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BEHAVIOUR OF TRANSPORT COEFFICIENTS OF SIMPLE FLUIDS IN THE CRITICAL REGION

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RESUMEN

En este trabajo se exhiben las inconsistencias que aparecen al intentar explicar las anomalías que presentan los coeficientes de transporte de un fluido simple en la vecindad del punto crítico cuando se utiliza la suposición de que las fluctuaciones en densidad evolucionan en el tiempo de acuerdo con las ecuaciones de la hidrodinámica. También se hace ver, contrario a lo que se supone en los modelos relevantes, que los detalles de la forma del potencial intermolecular sí juegan un papel importante en este problema. Los potenciales que aquí se consideran son el de Yukawa, el Gaussiano y el potencial de Lorentz.

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ABSTRACT

We show, in this paper, the inconsistencies that appear when one is trying to explain the anomalies in the transport coefficients of a simple fluid in the vicinity of the critical point, when one makes the assumption that the density-density fluctuations obey the hydrodynamical equations. We also show, against what is normally assumed, that the form of the intermolecular potential plays an important role in this problem. The potentials considered are the Yukawa, the Gaussian and the Lorentz potentials.

I. INTRODUCTION

For the past two decades the behaviour of matter in the neighbourhood of critical points has received considerable attention. In particular, the behaviour of transport coefficients of fluids has been analyzed both through theory and experiment, the subject still remaining in a very controversial stage. On the one hand, the experimental data is scarce and somewhat innacurate. Indeed, as it has been indicated by Sengers,[1,2] in his thorough and extensive analysis of the existing data, the viscosity of a simple gas does not show anomalies in the vicinity of the critical point and at the critical point itself the anomaly is very small, if it exists at all. The thermal conductivity does show an anomalous behaviour in the vicinity of the critical point, but the result has not yet been completely confirmed. Neither has the shape of such an anomaly. Furthermore, the experimental evidence is based only on work performed mainly with CO_2. On the other hand, a certain ammount of theoretical work trying to explain these experimental results has been developed[3]. However, the situation is very far from being at all satisfactory.

Several of the theoretical models which have been proposed to deal with this problem are somewhat related to the idea that the qualitative features shown by a fluid in the neighbourhood of a critical point should be independent of the specific shape of the intermolecular potential acting between the molecules and depend only on its long range contribution. This idea was exploited by van Kampen[4] in his work on the classical gas in equilibrium and was extended to non-equilibrium phenomena by Mountain and Zwanzig[5] and more recently by De Sobrino[6].

Following Mountain and Zwanzig's approach, the contribution of the long-range potential to the shear viscosity and thermal conductivity of a simple gas can be obtained by evaluating the time-correlation functions which are known to relate these properties to microscopic currents characteristic of the system itself[7]. This approach is mainly based on the two following assumptions:

a) The anomalous behaviour of the transport coefficients arises from the density-density fluctuations, which the system displays in the vicinity of a critical point.

b) These density-dendity fluctuations are described through a microscopic density operator which appears in the expression for the current in the time-correlation function. The assumption is then made, that this operator can be substituted by the local macroscopic density fluctuation which is found by solving the linearized equations of hydrodynamics.

Regarding assumption (b) one immediately falls into an inconsistent scheme. In fact, the linearized equations of hydrodynamics[8, 9] involve the transport coefficients themselves and when solving them one assumes that these quantities show no anomalies, i.e. are well behaved near the critical point. Afterwards, one uses these results to evaluate the time-correlation functions in order to exhibit their anomalous behaviour in the vicinity of such a point.

In their work, Mountain and Zwanzig used a Yukawa potential to show how the shear viscosity and the thermal conductivity have the same qualitative critical behaviour as that indicated by experiment. The purpose of this paper is to extend these calculations considering two other potentials, the Gaussian and the Lorentzian, both having a long-range behaviour which is similar to the former one. The results obtained show that in none of the three cases the results coincide. Thus, one is led to the conclusion that the agreement obtained with experiment using Yukawa's potential is merely accidental. Also, the inconsistency of the model pointed out above, shows up in an explicitly way, namely, within the proposed model the shape of the attractive part of the potential strongly influences the expressions for the transport coefficients near the critical point and, moreover, we do not get a unique behaviour of such quantities.

