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Scaling function for the critical diffusion coefficient of a critical fluid in a finite geometry

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The long-wavelength diffusion coefficient of a critical fluid confined between two parallel plates, separated by a distance *L*, is strongly affected by the finite size. Finite size scaling leads us to expect that the vanishing of the diffusion coefficient as ξ^{-1} for $\xi \ll L$, ξ being the correlation length, would crossover to L^{-1} for $\xi \gg L$. We show that this is not strictly true. There is a logarithmic scaling violation. We construct a Kawasaki-like scaling function that connects the thermodynamic regime to the extreme critical $(\xi \gg L)$ regime.

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One of the earliest and certainly one of the most frequently used scaling functions in critical dynamics is the scaling function for the thermal conductivity/concentration diffusivity in a single component/binary fluid near the gas-liquid critical point/critical mixing point. This is the well known Kawasaki function, which describes the passage of the diffusion coefficient (we will use binary liquid language) from a long-wavelength, finite correlation length regime to a finite-wavelength, infinite correlation length regime. When the wavelength is very large (k, the wave number→0), the diffusion coefficient D vanishes as $\xi^{4-d} = \kappa^{d-4}$, where ξ is the correlation length, κ is the inverse correlation length, and d is the dimensionality of space. At the critical point (κ=0), this behavior changes to k^{d-4}. In the physical $(d=3)$ situation, we have the passage described by the Kawasaki function $K(x)$ [1]:

$$D(k,\kappa) = \frac{k_B T}{6\pi\eta_0 \xi} K(k\xi) \tag{1}$$

with

$$K(x) = \frac{3}{4x^2}\left[1 + x^2 + \left(x^3 - \frac{1}{x}\right)\tan^{-1}x\right]. \tag{2}$$

If $k \to 0$, $D(\kappa) = k_B T/6\pi\eta_0\xi$ and for $\kappa \to 0$, $D(k) = (k_B T/6\pi\eta_0)(3\pi/8)k$. In the above, η_0 is the background critical viscosity. The small divergence of the critical viscosity is ignored in this paper. A practical approximation to the Kawasaki function is to write it as

$$D(k,\kappa) = \frac{k_B T}{6\pi\eta_0} \frac{Ł(k,\kappa)}{\chi(k,\kappa)} \tag{3}$$

with Ł having the property that

$$\frac{Ł}{\chi} \to \kappa \text{ as } k \to 0 \to \frac{3\pi}{8}k = 1.18\ k \simeq k \text{ as } \kappa \to 0 \tag{4}$$

and χ is the susceptibility. The first correction being known to be of the form k^2/κ^2 about the $k=0$ limit, we can use the approximation $Ł(k,\kappa)/\chi(k,\kappa) = (k^2+\kappa^2)$ and so the diffusion coefficient becomes

$$D(k,\kappa) = \frac{k_B T}{6\pi\eta_0}(k^2+\kappa^2)^{1/2}. \tag{5}$$

This is exact for $k \to 0$ and over the range of practical values of the k/κ ratio, is accurate to about 5%. This makes it a very useful approximation.

In this paper, we want to look at the diffusion coefficient in a finite geometry [2–4]—the fluid contained between two slabs separated by a distance L. Recently Koch and Dohm [5] have explored finite size effects on the diffusion coefficient in three dimensional Ising-like systems. Unlike their situation, we will show that our system exhibits a small scaling violation. This is a physical model and hence this violation should be experimentally accessible. The hydrodynamic limit is taken to hold, i.e., we are in the long wavelength limit (i.e., $k=0$). For $L \gg \xi$, the diffusion coefficient will be governed by $D(\kappa) = (k_B T/6\pi\eta_0)\kappa$. In the finite geometry, the leading correction to this result was first obtained by Calvo and Ferrell [6]. The result was a bit of a surprise in the presence of a logarithmic factor

$$Ł(\kappa,L) = \kappa^{-1}\left[1 - \frac{\ln \kappa L}{2\kappa L}\right], \quad \kappa L \gg 1. \tag{6}$$

