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Nonideal gas of clusters at equilibrium

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Good agreement is obtained between the predictions stemming from a theoretical framework to derive the cluster concentration and the pressure of a gas at low temperature with molecular-dynamic simulations of a simple fluid system. The theory is based upon a rigorous study that considers the nonideal contributions. In particular it is derived that the pressure is not simply the sum of partial pressures but it also includes a nonideal term. The present scheme represents an improvement over the ideal gas mixture approximation used in the *homogeneous nucleation theory*. [S1063-651X(97)09408-7]

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I. INTRODUCTION

Molecules in a gas at equilibrium and not too far from the liquid-gas transition line tend to form microscopic clusters. These clusters stem from local fluctuations of the thermodynamic variables and can be thought of as microscopic domains of the liquid phase. A gas, far from the critical point, that cannot be described ignoring the presence of these clusters will be called a *vapor* in the sense that it is a nonideal gas, but the nonideal effects come from low-temperature effects rather than from high density. In order to have a satisfactory description of a vapor at equilibrium or of the dynamics of condensation, it is necessary to understand the dynamics of clusters in the gaseous phase.

The theory that conceptually best describes the dynamics of these clusters is the homogeneous nucleation theory (HNT) [1–4]. This theory yields the evolution of the concentrations $N_k(t)/N$ of clusters of size k once some data are externally provided. These data are the concentration at (stable or metastable) equilibrium, $N_k(\infty)/N$, and the rate at which a cluster absorbs a monomer to become larger, also called the rate of *successful reactions*. The rate at which a cluster evaporates a monomer can be obtained from the previous data using detailed balance arguments. HNT is then a combination of kinetic considerations that determine the absorption of monomers by a cluster and thermodynamic considerations that allow the derivation of the concentrations at equilibrium associated with each cluster size.

Classical HNT uses the *capillary approximation* to determine the free energy of cluster formation, from which it is possible to derive the concentrations N_k/N. In this approximation it is assumed that the free energy is the sum of a volumetric and a surface term. In some cases the predictions that emerge from this construction differ by several orders of magnitude from the experimental values [5–9]. These discrepancies have led to a variety of modifications. Lothe and Pound [10] suggested improving the evaluation of the free energy involved in the cluster formation process by taking into consideration the conversion of the vibrational degrees of freedom into rotational ones. They managed to significantly improve the theoretical predictions, but later there was a polemic regarding the possibility that some terms are being counted twice. Blander and Katz [11] made a rigorous thermodynamic analysis of the expression for the free energy and concluded that the classical expression is not consistent with the definition. Later Dillmann and Meier [12,13] used Fisher's drop model to include curvature effects on the surface tension of a cluster. In a review article Oxtoby [14] clearly underlines that the process of nucleation is not well understood yet. There are many works that try to improve the thermodynamic description of clusters [5,15–19].

In the present article we study the nonideal behavior of a vapor, with particular attention to the pressure and the cluster concentrations N_k/N. With this aim we work with a formal virial expansion and find an expression for the pressure that differs significantly from the usual sum of partial pressures. All the works mentioned above assume that a vapor can be considered as an ideal mixture of k cluster gases.

II. CLUSTER DEFINITION

In the following we study a gas of clusters at equilibrium considering nonideal contributions up to first virial corrections. Microscopically, a vapor will be considered as a nonideal gas mixture in which 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 only have 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 [20,4]. Usually a cluster is understood either as a set of molecules that are closer to each other than a specified distance [21] or as a set of molecules inside a spherical shell [22], or a density fluctuation that exceeds a certain threshold [23]. One can also require that, besides proximity, the particles satisfy some energy requirement associated with the idea of forming a bound state.

We shall define a cluster as a set of particles that in some sense are bound together. For the moment, and without having to define every detail, it will suffice to use 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 or 0 with a well-defined criterion. We assume that $C(\mathbf{r},\mathbf{v})$ is of short range in positions. To define clusters we introduce the con-

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*Electronic address: rsoto@cec.uchile.cl cept of *linked* particles as follows: (i) If $C(\mathbf{r}_{ab},\mathbf{v}_{ab})=1$ then by definition a and b are *linked* and (ii) if particle a is linked with b and b is linked with c then a and c are linked. Finally, *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. One criterion used in the literature is equivalent to assuming that two particles are linked if they are closer than a certain distance r_0, namely, $C(\mathbf{r},\mathbf{v})=\Theta(r_0-r)$, where Θ is the Heaviside step function.

