EFFUSION OF A DILUTE GAS REVISITED : VAN KAMPEN'S EXPANSION

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Abstract

We have studied the problem of effusion of a dilute gas through a hole by means of van Kampen's systematic Ω-expansion. In this way, the macroscopic equation as well as the Fokker-Planck equation for the fluctuations around the macroscopic behaviour have been obtained and some dubious points in a recent analysis of the problem clarified.

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I. INTRODUCTION

Quite recently[1], the problem of effusion of a low pressure gas through a hole, connecting two volumes V_A and V_B, has been analyzed in a stochastic framework. Using some simple probability concepts, the master equation[2] for the probability density $P(N_A,t)$ of having N_A molecules in volume V_A at time t, has been found. As was remarked in Ref.[1], the question of how this phenomenon proceeds in time, is not found in the elementary literature. Also, the author states that this is a **most transparent application of the Fokker-Planck equation** (FPE), **still not completely trivial**. He then proceeds with a Taylor like expansion up to terms of order 1/N (N being the total number of molecules), obtaining in this way a FPE for the process. However, the method used is clearly not systematic and some inconsistencies can be pointed out.

We, on the other hand, believe that this problem configures a clean and very clear classroom introduction to van Kampen's Ω-expansion method for the master equation[2,3]. Within this scheme one is able to show how to extract the macroscopic equation that drives the process as well as the FPE for the fluctuations around such macroscopic behaviour. This approach has become a standard technique and is one of the most efficient methods to extract a FPE from a master equation (if the latter fulfills some conditions). With few

exceptions[3], it has not been discussed in textbooks of statistical mechanics. It is with the aim of providing a didactic example to introduce this expansion in statistical mechanics courses that we present the analysis of the effusion problem within the framework of the Ω-expansion method. In what follows we introduce the method by applying it to this problem. We show the resulting macroscopic equation and FPE, the way to solve them, and some results in the nonequilibrium situation. Also, some improvements on what, in our judgement, are failings in the previous analysis are pointed out.

II. THE METHOD

We will not repeat here the arguments used to derive the master equation, but will refer to the results of Ref.[1]. Also, we will use the same nomenclature (except that we adopt the usual P for the probability density instead of W). The master equation for the probability density $P(N_A,t)$ is then given by[1],

$$(d/dt)P(N_A,t)=(sv/a(1-a)V)\ \{(1-a)\ [(N_A+1)\ P(N_A+1,t)-N_A\ P(N_A,t)]$$

$$+\ a\ [(N-N_A+1)\ P(N_A-1,t)-(N-N_A)\ P(N_A,t)]\} \qquad (1a)$$

where s is the area of the hole, v the average value of the velocity component of the molecule along the normal to

s, $V = V_A + V_B$, N the total number of molecules and $a = V_A/V$. It is useful to introduce here the **step operator** $\mathbb{E}$, which is defined by[2],

$$\mathbb{E}\ g(N_A) = g(N_A + 1)$$

$$\mathbb{E}^{-1}\ (N_A) = g(N_A - 1)$$

where $g(N_A)$ is an arbitrary function of N_A. Then Eq.(1a) maybe written as

$$(d/dt)\ P(N_A,t) = (sv/a(1-a)V)\ \{(1-a)\ [\mathbb{E} - 1]\ N_A\ P(N_A,t)$$

$$+ a\ [\mathbb{E}^{-1} - 1]\ (N-N_A)\ P(N_A,t)\} \qquad (1b)$$

In order to illustrate the Ω-expansion method we will show how it works, by directly applying it, in this situation and making the relevant comments at each stage. The so called Ω parameter refers to a system's parameter that is "large", and such that its inverse, or more correctly $\Omega^{-1/2}$, being "small", could be used as an expansion parameter. The first point is that the rate for transitions from state n to state m in the master equation, $W(m|n)$, must have the (so called canonical) form[2], which essentially means a Taylor expansion of $W(m|n)$ in Ω^{-1} in which each term is a function of Ω only through the intensive variable m/Ω:

$$W(m|n) = f(\Omega)\ \{\Phi_o(m/\Omega,\ r) + (1/\Omega)\ \ \Phi_1\ (m/\Omega,\ r) + \ldots\}$$

