Connection between the virial equation of state and physical clusters in a low density vapor

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We carry out Monte Carlo simulations of physical Lennard-Jones and water clusters and show that the number of physical clusters in vapor is directly related to the virial equation of state. This relation holds at temperatures clearly below the critical temperatures, in other words, as long as the cluster-cluster interactions can be neglected—a typical assumption used in theories of nucleation. Above a certain threshold cluster size depending on temperature and interaction potential, the change in cluster work of formation can be calculated analytically with the recently proposed scaling law. The breakdown of the scaling law below the threshold sizes is accurately modeled with the low order virial coefficients. Our results indicate that high order virial coefficients can be analytically calculated from the lower order coefficients when the scaling law for cluster work of formation is valid. The scaling law also allows the calculation of the surface tension and equilibrium vapor density with computationally efficient simulations of physical clusters. Our calculated values are in good agreement with those obtained with other methods. We also present our results for the curvature dependent surface tension of water clusters. © 2007 American Institute of Physics.
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I. INTRODUCTION

Understanding the molecular association in vapor is of essential importance to a variety of scientific fields ranging from nanotechnology to climatology. The controlled production of nanoparticles has a large potential for medical and technological applications, and it requires detailed information of the energetics of small molecular clusters. This information is also vital for predicting the formation of atmospheric particles, which can act as cloud condensation nuclei and thus cool the climate. Yet, it is not known how to calculate the nanoscale particle energetics governing the stability and number distribution of small molecular clusters.

Here, we study the connection between energetics of small clusters and the virial equation of state of a nonideal vapor, described by the series

$$\frac{P_v V}{kT} = 1 + \sum_{n=1}^{\infty} \frac{B_n}{V^n}, \tag{1}$$

where P_v is the pressure of the vapor in volume V and temperature T, and k is the Boltzmann constant. Mayer,[1] who first showed how to calculate the unknown coefficients B_n from statistical mechanics, noted that these coefficients are connected to the number density N_{cn} of mathematical n-mer clusters in the vapor in such a way that N_{cn} is a function of the lowest virial coefficients up to i, $N_{ci} = f(B_1, B_2, \ldots, B_i)$.

The connection between the virial coefficients and the equilibrium constants describing the relative pressures exerted by monomers and n-mer clusters was first presented by Woolley.[2] These relations have been used to calculate the number density of clusters in the vapor.[3,4] The mathematical clusters described by the virial approach are, however, rather abstract objects; the molecules in one cluster do not need to be close to each other. On the other hand, physical clusters represent clear density fluctuations in the vapor. Lockett[5] developed a modified Mayer theory to describe the physical clusters in the vapor. The most widely used description of physical clusters is, however, based on the noninteractive cluster theories by Frenkel[6] and Band.[7,8] In these theories, the cluster-cluster interactions are neglected in order to simplify the partition function of the system. As discussed by Saltz,[9] the mathematical clusters by Mayer describe physical clusters by Frenkel and Band in the limit when the cluster-cluster interactions can be considered negligible. The assumption of noninteracting clusters is valid in systems where the intermolecular interactions are of short range and the vapor density is rather low; it is also intrinsically used in the classical nucleation theory (CNT), which describes the birth rate of small liquid or solid embryos in a supersaturated vapor. The comparison between the number densities of mathematical Mayer clusters and physical clusters as calculated with CNT, or its expansions, has not been successful;[10] this mismatch is only expected since CNT completely neglects the fine structure of molecular clusters, making its use unreliable for the smallest clusters. However, lately we showed that down to very small cluster sizes CNT accurately describes the work of adding a monomer to a cluster,[11] but the error made by CNT in modeling the smallest clusters results in an erroneous absolute value for the cluster work of formation throughout the size range. Hence, the McGraw-Laaksonen scaling law,[12,13] stating that at a constant temperature the nucleation barrier height given by CNT is offset

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from the simulated barrier height by a value independent of the saturation ratio, is valid as long as the critical clusters are larger than some threshold cluster size. The threshold cluster size ranges from only a few to some tens of molecules depending on the temperature and the interaction potential between the cluster molecules. The purpose of this paper is to show that the work of formation of the smallest clusters is accurately described by the virial equation of state in a low density vapor where the assumption of noninteracting physical clusters is justified. The virial coefficients, when obtainable from experiments, can be used for calculating energetics and densities of smallest physical clusters in the vapor. Vice versa, calculations with physical noninteracting clusters can provide the coefficients for the virial series. We will also discuss how the planar surface tension and the equilibrium vapor pressure can be calculated with Monte Carlo simulations of relatively small physical clusters.