III. STATISTICAL FORMULATION FOR A GAS OF CLUSTERS

We choose to describe each microscopic state Ψ using the generic concept of cluster given above. Instead of describing the microscopic state by giving the position and velocity of each molecule in the gas, we describe Ψ giving the number of clusters of each size and the values of the degrees of freedom for each separate cluster, ordered by their size k. For a k cluster its degrees of freedom are the position of its center of mass, its total momentum, and its internal degrees of freedom: variables ξ. In d dimensions a cluster of size k of point molecules has $(k-1)d$ internal degrees of freedom. Specifically, the state Ψ can be written as

$$\Psi=(N_k,\{\mathbf{r}_\mu^k,\mathbf{p}_\mu^k,\xi_\mu^k\}_{\mu=1,\dots,N_k})_{k=1,2,\dots}, \tag{1}$$

where N_k is the number of clusters of size k and $\mathbf{r}_\mu^k$, $\mathbf{p}_\mu^k$, and ξ_μ^k are the coordinate and momentum of the center of mass and the internal degrees of freedom variables for the μth cluster of size k. The letters k,ℓ refer to cluster sizes, the greek letters μ,ν label particular clusters, and the letters a,b,c label the molecules inside a cluster.

Since particles in two different clusters μ and ν, of sizes k and ℓ, respectively, cannot be *linked*, there is a restriction relating the values of the variables of the particles in each of the two clusters [the function $C(\mathbf{r},\mathbf{v})$ cannot be 1]. Instead of imposing this condition through the limits of integration in the partition function, we introduce a *constraint potential* $U_{k\ell}^{\rm constr}$ that becomes infinite if such restrictions are violated and zero otherwise:

$$U_{k\ell}^{\rm constr}(\mu,\nu)=U_{k\ell}^{\rm constr}(\mathbf{r}_\mu,\mathbf{p}_\mu,\xi_\mu;\mathbf{r}_\nu,\mathbf{p}_\nu,\xi_\nu)=\begin{cases}\infty & \text{if there are particles } a,b \text{ such that } \; C(\mathbf{r}_{ab},\mathbf{v}_{ab})=1\\ 0 & \text{if } \; C(\mathbf{r}_{ab},\mathbf{v}_{ab})=0, \; \text{for all } \; a,b\end{cases} \tag{2}$$

where a is a particle in cluster μ and b in cluster ν, with $\mu\neq\nu$.

Hence the effective Hamiltonian of the system is

$$H=H_0+V, \tag{3}$$

$$\begin{aligned}H_0&=\sum_k\sum_\mu\left(\frac{p_\mu^{k2}}{2km}+U^k(\xi_\mu^k)\right)\\&=\sum_k\sum_\mu H_0^k(\mathbf{r}_\mu^k,\mathbf{p}_\mu^k,\xi_\mu^k)\\&=\sum_k\sum_\mu H_0^k(\mu),\end{aligned} \tag{4}$$

$$V=\sum_{k,\ell}\sum_{\mu,\nu}V_{k\ell}(\mathbf{r}_\mu^k,\mathbf{p}_\mu^k,\xi_\mu^k;\mathbf{r}_\nu^\ell,\mathbf{p}_\nu^\ell,\xi_\nu^\ell)=\sum_{k,\ell}\sum_{\mu,\nu}V_{k\ell}(\mu,\nu), \tag{5}$$

where H_0 includes the translational energy of the center of mass and the internal energy of each cluster (the kinetic energies of the particles relative to the center of mass of the respective cluster plus the internal potential energy) and V is the sum of the effective potential energies $V_{k\ell}(\mu,\nu)$ between all pairs of clusters. More specifically, $V_{k\ell}(\mu,\nu)$ is the molecular potential energies between all possible pairs of particles in clusters μ and ν plus the constraint potential $U_{k\ell}^{\rm constr}$ between them.

