Diffusion from Sessile Droplets Through Membranes

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We analyze diffusion from a periodic array of hemispherical droplets through a membrane. We find that the multiple sources do not interact strongly, even when the droplets are closely spaced, so that the flux through the membrane appears nearly additive.

The solutions to differential equations involving complicated geometries and time-dependent boundary conditions are known to result in departures from Fickian scaling. One practical problem where these considerations are met is the diffusion from sessile aerosol droplets of, for example, environmental pollutants through permeable membranes.

Consideration of the microscopic structure of the polymer membrane leads to further complications. For example, in the case of rubbery polymers one is faced with a concentration-dependent diffusion coefficient, while in the case of glassy polymers one must explicitly introduce non-Fickian time-dependent relaxation terms to the diffusion equation.

The case of diffusion from a neat droplet, in which one encounters a moving boundary problem as the diffusant both evaporates and permeates the membrane, has been treated both analytically and numerically.

Another case is that of diffusion from a polymer-thickened droplet through a membrane. Here, the droplet retains its shape and the moving boundary problem is avoided. The geometry is that of a spherical cap of
radius $R$ and contact angle $\alpha$ attached by its base to a planar membrane of thickness $L$.

The problem of diffusion from a single hemispherical droplet ($\alpha = \pi/2$) has been solved analytically, and the more general case of arbitrary $\alpha$ has been investigated by direct numerical simulation.

An expected result, closely demonstrated by the simulation, is that the droplet can behave as a trapping site, particularly if the partition coefficient $K$, defined to be the ratio of the solubility of the diffusant in the droplet to that in the membrane, is large compared to unity and the ratio to the diffusion coefficient in the droplet to that in the membrane, $D_D/D$, is small.

It is interesting to ask the effect of multiple droplet sources on the time dependence of the flux of diffusant through the membrane. In particular, at high areal density, the trapping nature of the droplets is expected to become more pronounced.

We consider a periodic rectangular array of droplets atop a membrane of thickness $6R$, to which we have applied the random walk techniques of ref. 9. We present preliminary results for the case $D_D/D = 1$, $K = 1$, and $\alpha = \pi/2$. Shown in Fig. 1 are the total exit flux per droplet for lattice spacings $2R$, $4R$, and $10R$, as well as that for a single droplet.

Also shown in Fig. 1 is an approximation to the flux through an area $4R^2$ from a uniform film of thickness $\pi R/6$. This was found by computing the leading term of the Bromwitch integral of the Laplace transformation of the flux.

![Fig. 1. Total exit flux $J(t)$ per droplet for lattice spacings $2R$, $4R$, and $10R$, as well as that from a single droplet, through a membrane of thickness $6R$. The smooth curve corresponds to the flux from a uniform film.](image-url)