# Itinerant-Oscillator Model of Liquids

P. S. DAMLE* AND A. SJÖLANDER
*Institute of Theoretical Physics, Sven Hultins gata, Göteborg, Sweden*
AND
K. S. SINGWI
*Institute of Theoretical Physics, Sven Hultins gata, Göteborg, Sweden*
*and*
*Solid State Science Division, Argonne National Laboratory, Argonne, Illinois*

(Received 14 July 1967)

Sears's itinerant-oscillator model of liquids has been reexamined so as to be consistent with the fluctuation-dissipation theorem. An expression for the frequency spectrum of the velocity autocorrelation function is derived which is different from the one given earlier by other authors. Two cases have been considered, one corresponding to the exponential and the other corresponding to the Gaussian correlation in time of the stochastic force. Our calculated spectrum for liquid argon is in very good agreement with the machine computations of Rahman.

## 1. INTRODUCTION

DURING recent years, several different models[1] to describe the self-motion of an atom in a classical liquid have been proposed. One common feature of these models is that they attempt to take into account in some fashion both the vibratory and the diffusive kind of motions. By their very nature, these models involve parameters which are introduced in a rather *ad hoc* manner and cannot, therefore, easily be related to microscopic quantities.

Another variant of these models has recently been proposed by Sears[2] who calls it "the itinerant-oscillator model of liquids." In this model the concept of a "center of oscillation" is introduced. The latter is defined in such a way that the motion of an atom relative to its center represents the thermal vibration of the atom, whereas the motion of the center of oscillation represents the diffusive motion. The vibratory motion is described by the equation of motion of a damped stochastic harmonic oscillator, whereas the diffusive motion is described by the usual Langevin equation. Sears's basic equations are the following:

$$\ddot{\mathbf{R}}_0(t)+\mu\dot{\mathbf{R}}_0(t)+\omega_0^2\{\mathbf{R}_0(t)-\mathbf{R}(t)\}=\mathbf{A}(t)\,, \qquad (1)$$

$$\ddot{\mathbf{R}}(t)+\nu\dot{\mathbf{R}}(t)=\mathbf{B}(t)\,, \qquad (2)$$

and

$$\mathbf{R}(t)=\frac{1}{\tau_0}\int_{t-\tau_0/2}^{t+\tau_0/2}\mathbf{R}_0(t')dt'\,, \qquad (3)$$

where $\mathbf{R}_0(t)$ and $\mathbf{R}(t)$ are, respectively, the positions of the atom and the center of oscillation. $\mathbf{A}(t)$ and $\mathbf{B}(t)$ are stationary stochastic forces and $\mu$ and $\nu$ are friction coefficients. $\mathbf{R}(t)$ is defined through Eq. (3), where $\tau_0=2\pi/\omega_0$ is the mean period of oscillation of the central atom. The coupled equations (1) and (2) were solved by Sears to obtain the velocity autocorrelation function or rather its Fourier transform, which was then compared with the machine calculations of Rahman[3] for liquid argon. The latter were found to agree well with the predictions of the model.

One obvious objection which can be raised against the above starting equations of Sears is that, using Eqs. (1) and (3), one does not obtain Eq. (2). Since Sears does not make use of Eq. (3) in deriving his final result, one might argue that Eq. (3) is redundant and that his starting equations are indeed (1) and (2). In that case, it is not clear what the precise meaning of $\mathbf{R}(t)$ should be. Moreover, the latter equations are open to a basic objection which is that the stochastic force terms $\mathbf{A}(t)$ and $\mathbf{B}(t)$ are assumed not to have a white spectrum, whereas the friction terms $\mu$ and $\nu$ are assumed to be time-independent. This latter assumption of Sears, as has been pointed out by Nakahara and Takahashi,[4] violates the fundamental fluctuation-dissipation theorem of statistical physics. These authors have attempted to remedy this defect in the Sears model but in an incorrect way, which when properly treated modifies the structure of Sears's equations, as we shall see in the sequel.

Since the physical content of Sears model is very appealing, and since there seems to be some experimental interest[5] in it, we have in the present paper reexamined Sears model such that it is free from mathematical inconsistencies. Care has been taken in choosing the values of the parameters such that they are consistent with the second moment of the frequency spectrum of the velocity autocorrelation function and the observed diffusion coefficient. Two cases have been considered, one corresponding to an exponential and the other corresponding to a Gaussian correlation for the

* Permanent address: Physics Department, University of Poona, Poona 7, India.

