

# Evaporation of a liquid

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An evaporation mechanism involving fluctuations in the binding energy of atoms in a surface layer is discussed. An evaporation of clusters of several atoms becomes likely according to this mechanism. A qualitative analysis is supported by the results of a numerical simulation of a phase transition by a molecular-dynamics method.

Textbooks have traditionally described the evaporation of condensed media as a one-particle process, consisting of the escape of the fastest atoms from a potential well with a depth equal to the average binding energy  $U_0$ . In accordance with this picture, one calculates the flux of evaporated atoms as the integral of the quantity  $nv_z$  (the  $z$  axis runs along the normal to the interface) over the velocity  $v_z$  from a minimum value  $v_z^* = (2U_0/m)^{1/2}$  to infinity (Ref. 1, for example). This picture is of course an extreme simplification. Actually, the binding energy  $U$  for atoms which are in the surface layer and which make up most of the evaporated flux is not a fixed quantity. It depends on the structure of the nearest neighborhood of the given atom. It is equal to  $U_0$  only in order of magnitude. There is an important circumstance here: A surface atom which has a binding energy  $U$  must undergo an average of  $\exp(U/kT)$  oscillations before it escapes into the gas phase. In other words, it must remain in a bound state for a time on the order of  $\nu^{-1}\exp(U/kT)$ , where  $\nu$  is a frequency on the order of the Debye frequency. At temperatures  $kT \ll U$  this time is clearly much longer than the time scale for structural changes in the nearest neighborhood of a surface atom, i.e., the time scale for a change in the binding energy  $U$  itself. The evaporation process is thus a collective process. Because of fluctuations in the binding energy, the surface layer acquires atoms or groups of atoms which can be detached by an energy on the order of the average thermal energy, and the lifetime of these atoms or groups in the bound state is on the order of  $\nu^{-1}$ . These atoms determine the evaporated flux. If we adopt this mechanism for the transition of atoms from the condensed phase to the gas phase, then the complex question of the formation of a high-energy tail on a Maxwellian distribution of atoms in the surface layer—a problem which has been discussed repeatedly in the literature but has yet to be resolved—drops out of the picture.

Let us consider at the fluctuations in the binding energy of the surface atoms from the macroscopic standpoint. In actuality, the interface between a liquid and vapor is neither planar nor in a steady state. Long-wave perturbations of the boundary are capillary waves with a dispersion relation  $\omega^2 = \sigma k^3 / \rho$ , where  $\sigma$  is the surface tension. On parts of the boundary which are convex toward the gas phase the binding energy decreases by an amount on the order of  $\sigma kV$ , where  $V$  is the volume per atom. This quantity becomes comparable to  $U_0$  at wavelengths on the order of interatomic dis-

tances. It would of course not be correct to describe such waves at a macroscopic level. For a qualitative discussion of the evaporation mechanism, however, it is convenient to say that waves whose spectrum extends to wavelengths comparable to the thickness of the boundary are excited at the interface (whose thickness far from the critical point is on the order of interatomic distances). As time elapses, the interaction of such surface modes leads to a complex, stochastic change in the shape of the boundary—a sort of surface turbulence. In the course of this motion, short-wave modes give rise to regions of the boundary which have a large local curvature and which contribute substantially to the flux of evaporated atoms. For wavelengths several times the interatomic distances, the motions of several atoms in a wave are correlated. Along with the evaporation of individual atoms, we could thus expect the detachment of small groups or clusters of atoms from the surface.

These simple qualitative considerations have found support in a numerical simulation of the evaporation process by a molecular-dynamics method. Calculations were carried out for a system of 8000 particles with a Lennard–Jones (6–12) potential. The parameters of the potential corresponded approximately to the interaction of argon atoms. Periodic boundary conditions in the  $(x, y)$  plane were imposed on the system. The period was about  $20d$ , where  $d$  is an average interatomic distance. Calculations were carried out for a closed volume with a fixed number of particles and also under conditions such that particles could escape from the computation region. The results of these calculations show that the local thickness of the interface is smaller than the average thickness of the transition layer between the liquid and the gas by a factor of several units (the averaging was carried out over cross sections of the computation region perpendicular to the  $z$  axis). The surface layer is thus inhomog-