II. THEORY

The pressure P_v of a system consisting of N identical molecules in volume V and at temperature T is given in terms of the Helmholtz free energy F as

$$P_v = -\left(\frac{\partial F}{\partial V}\right)_T. \tag{2}$$

The Helmholtz free energy F is given by

$$F = -kT \ln Q, \tag{3}$$

where k is the Boltzmann constant and Q is the classical partition function of the system given by

$$Q = \Lambda^{3N} Q_N / N!. \tag{4}$$

In the above equation, Λ is the thermal de Broglie wavelength and Q_N is the classical configuration integral taken over the whole volume of the system,

$$Q_N = \frac{1}{N!} \int_V \cdots \int \exp\left[\frac{-U(\mathbf{r}_1, \ldots, \mathbf{r}_N)}{kT}\right] d\mathbf{r}_1 \cdots d\mathbf{r}_N. \tag{5}$$

If the potential energy U of the system is zero, Eqs. (2)–(5) result in the ideal gas law, $P_v V = NkT$. If there exists some interaction between the particles, the system deviates from the ideal in a complex manner. In the late 1930s, Mayer[1] showed that the configuration integral in the above equation can be developed into a series, which results in[14]

$$\frac{P_v V}{kT} = \ln\left[1 + \sum_{N \geq 1} Q_N z^N\right] = \sum_{i \geq 1} V b_i z^i, \tag{6}$$

where $z = \Lambda^{-3} \exp(\mu/kT)$ is the fugacity of a vapor with chemical potential μ, and b_n is called the cluster integral. Indeed, Mayer interpreted the above equation to describe the number of clusters in the vapor with their number density given by

$$N_{c,\text{tot}} = N_{c1} + N_{c2} + N_{c3} + \cdots = \sum_{n=1}^{\infty} b_n z^n, \tag{7}$$

where N_{cn} is the number density of n-mer clusters. It is important to note that these clusters are not "physical," in the

sense that they do not have any boundaries. Rather, they are mathematical objects, since a mathematical cluster integral b_n contains contributions from all sets of n molecules that can be found in the system; one is not able to distinguish the Mayer clusters from a snapshot of vapor. As the first integral $b_1 = 1$, the fugacity z can be identified with the number density of monomers N_{c1} in the system. The Mayer expansion is exact, since it does not make any approximations concerning the partition function of the system.

Shortly after Mayer developed his theory of mathematical clusters, Frenkel[6] and Band[7,8] independently formulated an expression for the distribution of clusters in vapor; in these approaches, the molecules in the same cluster are in close vicinity of each other. It should be noted that Frenkel and Band both considered their theories simplifications of the more rigorous Mayer theory. If the vapor is considered to consist of physical clusters, the total energy can be written as[15]

$$U = \sum_{\lambda} U_{\lambda}(\mathbf{r}_{1_{\lambda}}, \ldots, \mathbf{r}_{n_{\lambda}})$$
$$+ \sum_{\lambda < \mu} U_{\lambda\mu}(\mathbf{r}_{1_{\lambda}}, \ldots, \mathbf{r}_{n_{\lambda}}, \mathbf{r}_{1_{\mu}}, \ldots, \mathbf{r}_{n_{\mu}}), \tag{8}$$

where U_{λ} describes the interactions between the molecules in the same cluster and $U_{\lambda\mu}$ describes interactions between molecules in different clusters. The corresponding configurational integral is

$$Q_c = \sum_{\mathcal{N}_n} \frac{1}{\prod_n \mathcal{N}_n!} \int_V \cdots \int \exp(-U/kT) \prod_{\lambda=1}^{\mathcal{N}_{\infty}} \frac{d\mathbf{r}_{\lambda,1} \cdots d\mathbf{r}_{\lambda,n_{\lambda}}}{n_{\lambda}!}, \tag{9}$$

where $\mathcal{N}_n$ is the number of n-mers in volume V. Furthermore, if the interactions between the clusters are considered negligibly small, the second term in Eq. (8) vanishes and the configuration integral can be written in a simple form,

$$Q_c = \sum_{\mathcal{N}_n} \prod_n \frac{[q(n)]^{\mathcal{N}_n}}{\mathcal{N}_n!}, \tag{10}$$

where $q(n)$ is the configuration integral of a physical cluster of n molecules,

$$q(n) = \frac{1}{n!} \int_{\text{cluster}} \cdots \int \exp\left[\frac{-U_n(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n)}{kT}\right] d\mathbf{r}_1 \cdots d\mathbf{r}_n. \tag{11}$$

The most probable set of values $\mathcal{N}_n$ is the one that maximizes the term in the summation of Eq. (10) subject to constraint

$$\sum_n n\mathcal{N}_n = N. \tag{12}$$

This leads to the law of mass action,[15]

$$\frac{\mathcal{N}_n}{q(n)} = \left[\frac{\mathcal{N}}{q(1)}\right]^n. \tag{13}$$

Taking into account that $q(1) = V$, Eq. (13) can be rewritten as a cluster distribution,

$$\frac{\mathcal{N}_n}{\mathcal{N}_1} = \exp\left(-\frac{\Delta W_n}{kT}\right), \tag{14}$$

where ΔW_n is the cluster work of formation (also referred to as the *internal* work of formation[16]) given by

$$\Delta W_n = -kT \ln\left[\frac{q(n)}{V} N_{c1e}^{n-1}\right] - (n-1)kT \ln S, \tag{15}$$

where the saturation ratio is defined as $S = N_{c1}/N_{c1e}$ and N_{c1e} is the saturated number density of monomers. Using Eqs. (14) and (15) we can write the equation for the total density of clusters in the same form as Eq. (7),

$$N_{c,\text{tot}} = N_{c1} + N_{c2} + N_{c3} + \cdots = N_{c1}\sum_n \exp\left(-\frac{\Delta W_n}{kT}\right). \tag{16}$$

