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Monte Carlo Calculation of Argon Clusters in Homogeneous Nucleation

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Monte Carlo calculations of the free energy of argon clusters are presented. The resulting homogeneous nulceation rates are in reasonable agreement with the experimental data over a wide range of pressures (10^{-4} atm $< p < 2\times10^{-1}$ atm) and temperatures (25 °K $< T <$ 60 °K) at the onset of condensation.

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Precise experiments on argon condensation by isothermal, steady-state, homogeneous nucleation from a supersaturated vapor have been carried out by Stein[1] and Wu, Wegener, and Stein.[2] Argon seems to be one of the easier vapors to study theoretically because of its simple Lennard-Jones interaction potential. Nevertheless up to now no calculation has given agreement with experiments over a wide range of temperatures (25 °K $< T <$ 60 °K) and pressures (10^{-4} atm $< p < 2\times10^{-1}$ atm) at the onset of condensation. Recently Hoare, Pal, and Wegener[3] have calculated free energies and nucleation rates for argon microclusters using an icosahedron-based packing and the harmonic approximation. It is known by comparisons with "exact" Monte Carlo calculations[4,5] that the harmonic approximation underestimates the free energies of cluster formation because it does not include anharmonicity or the entropy due to shape change. But it should be said that the point of view in Ref. 3 is a step forward in treating this problem by calculating the free energies.

In this work we report on a Monte Carlo calculation of free energies of formation of argon microclusters. The intermolecular potential is a Lennard-Jones potential. The cluster sizes go from two to thirty-seven molecules and the reduced temperature $T^* = kT/\epsilon$ (where ϵ is the Lennard-Jones well depth) varies between 0.2 and 0.7 with intervals $\Delta T^* = 0.05$.

Knowing the free energies it is possible to obtain nucleation rates and to compare them to experimentally obtained rates. Our calculated rates prove to be in good agreement with the reported data.[1,2]

We assume that cluster growth takes place by monomer addition according to the reaction:

$$A_1 + A_{n-1} \rightleftharpoons A_n. \tag{1}$$

If we assume a steady-state solution, the nucleation rate J may be calculated from the equilibrium concentrations C_n of the n clusters. It reads[3,4,6]

$$J = \alpha\beta \Big/ \sum_{n=1}^{N} (O_n C_n)^{-1}, \tag{2}$$

where N is the maximum cluster size after which the nucleation rate is unaffected, α is the sticking coefficient and is taken to be equal to unity, β is the rate at which atoms of mass m at the state (p, T) impinge on a unit area, and O_n is the surface area of a cluster of size n. The quantities β and O_n are given by

$$\beta = p/(2\pi mkT)^{1/2}, \tag{3}$$

and

$$O_n = (36\pi V_c^2)^{1/3} n^{2/3}, \tag{4}$$

where V_c is the effective volume per molecule in the cluster. Finally, C_n can be obtained by the methods of statistical mechanics[4]; by using the law of mass action for the kinetics of the reaction (1), we have, in equilibrium

$$Q(n)/VC_n = [Q(1)/VC_1]^n, \tag{5}$$

where $Q(n)$ is the partition function of an n cluster. Following Ref. 5 we write the partition function as

$$Q(n) = \lambda^{-3n} V q_{\rm int}(n), \tag{6}$$

where λ is the thermal de Broglie wavelength of the single atom and

$$q_{\rm int}(n) = (n^3/n!) \int \cdots \int \exp\Big[-\sum_{i>j} V(r_{ij}')/kT\Big] d^3r_1' \cdots d^3r_{n-1}'. \tag{7}$$