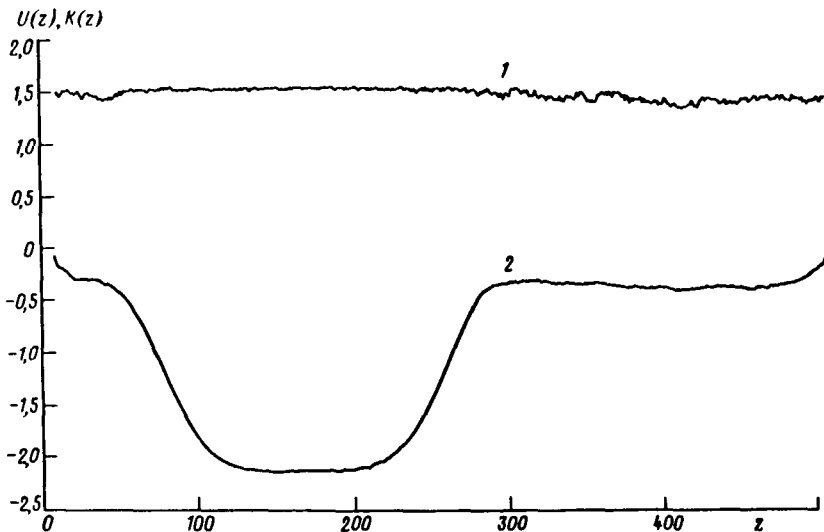


FIG. 1. Profiles of (1) the average kinetic energy in the  $(x, y)$  plane and (2) the potential energy along the coordinate  $z$ .

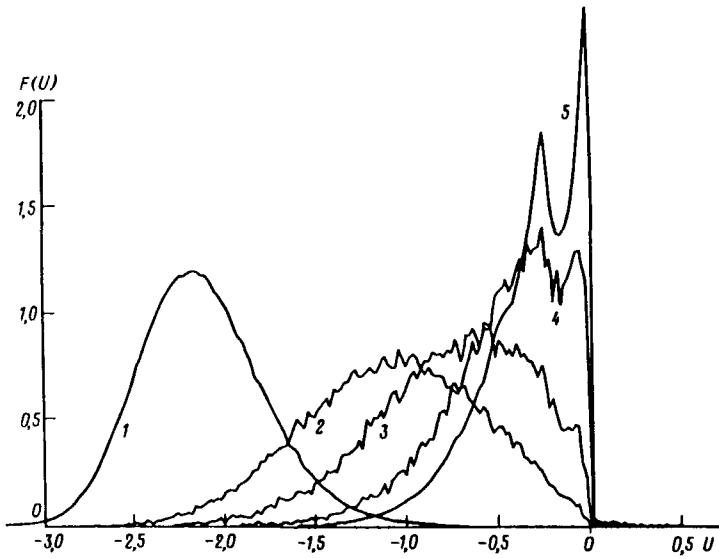


FIG. 2. Normalized probability density of the potential energy in the liquid (1), in the gas (5), and in the transition layer (2-4). The nucleation of clusters in the transition layer can be seen on curve 4.

enous. Oscillations with a length scale on the order of several interatomic distances are excited in this layer. The mechanism by which these motions are excited may be analogous in a qualitative sense to the mechanism for the instability of a plane evaporation front which was discussed in Ref. 2.

Let us look at some of the results of these calculations. Figure 1 shows the  $z$  profiles of the average potential energy in the  $(x, y)$  plane and the kinetic energy, per atom in both cases. The temperature here was fairly high, 0.77 of the thermodynamic critical temperature of argon. The average thickness of the transition layer under these conditions is about  $8d$ . It is clear from these calculated results that fairly large clusters (with something on the order of ten atoms) sometimes detach from the surface. They are usually in a vibrationally excited state, and in the gas phase they break up into smaller clusters. Near the surface, the number of "geometric" clusters, defined as groups of close-lying atoms, is considerably higher than the number of stable clusters, which have a negative total energy in the coordinate system moving with the center of gravity of the cluster.

Figure 2 shows the normalized probability density for the potential energy per atom in the liquid (curve 1), the gas (curve 5), and the transition layer (2-4) according to these calculations. The energy was averaged over a layer with a thickness on the order of  $0.2d$  in the  $(x, y)$  plane. In the gas phase the potential energy distribution has several characteristic features associated with the formation of diatomic and larger clusters. The potential energy distribution for the gas has a well-expressed tail in the region of negative energies. The average potential energy per atom in the gas is negative (as can also be seen from Fig. 1). From Fig. 2 we see that the spread of

binding energies in the transition layer increases with decreasing average density. The observed deviations from a monotonic distribution indicate a nucleation of clusters in the transition layer.

The results of these calculations and also the calculation method will be reported in more detail in a separate paper.

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<sup>1</sup>J. Frenkel (Ya. I. Frenkel'), *Kinetic Theory of Liquids*, Dover, New York, 1955.

<sup>2</sup>S. I. Anisimov and M. I. Tribel'skii, *Sov. Sci. Rev. A (Phys. Rev.)* (ed. I. M. Khalatnikov) **8**, 269 (1987).

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