So far we have derived all the above equations purely by using statistical mechanics. An expression for the homogeneous nucleation rate obtained through kinetic treatment is given by

$$J = \beta_{n^*}\mathcal{Z}N_1 \exp(-\Delta W_n/(kT)), \tag{17}$$

where β_{n^*} is the collision rate of monomers with the critical cluster containing n^* molecules, and $\mathcal{Z}$ is the Zeldovich[18] nonequilibrium factor. It can easily be shown[17] that the total contribution of $\beta_{n^*}N_1\mathcal{Z}$ is proportional to S^2, and thus Eq. (15) for ΔW_n satisfies the nucleation theorem[16,19,20] for the homogeneous nucleation rate J,

$$\left(\frac{\partial \ln J}{\partial \ln S}\right)_T = n^* + 1. \tag{18}$$

On the other hand, the derivative of the work of formation [Eq. (15)],

$$\left(\frac{\partial \Delta W_{n^*}}{\partial \ln S}\right)_T = n^* - 1, \tag{19}$$

now represents the excess number of molecules in the critical cluster with respect to the monomer. The calculation of ΔW_n with the liquid drop (LD) model leads to the CNT. However, when Eq. (16) is applied with CNT, a prefactor of $1/S$ (S being the saturation ratio) should be included on the right hand side of the equation. This prefactor, dating back to Courtney,[21] arises from the internal consistency requirement of CNT. Here, we will include this factor to the exponential by writing

$$\Delta W_{n,\text{LD}} = A_n \gamma_\infty - (n-1)kT \ln S, \tag{20}$$

where A_n is the equimolar surface area of the cluster and γ_∞ is the planar surface tension. Including $1/S$ in the exponent retains the similarity of forms of Eqs. (16) and (20). Also, the functional forms of $\Delta W_{n,\text{sim}}$ obtained from Monte Carlo simulations [Eq. (23)] and $\Delta W_{n,\text{LD}}$ of Eq. (20) are then identical.

The expressions given by the Mayer cluster approach and the physical cluster approach should be identical in equilibrium vapor when the clusters are noninteracting,[9] $U_{\lambda,\mu}$

$=0$, and the excluded volume[22,23] occupied by the clusters can be considered negligibly small. Then, the coefficients B_i are related to the equilibrium constants

$$K_n = \frac{P_n}{P_1^i} = \frac{\exp(-\Delta W_n/kT)}{P_1^{n-1}}, \tag{21}$$

where P_n is the total pressure of n-mers, by

$$B_2 = -K_2 RT,$$

$$B_3 = [4K_2^2 - 2K_3](RT)^2,$$

$$B_4 = [-20K_2^3 + 18K_2K_3 - 3K_4](RT^3), \tag{22}$$

$$B_5 = [112K_2^4 + 18K_3^2 - 144K_3K_2^2 + 32K_2K_4 - 4K_5](RT)^4,$$

$$\begin{aligned}B_6 = [&-672K_2^5 + 1120K_2^3K_3 - 315K_2K_3^2 - 280K_2^2K_4 \\ &+ 60K_3K_4 + 50K_2K_5 - 5K_6](RT)^5,\end{aligned}$$

where R is the universal gas constant. The description for obtaining the above expressions has been given by Woolley.[2]

There are several essentially equal methods to calculate the work of formation of noninteracting clusters[24] with Monte Carlo simulations. Lately,[11,25] we have presented a method where ΔW_n is calculated as

$$\Delta W_{n,\text{sim}} = -kT\sum_{n'=2}^{n} \ln\left(\frac{\bar{G}_{n'-1}(T, S=1)}{\bar{D}_{n'}(T, S=1)}\right) - (n-1)kT \ln S. \tag{23}$$

In the above equation, $\bar{G}_n$ and $\bar{D}_n$ are, respectively, the average grand canonical growth and decay probabilities for the n cluster, for which the set of configurations is generated with canonical Metropolis Monte Carlo simulations. The cluster distribution is obtained by inserting the above expression into Eq. (16).

III. RESULTS

The first six virial coefficients have been recently calculated for Lennard-Jones (LJ) vapor for reduced temperatures above 0.625 and for SPC/E model water vapor for temperatures above 373 K with Mayer sampling,[4,26] based on Monte Carlo calculations using importance sampling. Here, we calculate the work of cluster formation with Monte Carlo simulations of physical noninteracting LJ and SPC/E water clusters. We then compare our results to Mayer sampling calculations using Eqs. (21)–(23).