Section II of this paper will be devoted to make a resumé of Mountain-Zwanzig's paper. In Section III we shall give the calculations of the transport coefficients with the two proposed potentials and finally some concluding remarks will be given in Section IV.

II. MODEL OF MOUNTAIN AND ZWANZIG[5*]

As it was mentioned in the previous section, the approach used by these authors is to evaluate the time-correlation functions which relate the shear viscosity and thermal conductivity of a simple fluid to the microscopic currents representing the response of the system to an external force. These expressions were derived long ago by Green[10] and Kubo[11] and are currently referred to in the literature as the Green-Kubo formulae. Explicitly,[7] the shear viscosity η is given by

$$\eta = \frac{1}{Vk_B T} \int_0^\infty dt < J^{xy}(0)\, J^{xy}(t) > \ , \tag{1}$$

where the current J^{xy} is:

$$J^{xy} = \sum_j \frac{p_j^x\, p_j^y}{m} + \sum_j F_j^x R_j^y \ , \tag{2}$$

$p_j^{x,y}$ being the x and y components of the linear momentum of the j-th particle, F_j^x the x component of the force acting on it and R_j its position vector. The brackets $< >$ indicate that an average is to be taken over an equilibrium canonical en-

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[*] Hereafter referred to as MZ.

semble with temperature T and volume V. Also, k_B is Boltzmann's constant.

The thermal conductivity λ is defined through,

$$\lambda = \frac{1}{3Vk_B T^2} \int_0^\infty dt \, < \mathbf{S}(0) \cdot \mathbf{S}(t) > \tag{3}$$

where $\mathbf{S}$ is the heat current defined by

$$\mathbf{S} = \sum_i (H_i - h) \frac{\mathbf{p}_i}{m} + \frac{1}{2} \sum_{i,j} \mathbf{R}_{ij} \mathbf{F}_{ij} \cdot \frac{\mathbf{p}_i}{m} \quad . \tag{4}$$

In equation (4), H_i is Hamiltonian of the i-th particle, h is the enthalpy per particle and the rest of the symbols are the same as the ones appearing in Eq. (2).

Rather than repeating unnecessary algebra we would like to emphasize upon the philosophy which lies behind the calculation of Eqs. (1) and (3). According to assumption (a) in the introduction, the first step is to express the operators J and S in terms of a microscopic density operator. This is easily achieved by using van Kampen's method, namely, to substitute the summation over particles of a long-range slowly varying function by a summation over conveniently defined cells, where the weight of the function is now the particle density inside each cell. Thus, if $w(r_{ij})$ is such a function,

$$\sum_{i,j} f[w(r_{ij})] \rightarrow \sum_{a,b} \Delta^2 f[w(r_{ab})] \, n(r_b) \quad , \tag{5}$$

where $a, b, \ldots.$ label the cells, Δ is the volume of each cell and $n(r_b)$ is the number density in the b-th cell. By Fourier-transforming the expressions thus obtained, one is led to consider summations in k-space, where statistical averages of products of the Fourier components $\nu_k(t)$ are involved, where

$$\nu(\mathbf{r}_b) = n(\mathbf{r}_b) - n_0 \ ,$$

n_0 being the equilibrium number density. The second step is to calculate these statistical averages involving the ν_k's. It is here where assumption (b) enters. In fact, one now assumes that in terms of a certain initial value $\nu_k(0)$, the time dependence of $\nu_k(t)$ is *identical* to that which corresponds to the Fourier transform of the macroscopic density fluctuation obeying the linearized hydrodynamic equations. The explicit form for $\nu_k(t)$, first derived by Landau and Placzek[12], has been discussed by several authors[13], the approximate expression used by MZ being[5]

$$\nu_k(t) = \nu_k(0) \ \exp \left\{ - \frac{\lambda k^2}{n_0 C_V} \left(\frac{k^2 + \kappa^2}{k^2 + \gamma \kappa^2} \right) t \right\} \ , \tag{6}$$

where λ is the thermal conductivity, C_V the specific heat at constant volume, γ the ratio of the heat capacities and κ^{-1} is the so-called correlation length defined a la Ornstein-Zernike[14].