Here $V(r_{ij})$ is a Lennard-Jones 12-6 potential with parameters $\epsilon/k = 119.4\,^\circ\mathrm{K}$ and $r_0 = 3.4$ Å, $\vec{r}_i'$ are the positions of the atoms referred to the center of mass of the cluster, and the integration is carried out over the volume of the cluster. By application of Eq. (5) we obtain

$$C_n = C_1 \exp[-\Delta F(n,p,T)/kT], \tag{8}$$

where $\Delta F(n,p,T)$ is the difference between the free energy of the cluster and that of a vapor of monomers in the state (p, T),

$$\frac{\Delta F(n,p,T)}{kT} = -\ln[q_i(n)] - (n-1)\ln\left(\frac{p}{kT}\right). \tag{9}$$

The value of $q_i(n)$ is calculated by Monte Carlo techniques which are similar to those used by Lee, Barker, and Abraham.[5] First we observe that

$$\frac{\partial \ln[q_{\rm int}(n,T)]}{\partial(1/kT)} = -\Big\langle \sum_{i>j} V(r_{ij})\Big\rangle_T, \tag{10}$$

where $\langle\ \rangle_T$ stands for mean value at temperature T. Then

$$\ln[q_{\rm int}(n,T)] = \ln[q_{\rm int}(n,T_0)] - \int_{1/kT_0}^{1/kT} \Big\langle \sum_{i>j} V(r_{ij})\Big\rangle_{T'} d(1/kT'). \tag{11}$$

For T going to infinity the system approaches an ideal gas and the integral (7) may be calculated exactly.[5] We set $T_0 = 100\ \epsilon/k$ and corrected the ideal gas approximation with the first and second virial coefficients. Then a chain of about one million states was generated by the Monte Carlo procedure and the potential energy was calculated at every step. The value of $1/kT'$ was linearly changed along this chain until $T = 0.2\ \epsilon/k$ was reached, and partial summations were stored for higher temperatures. In all the calculations, the cluster was confined to a volume which was taken to be $5nV_c$. Lee, Barker, and Abraham[5] have shown that the precise value of this restriction volume is not crucial in the evaluation of the free energy of the cluster, except for very small clusters and high temperatures (i.e., less than 10 atoms and more than 60 °K). Since only clusters of about the critical size are important in determining the nucleation rates, the conditions in our work are reliable with respect to the restriction volume. The statistical error for the Monte Carlo calculation of $\ln[q_{\rm int}(n,T)]$ depends somewhat on n and T, ranging approximately between 0.5% and 1.5%.

Our results agree for $n = 13$ with those of Ref. 5 which has been used as a check on our calculations. Other details of these calculations will be presented elsewhere.[7] Values of $\Delta F(n)/kT$ are presented in Fig. 1(a) for the two extreme temperatures $T = 30$ and 60 °K. The pressures have been chosen in order to yield a nucleation rate of $10^0\ \mathrm{cm^{-3}\,s^{-1}}$ ($p = 1.19\times10^{-4}$ atm) and $10^6\ \mathrm{cm^{-3}\,s^{-1}}$ ($p = 0.205$ atm), respectively. The values for clusters larger than 37 atoms have been taken from Ref. 5 to check their effect in the nucleation rates (see Table I). In order to extend the calculation up to cluster $n = 100$ we have linearly interpolated $\Delta F(n)/kT$ between the values of $n = 43$, 60, 70, 80, 87, and 100 available from Ref. 5. Figure 1(b) shows $\log_{10}J$ as a function of N [in Eq. (2)] for the same conditions as those in Fig. 1(a). Of course, the value of V_c in Eq. (4) depends on the temperature but we have taken a constant value of $4\times10^{-23}\ \mathrm{cm^3}$ since this introduces a negligible error in J. Although it may be argued that the existence of a critical cluster size is not