Unambiguous definition of a noninteracting physical cluster, separated with boundaries from the rest of the vapor, is not straightforward. It appears that a proper definition of a physical cluster requires coupling of the cluster to the vapor.[27,28] However, the boundaries of the noninteracting clusters have usually been selected rather arbitrarily, either based on the insensitivity of the cluster formation work with respect to the boundary location[29,30] or to the radial distribution function of the molecules in bulk liquid.[31] Here we define the noninteracting clusters with the Stillinger cluster definition, which describes the physical cluster as a con-
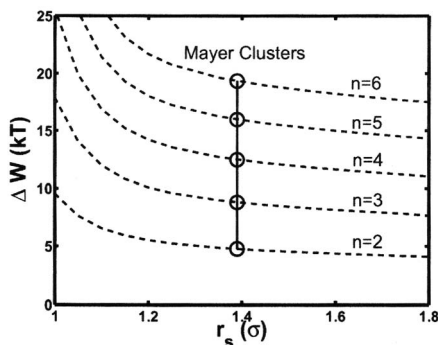
FIG. 1. The work of formation, ΔW_n, of physical Lennard-Jones clusters as a function of the Stillinger radius r_S defining the cluster boundaries. The number of molecules in the cluster is indicated above each line. Corresponding ΔW_n for Mayer clusters are marked with circles.

nected network of molecules separated no further than r_S from their nearest neighbors belonging to the same cluster. This cluster definition is commonly used in simulations of physical clusters, but it is important to realize how the selection of a specific value for r_S affects the cluster formation work. If the boundaries of the cluster are tight, the repulsion from overlapping of molecules makes their formation difficult and the number of clusters in the vapor is small. On the other hand, loose clusters are formed more easily, and at the limit of a physical noninteracting cluster with no boundaries the work of cluster formation approaches zero. In between, the formation work of clusters is only mildly sensitive to the selected value of r_S, as shown in Fig. 1 for LJ clusters at $T^* = 0.625$. At this temperature, the equilibrium vapor density of LJ vapor is relatively low and the average free space around the clusters is large. We can therefore estimate, with calculations similar to the ones presented by Oh and Zeng,[23] that the excluded volume work or the cluster-cluster interactions do not play a significant role. Figure 1 shows that the works of formation of Mayer clusters equal those for physical clusters with a unique value of r_S. For LJ clusters this value is $r_S = 1.39\sigma$, where σ is the LJ distance parameter. This value is slightly lower than the usual value of $r_S = 1.5\sigma$ applied for LJ clusters. Agreement with the Mayer approach is obtained with $r_S = 3.8$ Å for SPC/E water clusters at $T = 373$ K, where r_S refers to the distance between two oxygen atoms.

Using the above values of r_S, we carry out Monte Carlo simulations at reduced temperatures of 0.625, 0.75, and 1.0 with LJ clusters and at temperatures between 273 and 600 K with SPC/E water clusters. The work of adding a monomer to the mathematical Mayer clusters and physical clusters at a constant vapor pressure and temperature,

$$\delta\Delta W_n = \Delta W_n(P_v, T) - \Delta W_{n-1}(P_v, T), \qquad (24)$$

is shown in Fig. 2(a) and 2(b) for LJ and SPC/E water vapors, respectively, as a function of $n^{2/3} - (n-1)^{2/3}$ describing the change in surface area of the cluster. The curves are shown at equilibrium vapor pressures; however, similar correspondence is found at all pressures. Simulations at $T^* = 0.625$ for physical LJ clusters match the results for mathematical LJ clusters very accurately, but there is a slight deviation between the values for the dimer at $T^* = 0.75$. The
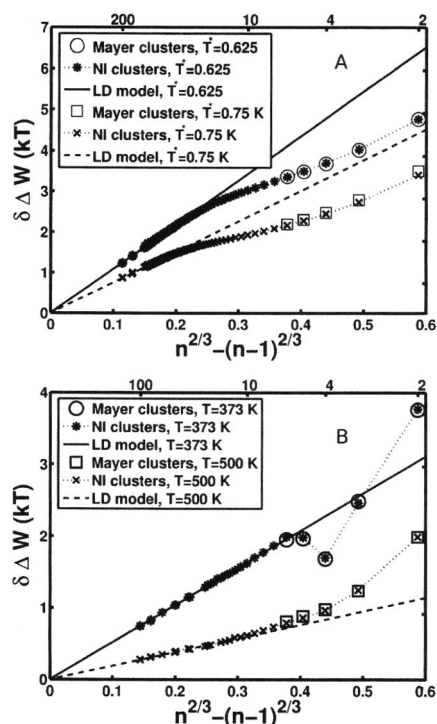

FIG. 2. The work of adding a monomer to the cluster, $\delta\Delta W_n$, with respect to the change in spherical surface area of the cluster, $n^{2/3} - (n-1)^{2/3}$, for our simulated noninteracting (NI) clusters and for Mayer mathematical clusters: (A) for LJ clusters and (B) for SPC/E water clusters. The top horizontal axis describes the cluster size n.