It is quite important to notice that the use of Eq. (6) implies two assumptions, namely, the validity of local and linear hydrodynamics in the vicinity of the critical point where the correlation length $\kappa^{-1} >> q^{-1}$, (the hydrodynamical length) and, furthermore, that the transport quantities η and λ are *finite* in that region.

The calculations of η and λ are rather straight-forward. Since λ depends upon C_V one begins by calculating this equilibrium quantity. From standard fluctuation theory we know that

$$C_V = \frac{1}{k_B T^2} < (\delta E)^2 > \ . \tag{7}$$

Expressing the contribution to δE coming from the long-range interaction and following the above scheme it is easy to show that

$$C_V^L = \frac{1}{2k_B T^2} \sum_{k=0} (w_k)^2 \left(|\varphi''| + \beta w_0 - \beta w_k \right)^{-2} , \tag{8}$$

where w_k is the k-th component of the Fourier transform of $w(r)$, the long-range potential, and $|\varphi''|$ is the magnitude of the second derivative of $(-\beta)$ times the free energy per unit volume. As usual, $\beta \equiv (k_B T)^{-1}$, and the superscript L indicates that we are only taking the long-range contribution.

If we take for $w(r)$ a Yukawa potential,

$$w_k = \frac{w_0}{1 + k^2 L^2} , \tag{9}$$

L being a constant, and substitute Eq. (9) back into Eq. (8), replace the summation by an integral whose evaluation is rather straightforward and take its limit when $T \to T_c$, we find that

$$C_V^L = \frac{V k_B}{16\pi L^4} \lim_{T \to T_c} \frac{1}{\kappa} , \tag{10}$$

where κ is for this potential the inverse of the correlation length, defined by

$$\kappa^2 = \frac{|\varphi''|}{L^2 (|\varphi''| + \beta w_0)} . \tag{11}$$

Since $|\varphi''|$ is proportional to $|T - T_c|$ in the vicinity of the critical point, κ^{-1} diverges in the same manner as the Ornstein-Zernicke's two-particle correlation length and hence C_V^L diverges as κ^{-1} near the critical region. This agrees qualitatively with some experimental results, but the point still remains unsettled[15]

When evaluating the time-correlation function for the shear viscosity one is led through the first step described above, to the following expression:

$$(J^{xy})^{L} = \frac{1}{2}\sum_{k\neq 0}(\mathrm{grad}_k\, w_k)^{y}\,(k)^{x}\left(|\nu_k|^2 - \langle|\nu_k|^2\rangle\right) , \qquad (12)$$

which combined with Eq. (6) and substituted in Eq. (1) leads, after the summation over k is replaced by an integral, to the following result,

$$\eta^{L} = \frac{n_0\, C_V}{120\pi^2\lambda}\int_0^{\infty}\frac{dk\, k^2\left[\dfrac{dw(k)}{dk}\right]^2}{\dfrac{k^2+\kappa^2}{k^2+\gamma\kappa^2}\left[\,|\varphi'' + \beta w_0 - \beta w(k)\,\right]^2} . \qquad (13)$$

Taking a Yukawa potential, the integral is evaluated straightforwardly and yields,

$$(\eta^{L})_{\mathrm{critical}} = \frac{k_B T}{30\pi^2}\left(\frac{3\pi}{16}\gamma\kappa + \frac{\pi}{4L}\right)\lim_{T\to T_c}\frac{n_0\, C_V}{\lambda} , \qquad (14)$$

which depends on the behaviour of $\gamma\kappa$ and C_V/λ at the critical point. In the MZ paper it is shown that these two quantities remain finite at the critical point and so does η^{L}, there upon agreeing with the experimental results. We shall come back to this point later on.

