



Kinetic effects in a non-ideal gas of clusters

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Abstract

The kinetic properties of clusters are studied taking into account non-ideal contributions. The velocity distribution functions are distorted Maxwellians. From these distributions it is possible to derive kinetic “temperatures” associated with each cluster species which are different from the thermodynamic temperature T . Molecular dynamics simulations confirm these predictions and show that the kinetic temperatures are larger than T . © 1998 Elsevier Science B.V. All rights reserved.

Molecules in a gas at equilibrium, and not too far from the liquid–gas transition, tend to form microscopic clusters. Clusters can be thought of as microscopic domains of the liquid phase. The study of the cluster properties is essential for understanding the condensation phenomena [1]. A lot of work has been done in predicting the clusters free energy [2] and their kinetic properties [3]. The effect of excluded volume is treated in [4]. In a recent paper, a new formalism based on a virial expansion that predicts the non-ideal effects in the concentration of clusters is used [5]. This formalism shows good agreement with molecular dynamics simulations.

In the following, we use the technique described in [5] to deduce new kinetic properties for the clusters, and compare the predictions to molecular dynamic simulations.

We simulate a two-dimensional system of hard disks interacting with a square well pair potential given by $\varphi(r) = [\infty, -\varepsilon, 0]$ depending on whether $r < \sigma$, $\sigma < r < \alpha\sigma$, or $r > \alpha\sigma$, respectively. We have chosen units so that $m = 1$, $\varepsilon = 1$, $\sigma = 1$, and we have set $\alpha = 1.5$.

We simulate systems of $N = 10^4$ hard disks at temperatures T and number densities n corresponding to the pure homogeneous gas phase with a non-negligible presence of clusters. The boundary conditions are periodic, to avoid heterogeneous condensation.

The system is described as a gas mixture of different cluster sizes, where we call cluster (*dynamical cluster*) a set of molecules that are energetically bound,

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making clusters to move as a whole allowing for an adequate kinetic study of them. Using this generic definition each microscopic state has a unique decomposition in clusters.

The gas of clusters is studied using the virial expansion based on a formal diagrammatic expansion for the case of gas mixtures [6,7]. The interactions between the different “particles” (clusters) take into account the full interaction between all the molecules composing each cluster. But, there is another interaction between clusters that come 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.

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

With this Hamiltonian, the grand partition function for this non-ideal gas composed of a mixture of different cluster sizes can be written. If the density is low, the diagrammatic method can be applied directly to this gas mixture. In this formalism it is possible to derive the distribution functions $f_k(\mathbf{r}, \mathbf{p})$ for clusters of size k [5]. Up to first virial correction,

$$f_k(\mathbf{r}, \mathbf{p}) = \frac{1}{k!} \lambda^k \left[\int e^{-\beta H_0^k(\mathbf{r}, \mathbf{p}, \xi)} d\xi + \lambda \int e^{-\beta H_0^k(\mathbf{r}, \mathbf{p}, \xi)} e^{-\beta v_1^2/2m} (e^{-\beta V_{k1}(\mathbf{r}, \mathbf{p}, \xi; \mathbf{r}_1, \mathbf{p}_1)} - 1) d\mathbf{r}_1 d\mathbf{p}_1 d\xi \right], \quad (1)$$

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 order zero f_k is directly a Maxwell–Boltzmann distribution. But when the non-ideal correction is included it becomes distorted.

We define the kinetic or *translational temperature* $T_k^{\text{trans}} = (mk/d) \langle v^2 \rangle_k$ and the *internal temperature* $T_k^{\text{int}} = 2K_k^{\text{int}}/[(k-1)d]$ where K_k^{int} is the internal kinetic energy. In classical systems these temperatures are equal to the thermodynamic temperature T , but for the energetically defined clusters they turn out to be different. Only T , of course, is a true temperature. From Eq. (1) T_k^{trans} can be calculated. After some algebra,

$$T_k^{\text{trans}} = T \left[1 + \lambda \frac{m^d}{k+1} \int d\mathbf{r}_0 d\mathbf{u} \langle e^{-\beta \tilde{V}_{k1}(\mathbf{r}_0, \mathbf{v}_0)} \rangle_\xi \left(\frac{2}{d} u^2 - 1 \right) e^{-u^2} \right], \quad (2)$$

where $\langle \dots \rangle_\xi$ is an average over the internal degrees of freedom of the cluster; \tilde{V}_{k1} is the effective potential between the cluster and the monomer in the reference system of the cluster, and $\mathbf{v} = \sqrt{2T(k+1)/(mk)} \mathbf{u}$. For energetically defined clusters, the average