This was later obtained using a different technique by one of the present authors [7]. The appearance of the logarithmic term prompted us to explore the limit $\xi \gg L$. In this limit, we find (as explained below)

$$Ł(\kappa=0,L) = \frac{L}{12}\ln\frac{1}{\kappa L}.$$

To arrive at the diffusion coefficient, one needs

$$D(\kappa,L) = \frac{k_B T}{6\pi\eta_0}\frac{Ł(\kappa,L)}{\chi(\kappa,L)},$$

where $\chi(\kappa,L)$ is the susceptibility in the finite geometry. The limiting form of $\chi(\kappa,L)$ are $\chi(\kappa,L\to\infty) = \kappa^{-2}$ and $\chi(\kappa \to 0,L) = L^2/12$, so that

$$D(k,\kappa)\to\frac{k_BT}{6\pi\eta_0}\kappa\left(1-\frac{1}{2}\frac{\ln\kappa L}{\kappa L}\right),\quad\text{for }\kappa^{-1}<L$$
$$\to\frac{k_BT}{6\pi\eta_0}\frac{1}{L}\ln\frac{1}{\kappa L},\quad\text{for }\kappa^{-1}\gg L.\tag{7}$$

We combine the two forms to propose the scaling function

$$D(k,\kappa)=\frac{k_BT}{6\pi\eta_0\xi}\left(1+\frac{1}{\kappa^2L^2}\right)\frac{1+\frac{1}{8}\left[\ln\left(1+\frac{1}{\kappa^2L^2}\right)\right]^2}{1+\frac{1}{2\kappa L}\ln\left(\kappa L+\frac{1}{\kappa L}\right)}$$
$$=\frac{k_BT}{6\pi\eta_0\xi}F(\kappa L),\tag{8}$$

which is the (κ,L) analog of the Kawasaki scaling function, given in Eq. (2).

In the thermodynamic limit $(\kappa L\to\infty)$, $F(\kappa L)=1$ and rises to $(1/\kappa L)\ln(1/\kappa L)$ as $\kappa L\to 0$. The change in κL is brought about by varying ξ at a fixed L. At $\kappa L=1$, $F(\kappa L)=1.57$, significantly different from its value in the thermodynamic limit. This should make the effect observable. To see the existence of the logarithmic terms, one would need a fairly high degree of accuracy. Now we outline the technical details.

The free energy functional that governs the static fluctuation of the order parameter ψ can be taken to be quadratic and is given by [8,9]

$$F=\int d^{D-1}r\int_0^L dz\left[\frac{\kappa^2}{2}\sum_{i=1}^{n}\psi_i^2+\frac{1}{2}\sum_{i=0}^{n}(\vec{\nabla}\psi_i)^2\right]$$
$$+\frac{c}{\lambda}\int d^{D-1}r[\psi^2(\vec{r},z=0)+\psi^2(\vec{r},z=L)].\tag{9}$$

Since the anomalous dimension index η plays an insignificant role in the study of dynamics, we can work with this quadratic expression for F. Here the geometry is restricted in the z direction between $z=0$ and $z=L$. The second term on the right hand side of Eq. (9) is a surface contribution, "c" is a constant and λ, an extrapolation length. For $\lambda\to 0$, ψ^2 must vanish at $z=0$ and $z=L$ in order to satisfy the Dirichlet boundary conditions. We set $\lambda=0$.

We introduce the Fourier transform of $\psi(\vec{r},z)$ through the relation

$$\psi(\vec{r},z)=\frac{1}{(2\pi)^2}\int\psi(\vec{k},z)e^{i\vec{k}\cdot\vec{r}}d^2k,\tag{10}$$

where $\vec{k}$ is the wave vector in the two-dimensional space. The two-point correlation function $G(\vec{k},z_1,z_2)$ is the solution of the differential equation

$$\left(\frac{d^2}{dz^2}-k^2-\kappa^2\right)G(k,z_1,z_2)=-\delta(z_1-z_2)\tag{11}$$

with $G(\vec{k},z_1,z_2)$ vanishing at $z=0$ and $z=L$ and is given by

$$G(\vec{k},z_1,z_2)=\frac{\sinh az_<\sinh a(L-z_>)}{2a\sinh aL}\tag{12}$$

with $a^2=k^2+\kappa^2$. For $L\to 0$ and $z_1>z_2$, Eq. (12) approximates to

$$G\sim\frac{z_<(L-z_>)}{2L}.\tag{13}$$

At this point it is easy to check that $\chi(\kappa,L)=(1/L)\int G(\vec{k}=0,z_1,z_2)dz_1dz_2$ gives the results mentioned above, Eq. (7).