where r=n-m is the step size, and $f(\Omega)$ is some arbitrary function of Ω. As can be seen from Eq.[1], adopting $\Omega = V$, this condition is fulfilled in our master equation, the arbitrary function f being $f(V)= sv/a(1-a)$. A second point is that we can assume that $P(N_A,t)$ is sharply peaked at values of $N_A \sim \langle N_A \rangle$, which is of (macroscopic) order "V"(or Ω), and will have, ccording to the Central Limit Theorem[2], a width of order $V^{1/2}$. Then, it is reasonable to make the separation of N_A into a macroscopic part of order V, and fluctuations around it of order $V^{1/2}$:

$$N_A = V\psi_A\ (t) + V^{1/2}\xi \qquad (2)$$

We can now rewrite the master equation in terms of ξ rather than N_A. The probability of finding the system with a value of the stochastic variable N_A in the range $(N_A,\ N_A+1)$ is related to the corresponding probability for the new stochastic variable ξ by,

$$W(N_A,\ t)\ \Delta N_A = \Pi\ (\xi,\ t)\Delta\xi \qquad (3a)$$

where

$$\Pi(\xi, t) = P(V\psi_A(t) + V^{1/2}\xi, t) \qquad (3b)$$

It is clear that we have

$$\frac{\partial \pi}{\partial t} = V^{1/2}\, \partial P/\partial N_A \qquad (4a)$$

and

$$\frac{\partial \Pi}{\partial t} = \partial P/\partial t + V^{1/2}\frac{\partial \Pi}{\partial \xi}\, d\psi_A/dt = \partial P/\partial t + V\partial P/\partial N_A\, d\psi_A/dt \qquad (4b)$$

We can rewrite the form (2) and relations (4a,b), as well as the form of the shift operator $\mathbb{E}$ in Eq. (1b), in terms of the variable ξ, giving

$$\mathbb{E}^{\pm 1} = \exp\{\pm V^{-1/2}\,\partial/\partial\xi\} = 1 \pm V^{-1/2}\frac{\partial}{\partial\xi} + 1/2\, V^{-1}\frac{\partial^2}{\partial\xi^2} + \ldots \qquad (5)$$

After scaling the time variable: $t \longrightarrow \tau = (sv/a(1-a)V)t$, the master equation (1b) has the expanded form (with $N = nV$),

$$\frac{\partial \Pi}{\partial t} - V^{1/2}\dot{\psi}_A\frac{\partial \Pi}{\partial \xi} = \left[V^{-1/2}\frac{\partial}{\partial\xi} + \frac{V^{-1}}{2}\frac{\partial^2}{\partial\xi^2} + \ldots\right](1-a)\left[V\psi_A + V^{1/2}\xi\right]\Pi$$

$$+\left[-V^{-1/2}\frac{\partial}{\partial\xi}+\frac{V^{-1}}{2}\frac{\partial^2}{\partial\xi^2}+\ldots\right]a\left[V(n-\psi_A)-V^{1/2}\xi\right]\Pi \tag{6}$$

Collecting and equating powers of V, and in order that the large terms proportional to $V^{1/2}$ disappear from the Eq.(6), we ask that the following equation be fulfilled

$$\dot{\psi}_A(\tau)= n\,a-\psi_A \tag{7}$$

which is just the **macroscopic equation.** The solution of Eq.(7) will have then the form

$$\psi_A(\tau)=\psi^{\circ}_A e^{-\tau}+na(1-e^{-\tau}) \tag{8}$$

where ψ°_A is the initial condition. It is clear that for $\tau\longrightarrow\infty$, $\psi_A(\infty)\longrightarrow na$, which corresponds to the stationary equilibrium value. Here it becomes clear why $t_d = sv/a(1-a)V$ plays the role of a relaxation time as was suggested in Ref.[1]. Up to the next order ($V^{\circ}=1$), Eq.[6] will give

$$\frac{\partial\Pi}{\partial\tau}=\frac{\partial}{\partial\xi}\xi\Pi+\left[(1-2a)\,\psi_A(\tau)+na\right]\frac{\partial^2}{\partial\xi^2}\Pi$$

which is the desired FPE. As it is a **linear FPE** (however, with coefficients that are functions of time through its

dependence on the solution of the macroscopic equation, Eq.(7), ψ_A) it follows that its solution **must be a Gaussian**[3,5]. In order to have its form explicitly, it is enough to solve the equations for the first two moments, which can be obtained multiplying Eq.(9) by ξ and ξ^2, respectively, and integrating over ξ. The resulting equations are

$$\frac{d}{d\tau} \langle \xi \rangle = - \langle \xi \rangle \qquad (10a)$$

$$\frac{d}{d\tau} \langle \xi^2 \rangle = (1-2a)\ \psi_A(\tau) + na - 2 \langle \xi^2 \rangle \qquad (10b)$$