Finally, the expression for the thermal conductivity can be obtained by evaluating Eq. (3) following essentially the same steps as in the previous case. However, the calculations are longer, so that we shall avoid to sketch them here and refer the interested reader to the original source[5]. The final result is that, for a Yukawa potential close to the critical point, the thermal conductivity behaves as

$$\left(\frac{\lambda}{n_0 C_V}\right)^L_{\text{critical}} = \frac{8L^2 w_0}{3m\left(\frac{\lambda}{n_0 C_V} + \frac{\eta}{mn_0}\right)} \tag{15}$$

It is important to recall that the values of λ and η which appear in the denominator of Eq. (15), are a consequence of using the solutions of linearized hydrodynamics to calculate $\nu_k(t)$. In particular the shear viscosity enters because in the process of calculating $\mathbf{S}$, the particle current shows up, and its transverse part $\boldsymbol{J}_k^T$ is found to be given by[13]

$$\boldsymbol{J}_k^T = \boldsymbol{J}_k^0 \exp\left(-\frac{\eta k^2}{mn_0}\right)t \quad . \tag{16}$$

Thus, λ and η are assumed to be finite in the right hand side of Eq. (15) even in the vicinity of the critical point. Hence, this result is inconsistent. Indeed if λ^L is finite, then, since C_V diverges as κ^{-1},

$$\frac{\lambda}{n_0 C_V} \to 0 \text{ as } |T - T_c|^{-1}$$

and, therefore, η should diverge at the critical point contradicting Eq. (14), our former result. On the other hand, if λ^L diverges as $1/C_V$, then the left-hand side of (15) is finite. The result is consistent only if λ/C_V is also finite, which requires the inconsistent assumption of λ being infinite. In this case η is finite, which agrees with (14), and the total result agrees with experiment. This is essentially the MZ argument developed in Appendix **II**, of their paper, which, however, works only for the Yukawa potential. As we shall see later on, this is no longer true for a Gaussian potential.

III. THE GAUSSIAN AND LORENTZIAN MODELS

This section will be devoted to the calculation of the shear viscosity and the thermal conductivity for a simple fluid assuming that the long-range attraction between the molecules is given by·

a) a Gaussian potential

and

b) a Lorentzian potential, which, as depicted in Fig. 1, behave for large distances as the Yukawa potential, thus suggesting that within the present formulation one should be led to results similar to those obtained with the latter one.

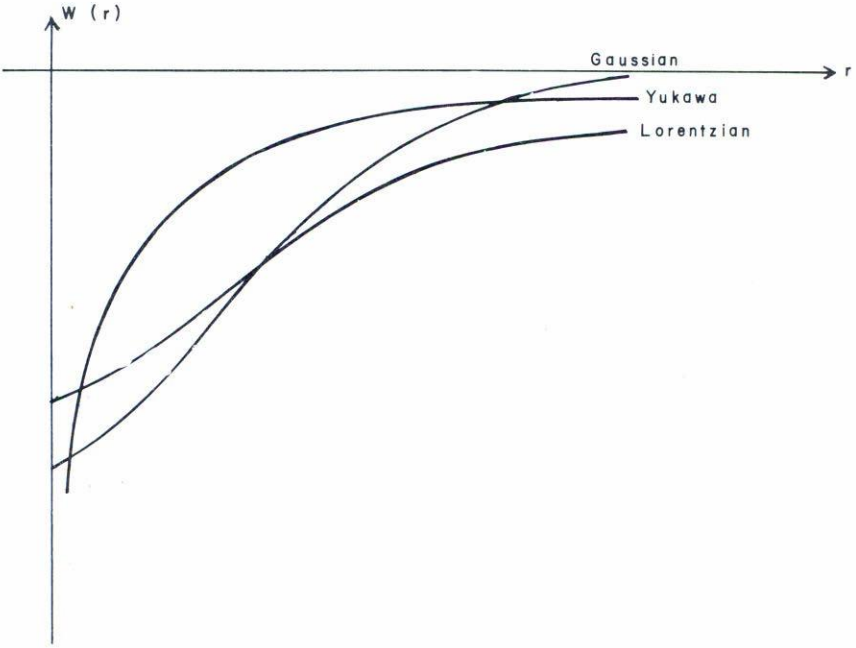

Fig. 1. The three potentials used in this paper, namely, the Yukawa, Gaussian and Lorentzian are shown on a comparative scale.

Let us start with the Gaussian potential, analytically defined by:

$$w(r) = A \exp(-a^2 r^2) , \tag{17}$$

where A and a are constants. Its Fourier transform is also a Gaussian function, namely,

$$w_k = w_0 \exp(-k^2/4a^2) , \tag{18}$$

where $w_0 = A\pi^{3/2} a^{-3}$.