With this Hamiltonian the grand partition function is

$$\begin{aligned}\Xi=&\sum_{N_1,N_2,\dots}\left(\prod_k N_k!(k!)^{N_k}\right)^{-1}\\&\times\int dX\prod_k\prod_\mu z_k(\mu)\prod_{k,\ell}\prod_{\mu,\nu}e_{k\ell}(\mu\nu),\end{aligned} \tag{6}$$

where the integral on dX means integration over all coordinates, momenta, and internal degrees of freedom. The internal degrees of freedom of a cluster have a restricted domain, otherwise the particles in it would not be linked. Since $V_{k\ell}^{\rm constr}$ may depend on momenta the (usually trivial) momenta integrals cannot be directly evaluated. Furthermore, the combinatorial factor $[\Pi_k N_k!(k!)^{N_k}]^{-1}$ takes into account the different but equivalent forms of assigning labels to the clusters and particles inside them and

$$\lambda=e^{\beta\mu}, \tag{7}$$

$$z_k(\mu)=\lambda e^{-\beta H_0^k(\mu)}, \tag{8}$$

$$e_{k\ell}(\mu,\nu)=e^{-\beta V_{k\ell}(\mu,\nu)}=h_{k\ell}(\mu,\nu)+1, \tag{9}$$

where $\beta=1/T$ since units of temperature are chosen so that $k_B=1$ throughout this article and μ is the chemical potential.

From Eq. (6) it is possible to derive the distribution functions for each cluster size [24]

$$f_k(\mathbf{r}_1,\mathbf{p}_1,\xi_1)=z_k(1)\frac{\delta\ln\Xi}{\delta z_k(1)}. \tag{10}$$

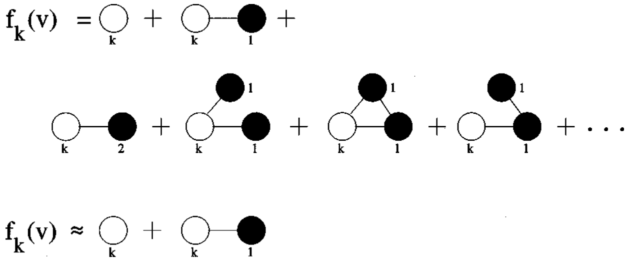

FIG. 1. Diagrams that represent the distribution function for clusters of size k. The upper figure represents the complete series and the lower one is the series truncated at the first virial order. See the text for an explanation of the different symbols.

Until now this description has been exact. Since we want to study low-density vapors we make a virial expansion of f_k and the technique used is the diagrammatic expansion defined in [24,25]. Given the form of the partition function (6), its logarithm has a simple diagrammatic expression

$$\ln \Xi = S, \tag{11}$$

where S is the sum of all the simply connected diagrams with black z_ℓ circles for all ℓ and $h_{k\ell}$ bonds between them.

We recall that a diagram is a compact notation to represent integral terms. Each diagram is formed by circles and bonds. Each circle represents a function that depends on the coordinates of only one cluster, while a bond represents a function that depends on the coordinates of two clusters. If the circle is black an integration over the variables associated with it is understood. There are some symmetry factors multiplying each expression.

Hence, from Eq. (10) the distribution function for clusters of size k is obtained from the sum of all the diagrams of $\ln \Xi$ that have at least one z_k circle. From each one of these diagrams one builds new diagrams transforming one black z_k circle to a white circle in all possible forms. Therefore,

$$f_k(r_1,v_1,\xi_1) = D, \tag{12}$$

where D is the sum of all the simply connected diagrams with one and only one white z_k circle plus any number of black z_ℓ circles (for all values of ℓ) and $h_{k\ell}$ bonds (see Fig. 1). Integrating this function over the internal degrees of freedom one, gets the distribution of positions and momenta for each species.

Each diagram in the expansion of f_k is of the order of a power of λ corresponding to the number of particles involved (the sum of the labels of each node). Since λ in a gas is proportional to the density, at low densities only the diagrams with lower powers of λ are kept. In this work we consider only the first virial correction, namely, we keep the first two powers of λ and therefore the only diagrams that are kept are of order λ^k and λ^{k+1}. Hence the distribution function to first order is the sum of a diagram consisting of a white z_k circle plus a diagram that consists of a white z_k circle, a black z_1 circle, and an h_{k1} bond (see Fig. 1).

This approximation corresponds to considering the clusters interacting only with a monomer. The explicit form for the distribution function is

$$f_k(\mathbf{r},\mathbf{p}) = \frac{1}{k!}\int z_k(\mathbf{r},\mathbf{p},\xi)d\xi + \frac{1}{k!}\int z_k(\mathbf{r},\mathbf{p},\xi) z_1(\mathbf{r}_0,\mathbf{p}_0) \times h_{k1}(\mathbf{r},\mathbf{p},\xi;\mathbf{r}_0,\mathbf{p}_0) d\mathbf{r}_0\, d\mathbf{p}_0\, d\xi. \tag{13}$$

The usual procedure found in the literature is equivalent to retaining only the lowest-order term (order zero), namely, an ideal gas of clusters, while we instead go one step further and consider the first-order contributions.