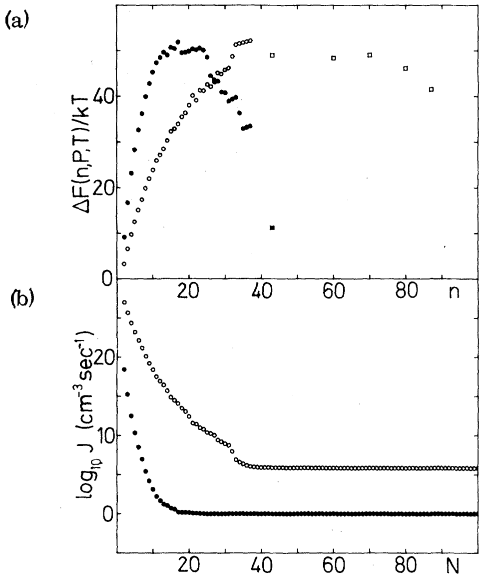

FIG. 1. (a) Difference between the free energy of the argon clusters and that of the corresponding vapor. Circles are calculations from this work and squares from Ref. 5. Full circles and squares are for T = 30 °K and $p = 1.19 \times 10^{-4}$ atm, while the open ones are for T = 60 °K and p = 0.205 atm. (b) Nucleation rates for the above conditions from Eq. (2) for varying N.

TABLE I. Pressures along the condensation curves $J = 10^0$ and 10^6 cm^{-3} s^{-1}. Also shown is the difference between summing up to N = 37 and N = 100 in Eq. (2).

		J (cm^{-3} s^{-1})	
T (°K)	$p \times 10^3$(atm)	N = 37	N = 100
25	0.0105	1.01×10^0	1.01×10^0
30	0.119	1.02×10^0	1.02×10^0
35	0.791	1.03×10^0	1.03×10^0
40	3.68	1.09×10^0	1.06×10^0
45	12.83	1.01×10^0	0.93×10^0
50	34.3	1.03×10^0	0.78×10^0
55	74.9	1.02×10^0	0.06×10^0
60	140.4	1.02×10^0	5.4×10^{-8}
25	0.0335	1.00×10^6	1.00×10^6
30	0.281	1.00×10^6	1.00×10^6
35	1.46	1.04×10^6	1.04×10^6
40	5.91	1.02×10^6	1.02×10^6
45	19.1	1.00×10^6	0.98×10^6
50	50.5	1.03×10^6	0.97×10^6
55	109.7	1.05×10^6	0.91×10^6
60	205	1.09×10^6	0.69×10^6

as distinct in Fig. 1(a) for $T = 60$ °K, it also should be seen that the logarithm of the nucleation rate remains practically constant after $N \simeq 37$. For the case of $T = 30$ °K the critical cluster is more distinct at $N \simeq 17$ after which the logarithm of J values remain constant. To analyze further the above points we present in Table I the difference in J obtained by summing up to $N = 37$ and $N = 100$ for various temperatures. We observe from the table that for the temperature range 25 °K $\leq T \leq$ 60 °K, the values of J obtained up to $N = 37$ are good except for $T \geq 55$ °K and $J \sim 10^0$ cm^{-3} s^{-1}. From Table I, we note that the summation for J can be truncated at $N = 37$ for the low-temperature experimental conditions. For the high-temperature experimental conditions, we note a discrepancy between the two sums for estimating J. While it would be desirable to extend the limit of the sum to much larger cluster sizes, the Monte Carlo free energies for these larger cluster sizes do not exist. However, it is apparent from the trend in the free energy dependence [Fig. 1(a)] that such an extension would not significantly change the estimate of J.