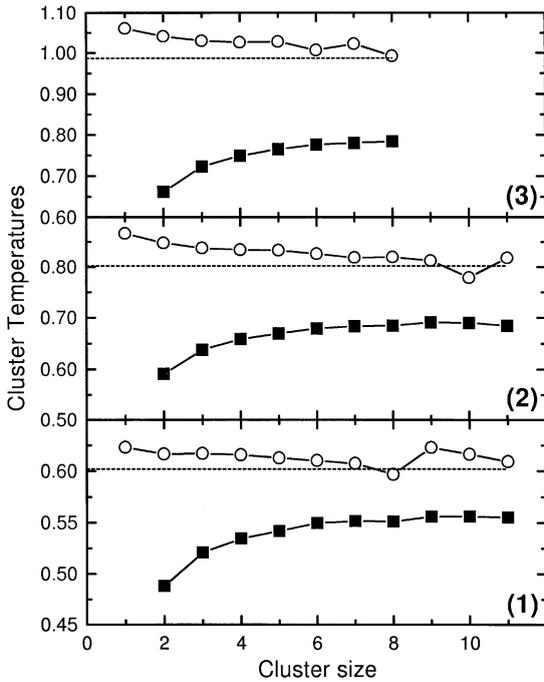


Fig. 1. Cluster temperatures as a function of cluster size. The open circles correspond to the translational temperature and the solid square to the internal temperature for different clusters sizes. The dash straight lines show the values of the thermodynamic temperature. The number densities and temperatures for the three simulations are: (1) $n = 0.02$, $T = 0.602$, (2) $n = 0.05$, $T = 0.802$, and (3) $n = 0.05$, $T = 0.987$.

in ζ depends non-trivially on velocities, so the above integral is generally not zero. Hence,

$$T_k^{\text{trans}} \neq T. \tag{3}$$

The difference comes from the existence of the *Constraint Potential* that depends on velocities. Fig. 1 shows the translational and internal cluster temperatures obtained in the simulations. They are different from T and satisfy the following inequality $T_k^{\text{int}} < T < T_k^{\text{trans}}$. This property can be understood in terms of the cluster definition. The restriction that the molecules inside a cluster have to be energetically bound puts an upper limit on the relative velocities of the molecules, 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 smaller energy in the internal degrees of freedom, the translational ones must have more than $T/2$, giving $T < T_k^{\text{trans}}$. In the case of monomers, it can be shown that $T_1^{\text{trans}} > T$. In fact, in this case the cluster (monomer) does not have internal degrees of freedom and Eq. (2) can be simplified

to

$$T_1 = \frac{m}{d} \langle v^2 \rangle_1 = T \left[1 + \lambda \frac{m^d}{2} \int d\mathbf{r}_0 d\mathbf{u} e^{-\beta \tilde{V}_{11}^{\text{constr}}(\mathbf{r}_0, \mathbf{v})} e^{-\beta \varphi(r_0)} \left(\frac{2}{d} u^2 - 1 \right) e^{-u^2} \right]. \quad (4)$$

But the first exponential factor in the integral 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. The integral in u from a finite value to infinity 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 and any cluster size, the monomers move (on average) faster than the thermal velocity associated to the temperature T of the system.*

To estimate the correction in the translation temperature for the case of large clusters it is necessary to model the effective potential between a cluster and a monomer.

The correction $\delta T_k/T = (T_k^{\text{trans}} - T)/T$ can be estimated for large clusters. When the temperature is low enough, the cluster is spherical and compact in the sense that the energy of the monomer inside the cluster would be infinite. Therefore, the average $\langle \exp(-\beta \tilde{V}_{k1}(\mathbf{r}_0, \mathbf{v}_0)) \rangle_{\xi}$ is zero inside the cluster, one outside it, and some undetermined value $F(\mathbf{r}_0, \mathbf{v}_0)$ in the surface. Using this approximation in Eq. (2), we have

$$\delta T_k/T = \lambda \frac{m^d}{k+1} A_{cl} \Delta \frac{1}{\Delta} \int d\mathbf{r}_0 d\mathbf{u} F \left(r_0 \hat{\mathbf{r}}, \sqrt{\frac{2T(k+1)}{mk}} \mathbf{u} \right) \left(\frac{2}{d} u^2 - 1 \right) e^{-u^2}, \quad (5)$$

where A_{cl} is the surface of the cluster, Δ the width of the interface and the integration is over the radial component only since the approximation $\Delta \ll R$ has been made. Then, the correction to the translational temperature comes only from the surface of the cluster. With the asymptotic values of A_{cl} and Δ in [8] the correction for large clusters is $\delta T_k/T = \mathcal{O}(k^{-1/4})$ in 2D and $\delta T_k/T = \mathcal{O}(k^{-1/3} \sqrt{\log k})$ in 3D. This result shows that both in two and three dimensions the correction to the translational temperature goes slowly down. The size dependence of the non-ideal correction to the translational temperature should be compared to the non-ideal correction to the cluster concentration [5], which increases linearly with the cluster size.

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