total hexamer formation works in equilibrium vapor are for Mayer clusters and noninteracting (NI) clusters $\Delta W_{6,\text{Mayer}}(T^* = 0.625) = 19.35kT$ and $\Delta W_{6,\text{NI}}(T^* = 0.625) = 19.35kT$, and $\Delta W_{6,\text{Mayer}}(T^* = 0.75) = 13.27kT$ and $\Delta W_{6,\text{NI}}(T^* = 0.75) = 13.04kT$. For water clusters, the correspondence in $\delta\Delta W_n$ is good between 373 and 500 K; the total formation works of hexamers are $\Delta W_{6,\text{Mayer}}(373 \text{ K}) = 11.84kT$ and $\Delta W_{6,\text{NI}}(373 \text{ K}) = 11.90kT$, and $\Delta W_{6,\text{Mayer}}(500 \text{ K}) = 5.89kT$ and $\Delta W_{6,\text{NI}}(500 \text{ K}) = 5.85kT$.

When we approach the critical temperatures T_c the $\delta\Delta W_n$ curves begin to diverge, as shown in Fig. 3 for LJ
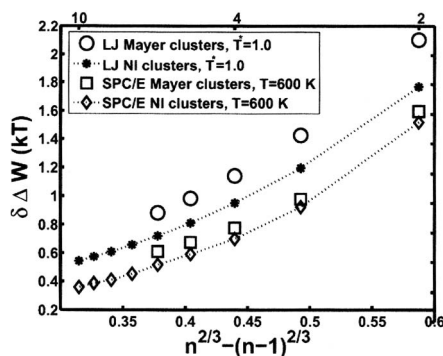

FIG. 3. The works of adding a monomer to the cluster for noninteracting (NI) cluster simulations and Mayer mathematical clusters for LJ vapor at $T^* = 1.0$ and SPC/E water vapor at $T = 600$ K. The lower horizontal axis describes the change in spherical surface area of the cluster; the top horizontal axis gives the corresponding cluster sizes n. Results are shown at arbitrary pressures of 0.023 for LJ vapor and at 50 Pa for SPC/E water.

TABLE I. Virial coefficients for SPC/E water. The units for the coefficients are (L/mol) for $B2$, $(L/mol)^2$ for $B2$, $(L/mol)^3$ for $B3$, $(L/mol)^4$, for $B4$, $(L/mol)^5$ for $B5$, and $(L/mol)^6$ for $B6$.

	T (K)									
	273	298	323	350	373	400	423	450	473	500
$B2$	−21.827	−9.6126	−4.9386	−2.7083	−1.7837	−1.1807	−0.8734	−0.645 2	−0.5167	−0.407 2
Lit.[a]					−1.8049		−0.8865	−0.652 88	−0.5189	−0.408 19
$B3$	−13 776	−1388	−210.7	−37.86	−11.02	−2.935	−1.080	−0.348	−0.132	−0.037
Lit.[a]					−10.29		−1.045	−0.347 906	−0.1373	−0.041 058
$B4$	-8.90×10^{7}	-1.40×10^{6}	−48 232	−2163	−230	−22.43	−3.454	−0.406 4	−0.0142	−0.022 6
Lit.[a]					−243		−2.85	−0.255 9	0.0335	0.049 757
$B5$	-3.22×10^{10}	-1.13×10^{8}	-7.80×10^{5}	−1069	621	80.90	14.34	2.355	0.5166	0.108 4
Lit.[a]					577		15.17	2.243 4	0.524	0.095 4
$B6$	3.01×10^{12}	9.26×10^{9}	6.51×10^{7}	5.68×10^{5}	17 800	507	26.5	0.110	−0.241	−0.083 9
Lit.[a]					15 000		16.7	−0.464	−0.472	−0.102

[a]Results obtained with Mayer sampling (Refs. 4 and 26).

clusters at $T^{*}=1.0$ [$T_{c}^{*}=1.30$ (Ref. 32)] and water clusters at $T=600$ K [$T_{c}=638.6$ K (Ref. 33)]. At high temperatures the results with noninteracting physical clusters and mathematical clusters cannot be matched merely by selecting a different value for r_{S}. The cluster-cluster interactions begin to play a significant role for LJ clusters around $T^{*}=0.75$ and for SPC/E water clusters at temperatures above 500 K. The virial coefficients for SPC/E water obtained from our calculations are compared to those obtained from the Mayer cluster simulations in Table I. Although a perfect one-to-one correspondence cannot be claimed, the physical cluster simulations can provide the magnitudes of virial coefficients with reasonable accuracy.