The solution of Eq.(10a) is clearly a decaying exponential. Solutions of Eq.(10b) for different values of the parameters (with zero initial conditions in $\langle \xi(o) \rangle$ and $\langle \xi^2(o) \rangle$) are depicted in Fig. I. There we see that, depending on the situation under study, we can find an increase of the fluctuations beyond the stationary value before the fluctuations decay reaching the stationary regime. With the above results we can write the solution of the FPE Eq.(9) as,

$$\Pi(\xi, \tau) = \left[2\pi\ \sigma^2(\tau)\right]^{-1/2} \exp\left\{ - \frac{[\xi - \langle \xi(\tau) \rangle]^2}{2\ \sigma^2(\tau)} \right\} \qquad (11)$$

where $\sigma^2(\tau) = \langle \xi^2 \rangle - \langle \xi \rangle^2$. In Fig. II we present results for this probability distribution $\Pi(\xi, \tau)$, at three different

times. The increase in the distribution width before reaching the smaller value corresponding to the stationary regime is clearly seen.

III. DISCUSSION

The procedure developed above makes clear that van Kampen's Ω-expansion method is a systematic procedure, which allows us to extract from the master equation, at different orders in $\Omega^{1/2}$, the macroscopic equation which drives the system towards the stationary equilibrium condition[5] and the FPE for the fluctuations around such macroscopic behavior. The form of the solution of the macroscopic equation Eq.(7), makes clear the interpretation of $t_d = sv/a(1-a)V$ as a relaxation time. For instance, if we start with the volume V_A empty (i.e.: $\psi^o_A = 0$), from Eq.(8) we see that the stationary value $\psi_A(\infty) = na$, will be reached only after a time of order t_d has elapsed. This point was not clear from the results of Ref.[1]. On the other hand, by means of this procedure we always obtain a linear FPE[5].

Next, we want to compare our result for the FPE, Eq.(9), with the corresponding result of Ref.[1] (Eq.(3) there). According to the change of variables done in Ref.[1], we can compare his variable z, with our variable ξ,

$$N_A = V\, n\, a + V^{1/2}\,(n^{1/2}\, a\, z) \qquad \text{(Ref.[1])}$$

$$N_A = V\, \psi_A + V^{1/2}\xi \qquad \text{(Ours)}$$

This seems to indicate that the expansion in Ref.[1] has been done around the stationary value =a n V. Also we could identify ξ <--> $n^{1/2}$ a z, and then rewrite Eq.(9) in terms of the variable z,

$$\frac{\partial P}{\partial z} = \frac{\partial}{\partial z}\, zP + \left[\frac{1-a}{a} + \frac{1-2a}{2a}\;\frac{\psi_A - na}{na}\right]\frac{\partial^2}{\partial z^2}P \qquad (12)$$

This point as well as his comment before Eq.(3), clearly indicate that, since his expansion is not systematic, he found terms with mixed orders. Also comparing with our results and eq. (12) , his FPE Eq.(3), will correspond to an expansion around the stationary value ($\psi_A(\infty) = na$). Of course, it is clear that the stationary probability distribution will agree in both cases,

$$\Pi(\xi,\infty) = \Pi^{st}(\xi) = \left[2\Pi\, an(1-a)\right]^{-1/2} \exp\left\{-\frac{\xi^2}{2an(1-a)}\right\} \qquad (13)$$

However, the results obtained in the present paper, based on van Kampen's systematic method, are more general and thus more adequate to describe the time evolution of the

effusion process. It is also simple if required, and without the need of extra calculations, to obtain the correlation of the fluctuations in the stationary state[2].

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REFERENCES

1) C. Bernardini, Am. J. Phys. 57, 1116 (1989).

2) N.G. van Kampen, "Stochastic Processes in Physics and Chemistry" (North Holland, Amsterdam, 1981).

3) L. E. Reichl, "A Modern Course in Statistical Physics" (Univ. Texas Press, Austin, 1980).