IV. CLUSTER CONCENTRATIONS

The number of clusters of size k in the system is given by

$$N_k = \int f_k(\mathbf{r},\mathbf{v}) d\mathbf{r}\, d\mathbf{v}, \tag{14}$$

which can be expressed as

$$N_k = Z_k \lambda^k + Z_{k1}\lambda^{k+1}, \tag{15}$$

while the partition functions Z_k and Z_{k1} are

$$Z_k = (2\pi k m T V) q_k, \tag{16}$$

$$Z_{k1} = [2\pi(k+1) m T V] q_{k1}, \tag{17}$$

$$q_k = \frac{1}{k!}\int d\xi\, e^{-\beta U(\xi)}, \tag{18}$$

$$q_{k1} = \frac{1}{k!}\int d\xi\, d\mathbf{r}\, d\mathbf{p}\, e^{-\beta U(\xi)} e^{-\beta p^2/2\mu}(e^{-\beta V_{k1}} - 1), \tag{19}$$

where V is the volume of the system, $\mu = mk/(k+1)$ is the reduced mass of the monomer-cluster system, and $\mathbf{r},\mathbf{p}$ are the phase-space coordinates of the monomer with respect to the cluster.

The total number of particles of the system up to the first virial correction is

$$N = N_1 + 2N_2 = Z_1\lambda + (Z_{11} + 2Z_2)\lambda^2. \tag{20}$$

The previous relation can be inverted to express λ in terms of the density $n = N/V$. The sign ambiguity is solved requiring that the ideal gas result is recovered in the low-density limit

$$\lambda = \frac{n}{2\pi m T}[1 + 2B(T)n], \tag{21}$$

where $B(T) = -(q_{11} + 2q_2)/2\pi T$ is, as we will see, the second virial coefficient.

Replacing this expression and Eqs. (16)–(19) in Eq. (15), it is possible to get the concentration of clusters in terms of