Recently, we showed[11] that the following scaling law holds for clusters larger than some threshold size n^{thr}:

$$\Delta W_{n}(n \geqslant n^{\text{thr}}) = \Delta W_{n,\text{LD}} - D(T), \qquad (25)$$

where $\Delta W_{n,\text{LD}}$ is given by Eq. (20) and $D(T)$ is a constant independent of the cluster size. This law is observed as the linearization of $\delta\Delta W_{n}$ curves at larger cluster sizes as shown in Figs. 2(a) and 2(b); for clusters larger than n^{thr}, $\delta\Delta W_{n}$ resulting from simulations is accurately given by $\delta\Delta W_{n,\text{LD}}$. This law is equivalent with the scaling law proposed by McGraw and Laaksonen,[12,13] which is given by

$$\Delta W_{n}^{*} = \Delta W_{n,\text{LD}}^{*} - D(T), \qquad (26)$$

where ΔW_{n}^{*} is the work of formation of a critical cluster, representing a cluster in an unstable equilibrium with the supersaturated vapor. Our expression given by Eq. (25) states that this law applies to all clusters above n^{thr}, and not only to the critical cluster. Due to equivalence of the properties and number densities of physical clusters and Mayer clusters, Eq. (25) suggests that the higher order virial coefficients B_{n} are functions of lower order coefficients for clusters larger than n^{thr}. One can also apply the above law to calculate the higher order virial coefficients in cases where cluster surface area A_{n} and planar surface tension γ_{∞} are not known. Using the property of linearization of $\delta\Delta W_{n}$ curves, Eq. (25) can be written in a general form as (see the Appendix)

$$\delta\Delta W_{n+1}(n > n^{\text{thr}}) = f(n)(\delta\Delta W_{n} - \delta\Delta W_{n-1}) + \delta\Delta W_{n}, \qquad (27)$$

where $f(n)$ is a function of n only. The high order coefficients can be calculated by using the above expression together with Eqs. (21) and (22) as long as we know the formation work for one cluster size above the threshold value.

These scaling properties can also be used to accurately calculate the values for planar surface tension γ_{∞}, saturated vapor density of monomers ρ_{1}^{eq}, and the saturated vapor pressure of monomers P_{1}^{eq}, as well as the corresponding values for the full vapor with contributions from all cluster sizes, ρ_{v}^{eq} and P_{v}^{eq}. The calculation details are given in the Appendix. Since these values are calculated with simulations of small physical clusters, there is no need to truncate the interaction potential. The equilibrium vapor pressure can be found by locating the monomer pressure for which $\delta\Delta W_{n}$ approaches zero as $n \rightarrow \infty$.[11] Generally, the $\delta\Delta W_{n}$ curve crosses the horizontal axis at the critical cluster size, which depends on the vapor density; for equilibrium vapor this size is infinite. Our calculated values are compared against values obtained with other simulation methods in Table II, together with the observed values for the threshold sizes. For the calculation of γ_{∞} we need to know the equimolar surface of the cluster, A_{n}, which can be calculated from the literature values for the bulk liquid density also shown in Table II. Our calculated values for equilibrium vapor properties and surface tension agree well with the literature data.

We also wish to highlight a potentially significant aspect related to the comparisons between the theoretical and experimentally measured nucleation rates. The saturation ratio used in the theoretical nucleation calculations always corresponds to the saturation ratio of monomers,[9,34] $S=\rho_{1}/\rho_{1}^{\text{eq}}=P_{1}/P_{1}^{\text{eq}}$, and not to the full vapor values $S_{P}=P_{v}/P_{v}^{\text{eq}}$ or $S_{\rho}=\rho_{v}/\rho_{v}^{\text{eq}}$, from which S_{ρ} deviates from the true value of S more than S_{P}. The deviations become larger at higher saturation ratios and lead to errors in calculating S when a significant proportion of molecules is bound to clusters larger than monomers. For example, at saturation ratio $S=2$ for SPC/E water, $S_{\rho}=2.15$, and for $S=3$, $S_{\rho}=3.63$. The value normally measured in nucleation rate experiments is ρ_{v} and

TABLE II. The thermodynamic parameters for equilibrium Lennard-Jones (LJ) and SPC/E water vapors obtained from the physical clusters simulations. The LJ values are in reduced units. The parameters for SPC/E water are monomer vapor pressure P_1 (bar), total vapor pressure P_v (bar), monomer vapor density ρ_1 (g/cm^3), total vapor density ρ_v (g/cm^3), bulk liquid density ρ_l (g/cm^3), and planar surface tension γ_∞ (10^{-3} N/m).

Model	T	n^{thr}	P_1^{eq}	P_v^{eq}	ρ_1^{eq}	ρ_v^{eq}	ρ_l^{eq}	γ_∞
LJ	0.625	40	0.000 438	0.000 441	0.000 700	0.000 712		1.285
Lit.				0.000 48[a]			0.873[b]	1.266[a]
LJ	0.75	48	.002 573	0.002 664	0.003 43	0.003 683		1.025
Lit.			0.002 558[c]	0.002 86[a]	0.003 41[c]	0.003 67[c]	0.8213[c]	1.058,[c] 1.060[a]
SPC/E	373	8	40.0	41.0	0.000 232	0.000 245		55.0
Lit.				43[d]		0.000 24[d]	0.945[d]	58,[e] 57,[f] 51[g]
SPC/E	500	14	13.95	16.78	0.006 045	0.009 214		23.2
Lit.				16.25,[h] 7.0[g]		0.0088,[h] 0.010[g]	0.794[h]	31,[e] 25,[f] 25.9[g]