Also notice that $\Delta F(n, p, T)$ has small oscillations for $n \gtrsim 11$. Although partly obscured by the statistical errors, they have physical significance: They describe the variation in free energy with the number of particles which results from layering and packing in the cluster, when that number is a small integer. Similar oscillations have been observed for water and xenon clusters.[8,9] But these features do not affect the value of J [see the smooth behavior of Fig. 1(b)]. As expected, the calculations presented here yield larger free internal energies of cluster formation (i.e., smaller values of ΔF) than those of Ref. 3; this reflects the underestimation of the entropy in that calculation. The consequences are that our calculations yield larger values of J than Ref. 3 for the same conditions. The values of V_c and α do not affect the calculation of J very much because it is dominated by the value of C_n at the maximum in the curves of Fig. 1(a). Knowing the concentrations of the n clusters it is straightforward to calculate the onset of condensation (p, T) curves for a constant nucleation rate. Three sets of curves are presented in Fig. 2 for the values of $J = 10^0$ and 10^6 cm^{-3} s^{-1}. The dashed lines represent the results by Hoare, Pal, and Wegener[3] and seem to be reasonable for $T \simeq 30$ °K. However, it should be said that even at 30 °K the smallest clusters should be melted[5,10] and the quasiharmonic approximation should be a very poor one. Also, these authors do not report calculations of free energies for $n > 20$ or $T > 35$ °K and their results should not be valid for T

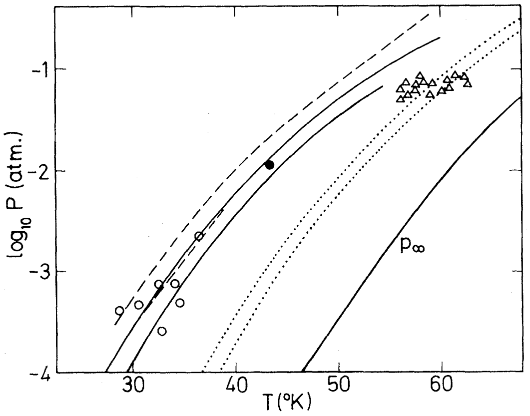

FIG. 2. Comparison of different calculations with experimental data for the onset of condensation. Dotted lines: classical theory; dashed lines: harmonic approximation (both from Ref. 3); continuous lines: this work. In each case the lower and upper curves are for $J = 10^0$ and 10^6 cm^{-3} s^{-1}, respectively. Open triangles and full circles are for pure argon and open circles for argon in helium as a carrier gas (from Ref. 2). p_∞ is the vapor pressure given by Eq. (12).

>35 °K. Even if calculations were performed at higher temperatures, it would be necessary to extend the summation in Eq. (2) to more than $N = 20$ and then their nucleation curves would bend up even more. But even if one does not consider the above points, the curves for constant J in Ref. 3 go far away from the high-T experimental points. The dotted lines are obtained with the classical approximation[3] as used in Ref. 3 with a surface tension of $\sigma = 17.4$ dyn/cm and a vapor pressure given by the formula

$$\log_{10} p_\infty(\text{atm}) = -403.9/T(°\text{K}) + 4.653\,. \tag{12}$$

The results of that calculation do not agree with the measured data at low (p, t) while they fit the high data well. Our Monte Carlo calculations are the continuous curves for $J = 10^0$ and 10^6 cm^{-3} s^{-1}. These have been extended in temperature until the difference in J after summing in Eq. (2) up to $N = 37$ or up to $N = 100$ is by a factor of 2. This happens at 54 °K for $J = 10^0$ cm^{-3} s^{-1} and at 60 °K for $J = 10^6$ cm^{-3} s^{-1}. Note that a factor of 2 in J would shift the (p, T) curves inappreciably. It is clear that the Monte Carlo calculation fits better than the other curves. The reason is that the free energies are able to give a good description of a dominant potential energy at low (p, T) and a good account of the entropy at higher T.

In conclusion we have presented calculations for argon cluster formation in reasonable agreement with experiments over a wide range of (p, T) points without any adjustable parameter in the theory except for the sticking coefficient, taken to be unity, which does not seem to affect the numerical results significantly.[3,4,6] It must be stressed that still better agreement between theory and experiment should be searched for at high-(p, T) nucleation onset. But we strongly believe that this involves new precise experiments,[11] with carrier gas if possible, in the region of $T \simeq 60$ °K as well as better theoretical understanding of the kinetic and nonequilibrium processes which occur during the nucleation. A deeper knowledge of the meaning of clusters at high temperature is also necessary. These theoretical points are now under research. In any case the present results provide a starting point to understand the homogeneous nucleation processes for other more complex systems. Work is in progress for water and ammonia.