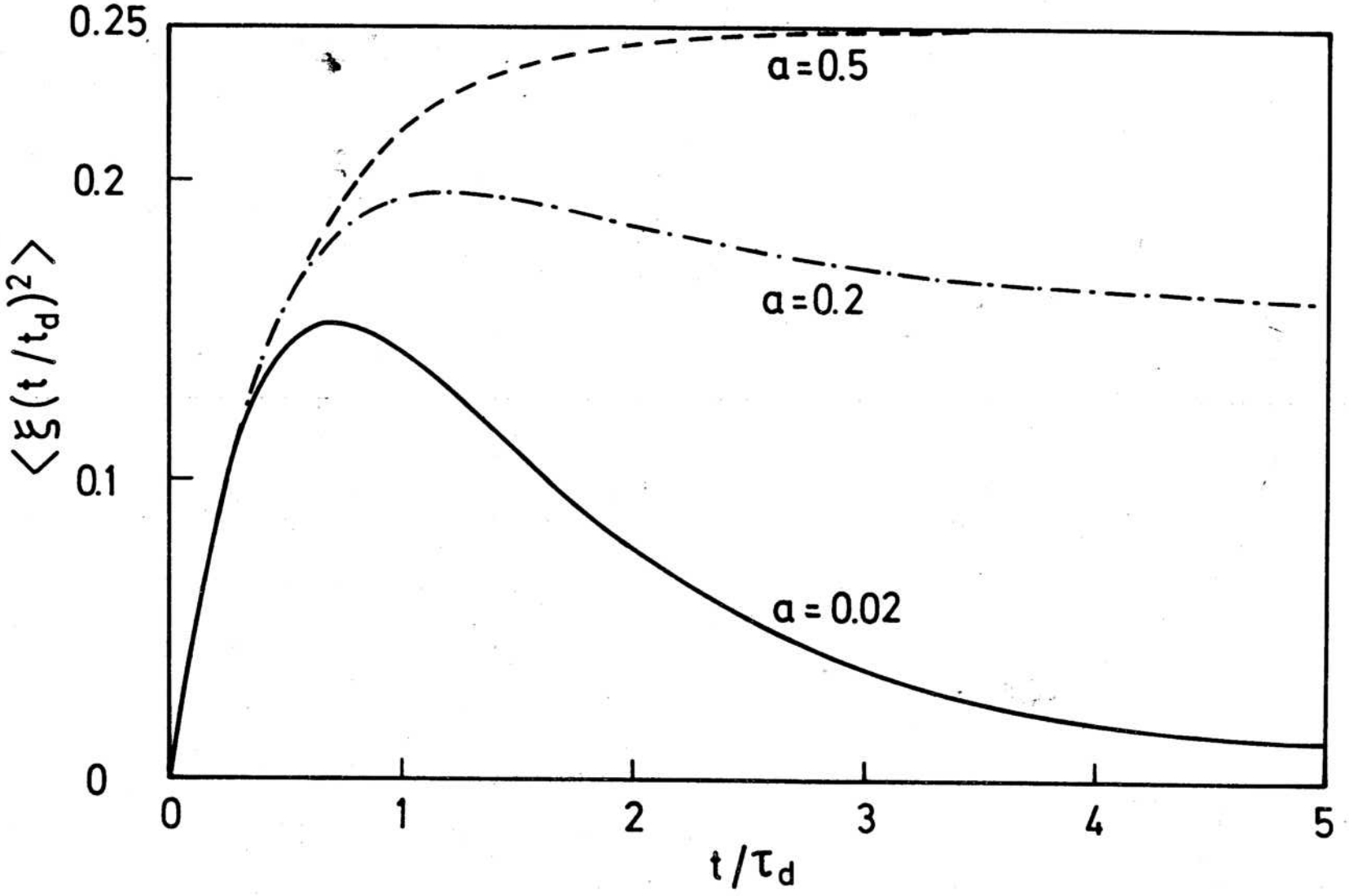
4) C.W. Gardiner, "Handbook of Stochastic Methods" (Springer-Verlag, Berlin, 1983).