[a]Reference 35 [P_v^{eq} using fit $P_v^{\mathrm{eq}}=\exp(0.0341-6.6674/T)\times 20.065$].
[b]Estimated from Ref. 36 and experimental temperature dependence of density of liquid argon from Ref. 37
[c]Reference 36.
[d]Reference 38.
[e]Reference 39.
[f]Reference 40.
[g]Reference 41.
[h]Reference 42.

should be corrected to ρ_1, which requires B_2 and, preferably, even higher virial coefficients of the vapor to be known. Since both the dimer work of formation and the slope of $\delta\Delta W_n$ are higher at lower temperatures, the effect is less significant at low temperatures.

Finally, we study the size dependence of the equimolar surface tension γ_n of clusters by calculating, as in our earlier paper,[11]

$$\gamma_n = \frac{\Delta W_n^{\mathrm{eq}}}{A_n}, \qquad (28)$$

where A_n is the equimolar surface area and ΔW_n^{eq} is the work of cluster formation in equilibrium vapor. Our results for mathematical and physical water clusters are shown in Fig. 4, together with the McGraw-Laaksonen expression[13]

$$\gamma_n = \gamma_\infty - \frac{D(T)}{A_n}, \qquad (29)$$

where our calculated values for

$$D(T) = A_1\gamma_\infty - \sum_{n'=2}^{n^{\mathrm{thr}}} \left[\delta\Delta W_{n,\mathrm{LD}} - \delta\Delta W_{n,\mathrm{sim}}\right] \qquad (30)$$

are $D(373\ \mathrm{K})=5.2kT\simeq A_1\gamma_\infty$ and $D(500\ \mathrm{K})=-0.1kT$. At 373 K, the largest contribution to $\delta\Delta W_4$ comes from the energetically favorable four-ring structure, and the summation in Eq. (30) results a value close to zero as different terms cancel each other [Fig. 2(b)]. In contrast, at 500 K, a more important contribution to $\delta\Delta W_4$ comes from other than four-ring configurations, so that the terms in Eq. (30) are monotonous and the summation results a value slightly exceeding the $A_1\gamma_\infty$ term. Therefore, $D(500\ \mathrm{K})$ becomes negative and a very different surface tension size dependence is observed at the two temperatures: the surface tension of clusters at 373 K gradually grows toward the planar surface value, but at 500 K the surface tension exceeds the planar surface value for clusters larger than 8 molecules. We observed a similar change in the value of $D(T)$ when the water clusters were simulated with the TIP4P water model. The results from our simulations are again nearly identical with the results obtained for Mayer clusters, and agree with the results of McGraw-Laaksonen expression when $n\geq n^{\mathrm{thr}}$. Distinctively, the surface tension obtained from calculations with physical or mathematical clusters becomes zero for a monomer cluster.
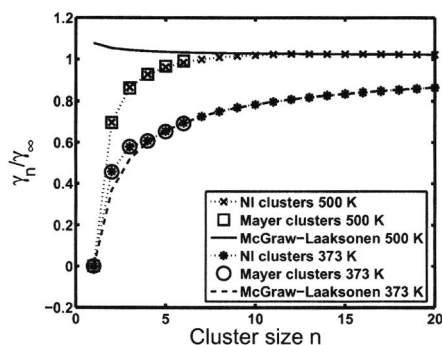

FIG. 4. The size dependence of the equimolar surface tension for SPC/E water obtained from the work of formation of physical clusters and Mayer clusters. The lines corresponding to McGraw-Laaksonen expression are also shown.

IV. CONCLUSION

We have examined the statistical mechanics treatment of the clusters in vapor and discussed the essential identity of the number of mathematical Mayer clusters and physical clusters of Frenkel and Band in a vapor where the cluster-cluster interactions can be neglected. We verify this identity for the first time for Lennard-Jones and water vapors by comparing our results with Monte Carlo simulations of physical clusters, defined according to the Stillinger cluster definition, to the results obtained with previously calculated

virial coefficients. The connection holds at temperatures clearly below the critical temperature and breaks down at high density vapors where cluster-cluster interactions become significant. Our results indicate that at moderate temperatures the nonideality of vapor is directly related to the formation of physical clusters. Therefore, there is a direct relationship between the virial equation of state and the work of cluster formation.

The calculation of virial coefficients with cluster integrals is a tedious task even with the recently presented Monte Carlo methods. The physical cluster simulations provide an efficient tool for extending the calculations to higher order coefficients. Besides, they predict the existence of a threshold size n^{thr} above which the higher order virial coefficients can be analytically solved from the lower order coefficients. This threshold size depends both on the interaction potential and on the temperature. For water, the threshold cluster contains only 8 molecules at temperatures at 373 K and 14 molecules at 500 K.