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Theory of Spin Relaxation by Magnetic Dipole Interaction in a Fermi Liquid: Application to ^{3}He

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We consider a system of fermions interacting via both strong spin-conserving and weak (spin-nonconserving) magnetic dipole forces. An expression for the spin relaxation rate $1/T_1$ in terms of the incoherent dynamic structure factor $S_I(q,\omega)$ is derived by treating the dipole interaction as a perturbation. We have calculated T_1 for normal liquid ^{3}He at all temperatures using the polarization-potential approach of Aldrich and Pines as well as the measured spin-diffusion coefficient and find good agreement with available data.

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Recently the dynamics of Fermi liquids on the atomic scale has attracted new interest due to both the first neutron scattering data for liquid ^{3}He (Ref. 1) and their theoretical interpretation in terms of the so-called polarization-potential theory.[2] Since neutron scattering experiments are difficult to perform, one may consider whether there are any other physical quantities that can be employed for probing the dynamics of the liquid at large frequency ω and/or wave vector $\vec{q}$. In this Letter, we want to show that one such quantity is the spin-relaxation time T_1, which samples the spin-density excitation spectrum of the liquid for wave vectors up to twice the Fermi wave vector k_F.

A nonequilibrium homogeneous spin polarization $\langle S\rangle$ of a Fermi liquid may relax in the bulk because of spin-orbit interactions such as the dipole interaction of the magnetic moments associated with the fermion spins. In the event that the dipole energy is small in comparison with the characteristic energies of the system (which is the case in ^{3}He), the time scales of the relaxation of the total spin and the motion of the other degrees of freedom (single-particle excitations, collective modes) are well separated and the spin-relaxation rate may be calculated in perturbation theory with respect to the dipole interaction. The elementary spin-relaxation process then consists in the decay of a homogeneous ($\vec{q}=0$) spin fluctuation into two spin modes with momenta $\pm\vec{q}$ via the spin-orbit force, a process by which spin angular momentum is transformed into orbital angular momentum.

We consider a system of fermions interacting via strong spin-conserving forces and the weak dipole-dipole forces associated with the spin magnetic moments, as described by the Hamiltonian

$$H_D = -\tfrac{2}{3}\pi\gamma^2\sum_{\vec{q}}[\vec{S}_{\vec{q}}\cdot\vec{S}_{-\vec{q}} - 3(\hat{q}\cdot\vec{S}_{\vec{q}})(\hat{q}\cdot\vec{S}_{-\vec{q}})].$$

Here $\vec{S}_{\vec{q}}$ is the Fourier component of the spin-density operator with wave vector $\vec{q}$, γ is the gyromagnetic ratio, and $\hat{q}=\vec{q}/|\vec{q}|$. The last term in the $\vec{q}$ sum in H_D clearly breaks spin rotation invariance. It is this interaction that governs the relaxation of the total spin operator $\vec{S}=\vec{S}_{\vec{q}=0}$:

$$\dot{\vec{S}} = 2\pi\gamma^2\hbar^{-1}\sum_{\vec{q}}[(\hat{q}\times\vec{S}_{\vec{q}})(\hat{q}\cdot\vec{S}_{-\vec{q}}) + \text{H.c.}]. \tag{1}$$

Our aim is to express the spin-relaxation rate $1/T_1$ in terms of the spin-density response function $\chi(z)$ defined by

$$\chi(\omega+i0) = (i/\hbar^2)\int_0^\infty dt\, e^{i\omega t}\langle[S^z(t), S^z(0)]_-\rangle \equiv \{M(\omega+i0)/[\omega+M(\omega+i0)]\}\chi(0), \tag{2}$$