To study the dynamics, we need to introduce the equation of motion for ψ field. We take this to be a Langevin [10] equation where the potential corresponds to the free energy functional of Eq. (9). For the nonconserved ψ field, this reads as

$$\frac{\partial\psi}{\partial t}=-\Gamma\left(k^2+\kappa^2-\frac{\partial^2}{\partial z^2}\right)\psi(\vec{k},z,t)+N(\vec{k},z,t),\tag{14}$$

where $N(\vec{k},z,t)$ is the noise, characterized by the correlation

$$\langle N(\vec{k}_1,z_1,t_1)N(\vec{k}_2,z_2,t_2)\rangle$$
$$=2\Gamma\,\delta(\vec{k}_1+\vec{k}_2)\,\delta(z_1-z_2)\,\delta(t_1-t_2).\tag{15}$$

If the order parameter field ψ is conserved, there will be an additional factor $(k^2-\partial^2/\partial z^2)$ multiplying Γ in Eq. (14). The dynamic correlation function reads

$$C(\vec{k},z_1,z_2)=\langle\psi(\vec{k},z_1,\omega)\psi(-\vec{k},z_2,-\omega)\rangle$$
$$=\frac{1}{\Gamma^2}\int dz'dz''R_+(z_1,z')R_-(z_2,z'')$$
$$\times\langle N(z')N(z'')\rangle$$
$$=\frac{2}{\Gamma}\int dz'R_+(z_1,z')R_-(z_2,z'),\tag{16}$$

where

$$R_\pm=\frac{\sinh a_\pm z_<\sinh a_\pm(L-z_>)}{2a_\pm\sinh a_\pm L}\tag{17}$$

with

$$a_\pm^2=\pm\frac{i\omega}{\Gamma}+k^2+\kappa^2.\tag{18}$$

We note that the current $\vec{j}(\vec{r},z,t)$ associated with a transport process is, in general, a bilinear combination of the order parameter field or a combination of the order parameter field with a secondary field. Then Kubo's formula yields the Onsager coefficient corresponding to the current $\vec{j}(\vec{r},z,t)$ as

$$\lambda \propto \frac{1}{V_2 L T}\int \langle \vec{j}(\vec{r}_1,z_1,t_1)\cdot \vec{j}(\vec{r}_2,z_2,t_2)\rangle \times d^2r_1 d^2r_2 dz_1 dz_2 dt_1 dt_2, \tag{19}$$

where V_2 is the volume in the two-dimensional space.

For the binary liquid system, the order parameter field ψ is the density difference between the liquid and gaseous phase and the relevant current is $\vec{j}=\psi\vec{v}$, where $\vec{v}$ is the velocity field. For the liquid-gas system, this current is proportional to the entropy current and so Kubo's formula yields the thermal diffusivity. For a binary mixture, the current is the mass current and Kubo's formula yields the mass diffusivity. Using $\vec{j}=\psi\vec{v}$ in Eq. (19), we have

$$\lambda \propto \frac{1}{V_2 L T}\int \langle \psi(\vec{r}_1,z_1,t_1)\vec{v}(\vec{r}_1,z_1,t_1)\cdot \psi(\vec{r}_2,z_2,t_2) \times \vec{v}(\vec{r}_2,z_2,t_2)\rangle d^2r_1 d^2r_2 dz_1 dz_2 dt_1 dt_2. \tag{20}$$

The decoupled mode approximation enables us to write the correlation function in Eq. (20) as a product of two correlation functions [11] viz. $\langle \psi(\vec{r}_1,z_1,t_1)\psi(\vec{r}_2,z_2,t_2)\rangle$ and $\langle \vec{v}(\vec{r}_1,z_1,t_1)\cdot\vec{v}(\vec{r}_2,z_2,t_2)\rangle$ and so finally we have

$$\lambda \propto \frac{1}{L}\int C_{\psi\psi}(\vec{k},z_1,z_2,\omega)C_{vv}(-\vec{k},z_1,z_2,\omega)d^2k\,d\omega\,dz_1 dz_2, \tag{21}$$

where $C_{\psi\psi}$ and C_{vv} , respectively, stand for the order parameter and velocity correlation functions.