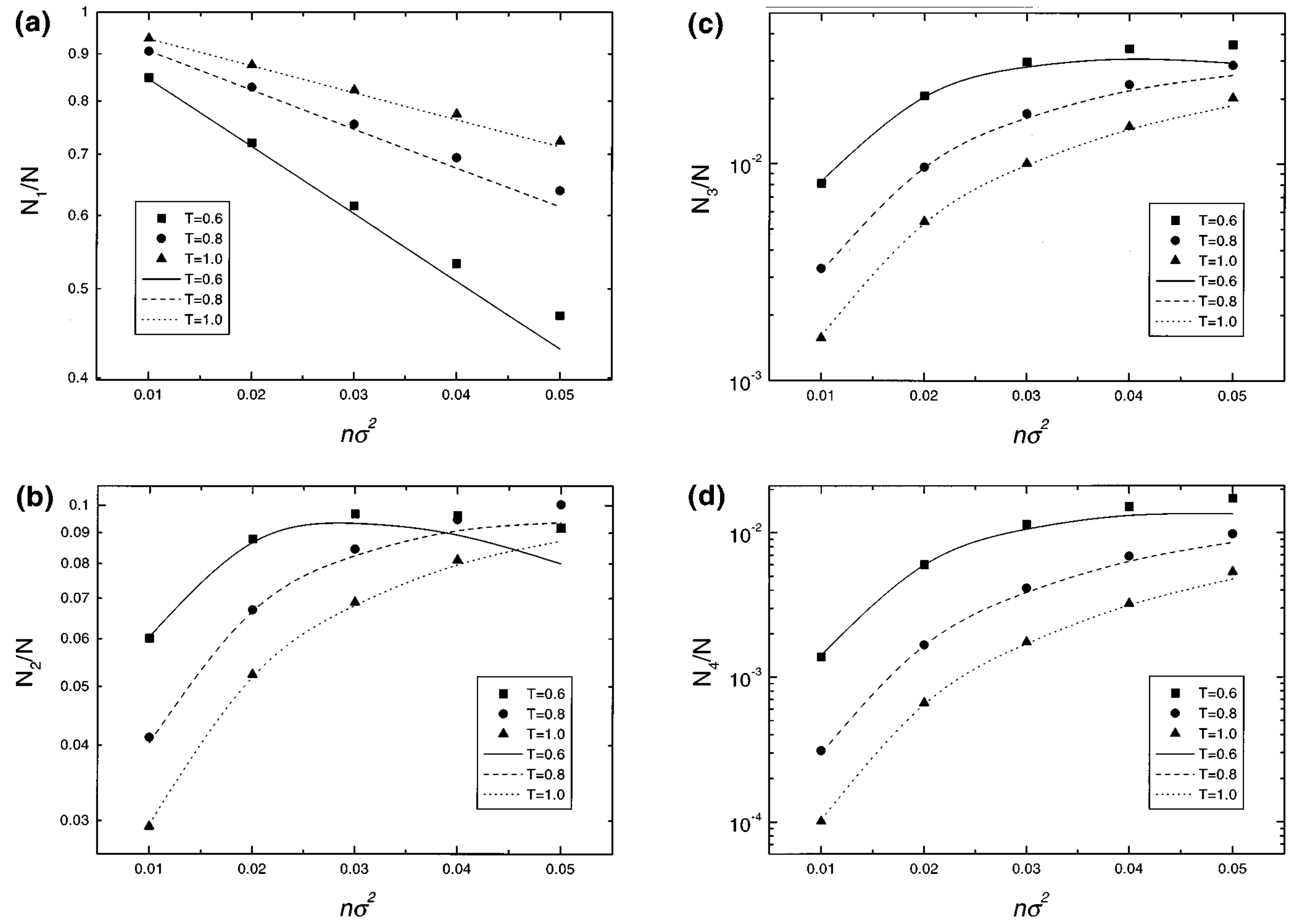

FIG. 2. Cluster concentrations for different sizes k as a function of the area density $n=N/V$. The symbol σ represents the disk diameter introduced in Eq. (31). The different curves correspond to three different temperatures. The symbols represent the results obtained directly from simulations, while the curves are our predictions up to the first virial correction for the potential (31). (a) Monomers, $k=1$, (b) dimers, $k=2$; (c) trimers, $k=3$; and (d) tetramers, $k=4$.

the density. In this expression only the first nonideal correction is kept, in order to be consistent with the order of the expansion. This correction is now written in an exponential form, instead of as a linear term, to be able to interpret it as a Boltzmann factor, as it will be explained later:

$$\frac{N_k}{N}=A_k(T)n^{k-1}e^{-C_k(T)n}, \tag{22}$$

with

$$A_k(T)=\frac{kq_k}{(2\pi mT)^{k-1}},$$

$$C_k(T)=-2kB(T)-\frac{(k+1)q_{k1}}{2\pi kTq_k}. \tag{23}$$

At low densities we recover the well known *law of mass action* [3]. The correction for finite densities corresponds to an excluded volume effect, which appears due to the nonideal free-energy cost necessary to make room for the cluster.

In the case of monomers $A_1(T)=1$ and therefore the relative concentration of monomers at low densities is almost one due to the negligible presence of clusters. At higher densities the exponential factor makes N_1 decrease, as expected. It is important to note that when nonideal contributions are not considered, the predicted relative concentrations of monomers is always one, independent of density.

After some algebra $C_k(T)$ can be written as

$$C_k(T)=-2kB(T)-\frac{\int d\mathbf{r}\,d\mathbf{v}\,e^{-\beta p^2/2\mu}\langle e^{-\beta V_{k1}}-1\rangle}{\int d\mathbf{v}\,e^{-\beta p^2/2\mu}}, \tag{24}$$

where μ, as before, is the reduced mass of the monomer-cluster system and the canonical average $\langle\ \rangle$ is over all the allowed configurations of the cluster. From this expression we see that both terms are proportional to the number of particles in the cluster plus a surface term, that is, $C_k(T)\sim Ak+Bk^{(d-1)/d}$.

V. VAPOR PRESSURE

Expressions for the vapor pressure can be obtained directly from Eqs. (11) and (19),

TABLE I. Comparison of the theoretical predictions for the concentrations of clusters (N_k/N) using the zeroth-order (ideal gas) and the first-order approximations (the latter being the present work) with the concentrations obtained in the simulations. The temperature is $T=0.8$ and the density goes from $n=0.01$ to $n=0.05$. For other temperatures the results are similar. Numbers in square brackets denote powers of 10 by which the preceding term is to be multiplied.