The specific heat at constant volume is readily obtained substituting Eq. (18) into Eq. (8). Introducing the variables,

$$x = \frac{k^2}{4a^2} \quad \text{and } G = \frac{\beta w_0}{|\varphi''| + \beta w_0}$$

and replacing the sum by an integral we get,

$$C_V^L = \frac{V w_0^2 a^3}{\pi^2 k_B T^2} \frac{1}{(|\varphi''| + \beta w_0)^2} \int_0^\infty \frac{\sqrt{x}\, e^{-2x}\, dx}{[1 - G e^{-x}]^2} \quad . \tag{19}$$

The integral appearing in Eq. (19) can be easily performed to yield the following result,

$$C_V^L = \frac{V w_0^2 a^3}{\pi^2 k_B T^2} \frac{1}{(|\varphi''| + \beta w_0)^2} \frac{\sqrt{\pi}}{2} \times 3.0300785 .$$

In the limit when $T \to T_c$, $\varphi'' \to 0$, and C_V^L remains finite with a value given by

$$(c_V^L)_{\text{crit.}} = V k_B a^3 \frac{2}{\pi^{3/2}} \times 3.03 \ldots , \tag{20}$$

a result which disagrees both with experiment and with Eq. (10), obtained using a Yukawa potential.

The formula for the shear viscosity is obtained through direct substitution of Eq. (18) into Eq. (5), yielding

$$\eta^L = \frac{n_0 C_V w_0^2}{120 (2\pi)^2 k_B T \lambda a^4} \int_0^\infty \frac{dk (k^6 + \gamma \kappa_1^2 k^4)\, e^{-k^2/2a^2}}{\left[(k^2 + \kappa_1^2) \;\; |\varphi''| + \beta w_0 \, e^{-k^2/2a^2} \right]^2} \tag{21}$$

where κ_1 is the inverse of the correlation length for this potential, whose behaviour in the critical region is analogous to the κ for the Yukawa potential because, by the nature of the approximations we have used, this characteristic length does not depend on the explicit form of the potential.[14]

To study the integral appearing in Eq. (21) let us introduce the following notation:

$$u(k) = k^6 + \gamma \kappa_1^2 k^4 \; ,$$

$$D = \frac{|\varphi''| + \beta w_0}{\beta w_0} \; .$$

Calling such an integral I, we have that

$$I = \frac{1}{\beta^2 w_0^2} \int_0^\infty \frac{u(k)\, dk}{(k^2 + \kappa_1^2) \left[D \exp (k^2/4a^2) - 1 \right]^2} \; . \tag{22}$$

Using the inequality,

$$\frac{u}{(k^2+\kappa_1^2)\,[D\exp(k^2/4a^2)-1]^2} \leqslant \frac{u}{\kappa_1^2\,[D\exp(k^2/4a^2)-1]^2}$$

one has that

$$I \leqslant \frac{1}{(\beta w_0 \kappa_1)^2}\int_0^\infty \frac{(k^6+\gamma\kappa_1^2 k^4)\,dk}{[D\exp(k^2/4a^2)-1]^2}$$

which may be transformed into

$$I \leqslant \frac{1}{(\beta w_0 \kappa_1)^2}\;\frac{a}{D^2}\int_0^\infty \frac{[(2a)^6 y^{5/2}+(2a)^4 y^{3/2}]\,e^{-2y}\,dy}{[1-D^{-1}e^{-y}]^2}$$

where $y = k^2/4a^2$.

The above integral can now be decomposed into two integrals of the type,

$$\int_0^\infty \frac{y^{\frac{2n+1}{2}}\,e^{-2y}\,dy}{[1-D^{-1}e^{-y}]^2} = \Gamma\left(n+\frac{3}{2}\right)\left[M\left(D^{-1};n+\frac{1}{2};1\right) - M\left(D^{-1};n+\frac{3}{2};1\right)\right]$$

for $n = 1, 2$; M denotes the confluent hypergeometric functions. Since D remains finite at the critical point, these integrals are simply constants and, hence, we have that

$$I \leqslant \frac{\text{const}}{\kappa_1^2}\;. \tag{23}$$

Substitution of Eq. (23) back into Eq. (21) yields,

$$\eta^{L} \leqslant \frac{w_0^2\, n_0\, C_V}{60 k_B T\,(2\pi^2)\, a^4}\;\frac{\text{const}}{\kappa_1^2\,\lambda}\quad . \tag{24}$$

