48**, 3620 (1993).
[19] D. I. Zhukhovitskii, J. Chem. Phys. **100**, 1 (1994).
[20] D. W. Oxtoby and R. Evans, J. Chem. Phys. **89**, 7521 (1988).
[21] T. L. Hill, J. Chem. Phys. **23**, 617 (1955).
[22] T. L. Hill, *Statistical Mechanics: Principles and Selected Applications* (McGraw-Hill, New York, 1956).
[23] F. H. Stillinger, J. Chem. Phys. **38**, 1486 (1963).
[24] P. K. Swaminathan and D. Poland, J. Chem. Phys. **69**, 3660 (1978).
[25] R. Soto and P. Cordero, Phys. Rev. E **56**, 2851 (1997).
[26] D. Lippmann and W. C. Schieve, J. Phys. Chem. **97**, 3978 (1993).
[27] C. F. Wilcox and S. H. Bauer, J. Chem. Phys. **94**, 8302 (1991).
[28] K. Binder and D. Stauffer, Adv. Phys. **25**, 343 (1976).
[29] H. Furukawa and K. Binder, Phys. Rev. A **26**, 556 (1982).
[30] H. Reiss, J. L. Katz, and E. R. Cohen, J. Chem. Phys. **48**, 5553 (1968).
[31] H. Reiss, A. Tabazadeh, and J. Talbot, J. Chem. Phys. **92**, 1266 (1990).
[32] T. Morita and K. Hiroike, Prog. Theor. Phys. **25**, 537 (1961).
[33] J.-P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, 2nd ed. (Academic, London, 1990).
[34] J. S. Rowlinson and B. Widom, *Molecular Theory of Capillarity* (Clarendon, Oxford, 1982).