For clusters larger than the threshold size, the McGraw and Laaksonen scaling law holds and the change in cluster work of formation, with respect to its size, is accurately given by the liquid drop model. This law is observed as the linear relation between the work of monomer addition and the corresponding change in spherical surface area of the cluster. By plotting this curve for different values of saturation ratio, one can accurately calculate the equilibrium vapor density from the curve which approaches the origin. Similarly, the bulk surface tension can be calculated from the slope of the linear part of the curve once the equilibrium bulk liquid density and, hence, the equimolar surface area of the drop are known. The calculations are both computationally economic and accurate—there is no need to truncate the interaction potential or to calculate a tail correction to the surface tension. One does not need to study all cluster sizes for the calculation of these values; one only need locate the threshold size and obtain the slope of the $\delta\Delta W_n$ curve from simulations with clusters somewhat larger than the threshold size. Also the equilibrium density of liquid can be obtained from the core density of the reasonably large droplet.[31] However, the McGraw-Laaksonen scaling law becomes valid before the droplets can be assumed to possess a liquidlike core.

In multicomponent cases, similar connections should be expected between the cross virial coefficients and the formation of clusters containing different species. Therefore, laboratory measurements of the cross virial coefficients can reveal new insight about the significance of different chemical species participating in atmospheric nucleation or about the possible carrier gas effect in nucleation experiments.[43,44]

Finally, we conclude that the picture of the cluster energetics in a low density equilibrium vapor, as gained from our simulations, is the following: the work of formation on the smallest clusters is directly related to the virial coefficients and, after a threshold size, the liquid drop model accurately describes the work of adding a monomer to the cluster. In CNT it is assumed that the steady state nucleation rate in a nonequilibrium vapor can be calculated with the means of the equilibrium distribution of clusters.[45] However, we stress that our results do not provide answers about the possible nonequilibrium effects in a supersaturated vapor where nucleation occurs, such as the effects of nucleation on cluster configurations.[46]

ACKNOWLEDGMENT

APPENDIX: CALCULATION OF THE EQUILIBRIUM VAPOR PRESSURE AND THE SURFACE TENSION

Above the threshold size $(n \geq n^{\text{thr}})$ the work of adding a monomer to the cluster is accurately given by the liquid drop model,

$$
\begin{aligned}
\delta\Delta W_{n,\text{sim}} = \delta\Delta W_{n,\text{LD}} &= \Delta W_{n,\text{LD}} - \Delta W_{n-1,\text{LD}} \\
&= A_1\gamma_\infty(n^{2/3} - (n-1)^{2/3}) - kT\ln S \\
&= \alpha x(n) + \beta,
\end{aligned}
\tag{A1}
$$

where

$$
x(n) = n^{2/3} - (n-1)^{2/3}, \tag{A2}
$$

and α is a constant independent of n,

$$
\alpha = A_1\gamma_\infty = \frac{\delta\Delta W_{n_1} - \delta\Delta W_{n_2}}{x(n_1) - x(n_2)}, \tag{A3}
$$

where $n_2 \neq n_1$ are arbitrary cluster sizes larger or equal to n^{thr}. Also β is a constant independent of n,

$$
\beta = -kT\ln S = \delta\Delta W_{n_1} - \alpha x(n_1). \tag{A4}
$$

From the above equations, the surface energy element $A_1\gamma_\infty$ and the saturation ratio $S = N_{c1}/N_{c1}^{\text{eq}}$ can be solved when α and β are known from plots like the ones shown in Figs. 2(a) and 2(b). The simulations are carried out at the monomer number density N_{c1}, which is related to the chemical potential μ as $N_{c1} = \exp(\mu/kT)/\lambda^3$. The number density of n-mers is given by $N_{cn} = N_{c1}\exp(\Delta W_{n,\text{sim}}/kT)$. Each n-mer population is considered to form an ideal gas of its own, so that $P_n = N_{cn}kT$, and the total pressure is given by the Dalton law $P_v = \Sigma_n P_n$. In a supersaturated vapor, $\delta\Delta W_n$ given by Eq. (A1) becomes zero at the critical cluster size.

Calculating Eq. (A1) for $\delta\Delta W_{n+1}$ by substituting $n_1 = n$ and $n_2 = (n-1)$ and using Eqs. (A2)–(A4) results in

$$
\begin{aligned}
\delta\Delta W_{n+1} &= \alpha x(n+1) + \beta \\
&= \frac{\delta\Delta W_n - \delta\Delta W_{n-1}}{x(n) - x(n-1)} x(n+1) + \delta\Delta W_n \\
&\quad - \frac{\delta\Delta W_n - \delta\Delta W_{n-1}}{x(n) - x(n-1)} x(n) \\
&= (\delta\Delta W_n - \delta\Delta W_{n-1})f(n) + \delta\Delta W_n,
\end{aligned}
\tag{A5}
$$

where

$$
f(n) = \frac{(n+1)^{2/3} - 2(n)^{2/3} + (n-1)^{2/3}}{n^{2/3} - 2(n-1)^{2/3} + (n-2)^{2/3}}. \tag{A6}
$$

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