In this case we find once more that the behaviour of the shear viscosity η^L in the vicinity of the critical point depends on

$$\lim_{T \to T_c} \frac{1}{\kappa_1^2\,\lambda}$$

i.e. on the knowledge of how the thermal conductivity behaves in such neighbourhood. When one investigates this quantity, it is found[16] by a process which is analogous to that described in MZ, and the use of Eq. (18), that

$$\lambda^{L} = \frac{n_0 w_0^2}{3\pi^2 m T} \times$$

$$\int_0^{\infty} \frac{\exp(-k^2/4a^2)(k^2+\gamma\kappa_1^2)\,dk}{\left[\frac{\lambda}{n_0 C_V}(k^2+\kappa_1^2)+\frac{\eta}{m n_0}(k^2+\gamma\kappa_1^2)\right]\left[\,|\varphi''| + \beta w_0 - \beta w_0 \exp(-k^2/4a^2)\right]} \tag{25}$$

This expression already gives rise to a difficulty similar to that pointed out in the case of a Yukawa potential. Indeed, if in the right-hand side λ and η are assumed finite and λ^L could be divergent as κ_1^{-2}, according to Eq. (24). This contradicts the experimental evidence. On the other hand if λ^L is infinite we get an inconsistency, because λ in the denominator of Eq. (25) has been assumed finite; however, qualitative agreement with experiment could be expected. Furthermore, since C_V is finite at $T = T_c$ we do not have the apparent consistency which shows up in the Yukawa potential.

Let us now consider the case of the Lorentzian potential. Here

$$w(r) = \frac{A}{a^2 + r^2} , \tag{26}$$

with a and A being constants. Its Fourier transform, as it is well known, is a Yukawa function in k-space, namely

$$w_k = 2\pi^2 A \frac{e^{-ka}}{k} , \tag{27}$$

so that when $k = 0$, irrespective of anything else, $w_0 = \infty$. This implies according to Eqs. (8), (13) and (25) (with $w(k)$ in general), that all the three quantities considered here vanish identically, namely,

$$C_V = \eta^L = \lambda^L = 0.$$

This is of course completely unphysical, but what is relevant here is that there exists a potential of the same long-range characteristics as Yukawa's and possessing a Fourier transform, for which the model fails. This result seems to point out the inconvenience of formulating these type of problems in k-space, instead of using directly the configuration space.

IV. CONCLUDING REMARKS

The results obtained in the preceeding section, together with those derived by MZ for the Yukawa potential, lead to the following remarks.

It is rather clear that the scheme described here is inconsistent in so far as the explanation of the apparent anomalies displayed by fluctuating quantities in the critical region. This was pointed out by Resibois[3] and it is explicitly exhibited by the results derived both for the Yukawa and the Gaussian potentials. Thus it is through the use of more basic approaches to this problem that one can expect to get better answers to this problem[17, 18]. Yet, the final and definite explanation is still a challenge.

Besides this general consideration, other feature of this paper is also relevant. In fact, even for fluctuating equilibrium properties, the model proposed by van Kampen seems to be inadequate, the specific heat at constant volume calculated for the three potentials considered here being different for them all. Hence, the details of the potential do matter in so far as the critical behaviour of such quantities. This point has been discussed by Mistura and Sette[19] in another context and seems to be related to the validity of the Ornstein-Zernike's expression for the two-body correlation function in the critical region. Finally, in a recent paper, De Sobrino[6] has attempted to calculate the transport properties of a gas in a non-equilibrium state using van Kampen's model, but starting not from the correlation function approach but by solving the first two equations of the BBGKY hierarchy using a linearization scheme to simplify the equation for the two-particle distribution function. His results are, for the equilibrium case, identical to those of MZ and hence subject to the same criticisms we have pointed out above. For the transport coefficients his results differ completely from those of MZ but, what is more interesting, he shows that the discrepancy arises from assuming that the density-density fluctuations obey the hydrodynamic equations with the obvious expressions for the transport coefficients. This is in agreement with the inconsistency pointed out above.

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