We note that the time scales associated with the velocity field and the density field are very different. The velocity field relaxes much faster and in the time scale (t_1-t_2), the density field changes hardly. As a result, the order parameter correlation function $C_{\psi\psi}(\vec{r}_1-\vec{r}_2,z_1,z_2,t_1-t_2)$ can be taken to remain at its static value and hence one needs the zero frequency limit of the velocity correlation function C_{vv}. Therefore Eq. (21) reduces to

$$\lambda \propto \frac{1}{L}\int d^2k\,dz_1 dz_2 C\psi\psi^{\rm static}(\vec{k},z_1,z_2)C_{vv}(-\vec{k},z_1,z_2,\omega=0). \tag{22}$$

The static correlation function for the order parameter ψ is given by Eq. (13). We now evaluate the zero frequency limit of the velocity correlation function $c_{vv}(-\vec{k},z_1,z_2,\omega)$. The relaxation dynamics of the $\vec{v}$ field is governed by

$$\frac{\partial \vec{v}}{\partial t} = -\Gamma_v\left(k^2-\frac{\partial^2}{\partial z^2}\right)\vec{v}(\vec{k},z,t)+\vec{N}_v. \tag{23}$$

The velocity field is solenoidal and so $\vec{\nabla}\cdot\vec{v}=0$. The above constraint tells us that we should work with a field $\vec{A}$, such that $\vec{v}=\vec{\nabla}\times\vec{A}$. The correlation function C_{AA} for the $\vec{A}$ field is given by Eq. (12) with $\kappa=0\Rightarrow T=T_c$. The velocity correlation function follows from

$$C_{vv}=\left(k^2+\frac{\partial^2}{\partial z_1\partial z_2}\right)C_{AA}. \tag{24}$$

In the limit $L\to 0$, it is found to be

$$C_{vv}=\frac{1}{2\Gamma}\left[\frac{1}{2k^2L^2}(4z_2-z_1)\right]. \tag{25}$$

Using Eqs. (13) and (25), the Onsager coefficient, in the three spatial dimensions, is

$$\begin{aligned}
\lambda &\propto \frac{1}{L}\int d^2k\,dz_1 dz_2 C^{\rm static}_{\psi\psi}(\vec{k},z_1,z_2)C_{vv}(-\vec{k},z_1,z_2,\omega=0)\\
&=\frac{1}{L}\int d^2k\int_0^L\left[\int_0^{z_1}+\int_{z_1}^{L}\right]dz_2\frac{1}{4\Gamma k^2L^2}(4z_2-z_1)\\
&\quad\times\frac{z_2(L-z_1)}{2L}\quad (z_1>z_2)\\
&=\frac{1}{4\Gamma L^4}\int\frac{d^2k}{k^2}\int_0^L(L-z_1)dz_1\int_0^{z_1}z_2(4z_2-z_1)dz_2,\\
&\quad\text{since}\int_0^L dz_1\left[\int_0^{z_1}+\int_{z_1}^{L}\right]dz_2\\
&=2\int_0^L dz_1\int_0^{z_1}dz_2\\
&=\frac{1}{4\Gamma L^4}\frac{5}{6}\int\frac{d^2k}{k^2}\int_0^L z_1^3(L-z_1)dz_1\\
&=\frac{L}{96\Gamma}\int\frac{d^2k}{k^2}.
\end{aligned} \tag{26}$$

Therefore, for $L\to 0$

$$\lambda \propto L\int_\kappa^{L^{-1}}\frac{dk}{k}\sim L\ln\frac{1}{\kappa L}. \tag{27}$$

This establishes the point we wanted to make in Eq. (7). Normalizing to the same prefactor for the large κ and small κ limits leads to the coefficients in Eq. (7).

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