	Monomers, $k=1$			Dimers, $k=2$			Trimers, $k=3$			Tetramers, $k=4$		
n	Order 0	Order 1	Simulation	Order 0	Order 1	Simulation	Order 0	Order 1	Simulation	Order 0	Order 1	Simulation
0.01	1	0.90683	0.90629	0.0489	0.04036	0.04122	0.00421	0.00317	0.00329	4.304[−4]	2.98006[−4]	3.11[−4]
0.02	1	0.82235	0.82828	0.0978	0.06661	0.06700	0.01682	0.00959	0.00965	0.00344	0.00165	0.00167
0.03	1	0.74573	0.75500	0.1467	0.08247	0.08459	0.03785	0.01629	0.01705	0.01162	0.00386	0.00412
0.04	1	0.67626	0.69406	0.1956	0.09075	0.09467	0.06729	0.02186	0.02330	0.02755	0.00633	0.00688
0.05	1	0.61325	0.63865	0.2445	0.09362	0.10024	0.10514	0.02578	0.02865	0.05380	0.00856	0.00982

$$
\begin{aligned}
p &= \frac{T}{V}\ln \Xi \\
&= \frac{T}{V}[Z_1\lambda + (Z_{11}+2Z_2)\lambda^2/2] \\
&= T\left(n_1 + n_2 - \frac{q_{11}}{2\pi T} n_1^2 \right),
\end{aligned}
\tag{25}
$$

which, once written in terms of the density, becomes

$$
p = T\left(n - \frac{q_{11}+2q_2}{2\pi T} n^2 \right). \tag{26}
$$

From here it follows that the second virial coefficient is

$$
B(T) = -\frac{q_{11}+2q_2}{2\pi T}. \tag{27}
$$

We can see from Eq. (25) that p is not equal to the sum of the partial pressures of monomers and dimers (as it is usually assumed in the HNT) since the nonideal contribution coming from the monomer gas is as important as the dimers' partial pressure [they are both $O(\lambda^2)$].

Since most articles on HNT work in the isobaric-isothermal ensemble it is convenient to express the cluster's density in this ensemble in order to be able to make comparisons,

$$
\frac{N_k}{V} = \exp\left[-\beta\left(\Delta G_k^{(0)} + \Delta G_k^{(1)} \frac{p_{\mathrm{sat}}}{T} S \right) \right], \tag{28}
$$

where

$$
\Delta G_k^{(0)} = -T\ln\left[2\pi T^2 k q_k \left(\frac{p_{\mathrm{sat}}}{2\pi T^2} \right)^k \right] - Tk\ln S \tag{29}
$$

is the exact (without the capillary approximation) ideal-gas-mixture-approximation result for the free energy of a cluster if the partition function q_k is known. p_{sat} is the saturation pressure, p is the total pressure given by Eq. (26), and $S=p/p_{\mathrm{sat}}$ is the supersaturation.

The nonideal contribution to the free energy of a cluster is

$$
\Delta G_k^{(1)} = -T\left(kB(T) + \frac{k+1}{2\pi Tk} \frac{q_{k1}}{q_k} \right). \tag{30}
$$

VI. SIMULATIONS

We have made molecular-dynamic simulations of a two-dimensional system of hard disks interacting with a square well pair potential given by

$$
\varphi(r) = \begin{cases} \infty, & r<\sigma \\ -\varepsilon, & \sigma<r<\alpha\sigma \\ 0, & r>\alpha\sigma, \end{cases} \tag{31}
$$

where we have chosen units so that $m=1$, $\varepsilon=1$, and $\sigma=1$ and we have set $\alpha=1.5$. We simulated systems of $N=10^4$ particles at temperatures and number densities n corresponding to the pure homogeneous gas phase with a non-negligible presence of clusters. The boundary conditions used were 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.

To get the results that follow we have defined clusters as sets of particles energetically bound, that is, we have chosen

$$
C(\mathbf{r},\mathbf{v}) = \Theta(\alpha\sigma - r)\Theta(\varepsilon - mv^2/4). \tag{32}
$$

This definition tends to guarantee a longer mean lifetime for clusters than the usual geometrical definition, where particles can be close just by coincidence, with no dynamical relation between them. This gives clusters an identity that lasts longer than the mere coincidence in space does because particles are in some sort of bound state. We must stress that such a choice of $C(\mathbf{r},\mathbf{v})$ is one possibility of many others equally valid and useful.