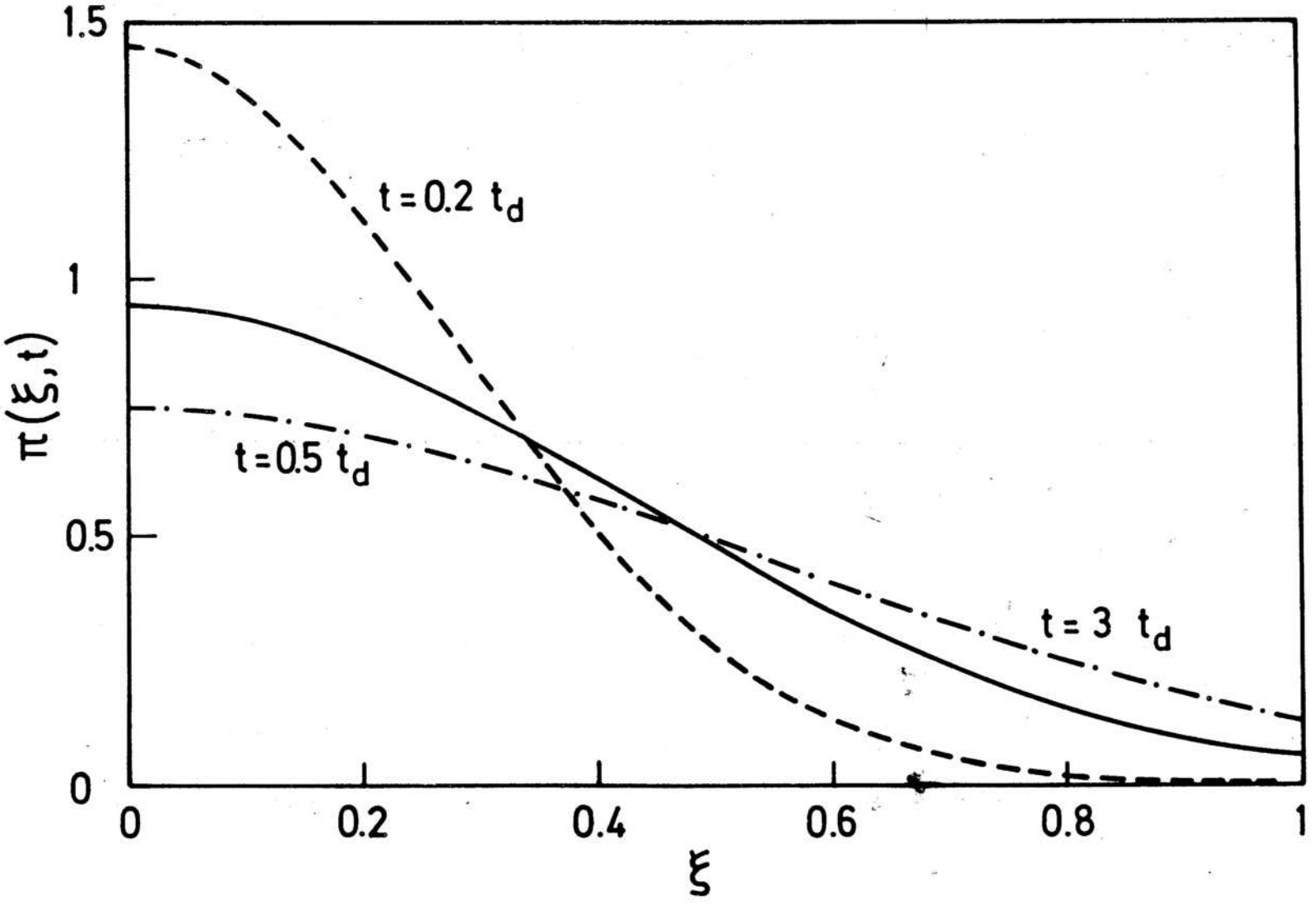
5) For those more involved situations where more than one stationary state exists; i.e.: bistability; or if the system is at a critical point we refer the reader to Ref. [2]

FIGURE CAPTIONS

FIGURE I: $\langle\xi^2\rangle$ as a function of time (in units of t_d), for different values of a (indicated in the figure), and other parameters equal to : V=5, $n_A(0)=0.6$, n=1, $\langle\xi^2(0)\rangle=0$.

FIGURE II: Probability density $\Pi(\xi,\tau)$ as function of τ, for different times. The values of the rest of the parameters are : V=5, $n_A(0)=0.6$, n=1, a=0.1, $\langle\xi^2(0)\rangle=0$, $\langle\xi(0)\rangle=0$.


0.25
0.2
0.1
0
$\langle \xi(t/t_d)^2 \rangle$
α=0.5
α=0.2
α = 0.02
0
1
2
3
4
5
t/τ_d


1.5
1
0.5
0
0
0.2
0.4
0.6
0.8
1
π(ξ,t)
ξ
t = 0.2 t_d
t = 0.5 t_d
t = 3 t_d