In each simulation the system was relaxed until it reached equilibrium (at least constant temperature and constant number of clusters of each size). Then the numbers N_k of clusters of size k were measured. These measurements were made taking snapshots of the system at regular intervals of about two collisions per particle. Given the microscopic state, it is possible to identify the clusters present in it and from here to determine the instantaneous value of their properties.

We made simulations for number densities (in units of σ^{-2}) $n=0.01$, 0.02, 0.03, 0.04, and 0.05 and temperatures (in units of ε) $T=0.6$, 0.8, and 1.0. These conditions ensure that the system is not in the coexistence zone. In each simulation we measured the number of clusters of each size. In the gaseous phase the free energy $\Delta G_k^{(0)} \sim Ak$ if k is large enough and A is a positive constant. Hence the number of clusters of size k decreases exponentially with k. It is understandable then that only the smallest size clusters could be studied reliably.

Using the potential (31) and the cluster definition given in Eq. (32), it is possible to study the functions q_k and q_{k1} for different temperatures using Monte Carlo integration [26]. These integrals are obtained by sorting coordinates and momenta for the particles belonging to the cluster and to the monomer. From these phase-space variables we evaluate the exponential of the internal energy $e^{-\beta U(\xi)}$ and the exponential of the interaction potential $e^{-\beta V_{k1}}$ and therefore the integrand.

Figure 2 presents a comparison of the simulational and theoretical results (22) and (23). It can be seen that the agreement is quite good even at relatively high densities. It is seen that our theory, which includes a nonideal correction, correctly predicts the saturation of the concentration of clusters when the density increases. This saturation occurs because the total number of particles is kept fixed and at higher densities more particles are part of larger clusters.

Table I gives a comparison for $T=0.8$ between simulations and theory using the zeroth-order approximation (usual in HNT applications) and the first-order approximation as presented in this work. It is seen that the zeroth-order approximation fails badly at higher densities even though the system is still a gas. The first-order approximation gives a notorious improvement with errors under 10%. The corresponding tables for the other temperatures considered in our study give equally good results.

TABLE II. Different expressions for the pressure as a function of the density for $T=0.8$: $p1$, exact pressure (up to the third virial correction); $p2$, sum of the partial pressures using the zeroth-order densities (HNT); $p3$, sum of partial pressures and the nonideal contribution from the monomers using the cluster densities predicted up to first order (present work).

n	$p1$	$p2$	$p3$
0.01	0.007739	0.00843	0.00768
0.02	0.014980	0.01789	0.01456
0.03	0.021755	0.02871	0.02050
0.04	0.028094	0.04129	0.02546
0.05	0.034032	0.05614	0.02945

Table II shows the pressure of the system at $T=0.8$ for different densities using the usual prediction of HNT $[p=T(N_1+N_2+N_3+\cdots)/V]$ using the zeroth-order prediction for the cluster densities and compares them to expression (25) that includes terms only up to the first virial correction. It is seen that even though it could seem that the first expression includes higher-order terms, the expression that we have derived gives better results because it considers all contributions up to order λ^2 in a consistent way.

Also, we have made simulations with $N=10^3$ particles using the geometrical definition of clusters $[C(\mathbf{r},\mathbf{v})=\Theta(\alpha\sigma-r)]$. Although statistics are poor, the results again are in good agreement with the theoretical predictions for this type of cluster.

VII. CONCLUSION

In this article there is a careful derivation of the relative number of clusters and the total pressure of a vapor with nonideal contributions coming from the presence of clusters. The theoretical framework is based on well-established tools from statistical mechanics. The diagrammatic expansion techniques deserve particular mention. Special care was taken to take into consideration all the contributions up to first order in the density. The resulting expressions for the concentration of clusters were rewritten in exponential form to be able to identify the implied correction with the free-energy cost necessary to create a cluster.

In HNT it is necessary to express the pressure in terms of the concentration of clusters. It was found that to be able to do so it is necessary to include both the clusters' partial pressures and the nonideal contributions from the clusters. In particular, up to second-order corrections the dimers' partial pressure is as important as the nonideal contribution coming from the monomers. All our results were corroborated with molecular-dynamic simulations of a simple system.

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