[1] See, e.g., A. Sjölander, in *Thermal Neutron Scattering*, edited by P. A. Egelstaff (Academic Press Inc., New York, 1965), Chap. 7, p. 291.

[2] V. F. Sears, Proc. Phys. Soc. (London) **86**, 953 (1965).

[3] A. Rahman, Phys. Rev. **136**, A405 (1964).

[4] Y. Nakahara and H. Takahashi, Proc. Phys. Soc. (London) **89**, 747 (1966).

[5] P. A. Egelstaff, Rept. Progr. Phys. **29**, 333 (1966); O. J. Eder, S. H. Chen, and P. A. Egelstaff, Proc. Phys. Soc. (London) **89**, 833 (1966); V. F. Sears, Can. J. Phys. **45**, 237 (1967).

fluctuating driving force. Our results calculated for liquids argon are in good agreement with the machine calculations of Rahman.[3]

## 2. MATHEMATICAL FORMULATION

As an atom moves, it drags along with it the surrounding fluid. In the present model the motion of an atom and its surroundings is assumed to be described by the following set of coupled equations:

$$\ddot{\mathbf{R}}_0(t)+\int_0^t \mu(t-t')\dot{\mathbf{R}}_0(t')dt' + \frac{\alpha^2}{M_0}[\mathbf{R}_0(t)-\mathbf{R}(t)]=\mathbf{F}_1(t), \quad (4a)$$

and

$$\ddot{\mathbf{R}}(t)+\int_0^t \nu(t-t')\dot{\mathbf{R}}(t')dt' - \frac{\alpha^2}{M}[\mathbf{R}_0(t)-\mathbf{R}(t)]=\mathbf{F}_2(t). \quad (4b)$$

$\mathbf{R}_0(t)$ denotes the position of the atom under consideration and $M_0$ its mass. The surroundings, here, have been replaced by a fictitious center whose coordinate is $\mathbf{R}(t)$ and whose mass is $M$. These equations are of the damped stochastic oscillator type with time-dependent friction coefficients $\mu(t)$ and $\nu(t)$. The above equations are the same as those of Nakahara and Takahashi[4] except for the presence of the restoring force term in (4b) which follows from Newton's third law of motion and is also a consequence of the fluctuation-dissipation theorem, as we shall see later.

Defining $\mathbf{R}_0(0)=\mathbf{R}(0)$, the above equations can be written as

$$\ddot{\mathbf{R}}_0(t)+\int_0^t [\mu(t-t')+\omega_0^2]\dot{\mathbf{R}}_0(t')dt' - \int_0^t \omega_0^2\dot{\mathbf{R}}(t')dt'=\mathbf{F}_1(t), \quad (5a)$$

$$\ddot{\mathbf{R}}(t)+\int_0^t [\nu(t-t')+\omega_1^2]\dot{\mathbf{R}}(t')dt' - \int_0^t \omega_1^2\dot{\mathbf{R}}_0(t')dt'=\mathbf{F}_2(t), \quad (5b)$$

where

$$\omega_0^2=\alpha^2/M_0 \quad \text{and} \quad \omega_1^2=\alpha^2/M.$$

For the sake of mathematical convenience, as will be evident from what follows, we have included the frequencies $\omega_0^2$ and $\omega_1^2$ with the friction terms.

Equations (5a) and (5b) can now be written as a single matrix equation

$$\dot{V}(t)+\int_0^t \Gamma(t-t')\cdot V(t')dt'=F(t), \quad (6)$$

where

$$V(t)=\begin{bmatrix}\dot{\mathbf{R}}_0(t)\\ \dot{\mathbf{R}}(t)\end{bmatrix}, \quad \Gamma(t)=\begin{bmatrix}\mu(t)+\omega_0^2 & -\omega_0^2\\ -\omega_1^2 & \nu(t)+\omega_1^2\end{bmatrix},$$

and

$$F(t)=\begin{bmatrix}\mathbf{F}_1(t)\\ \mathbf{F}_2(t)\end{bmatrix}. \quad (7)$$

Following Kubo[6] (see Appendix), we show from Eq. (6) that

$$\phi(p)=[p\mathbf{I}+\Gamma(p)]^{-1}\cdot\phi^0, \quad (8)$$

and

$$\Gamma(p)\cdot\phi^0=F(p), \quad (9)$$

where $\phi_{ij}(p)$, $\Gamma_{ij}(p)$, and $F_{ij}(p)$ are, respectively, the Laplace transforms of the matrix elements

$$\langle V_i(t)\cdot V_j(0)\rangle, \quad \Gamma_{ij}(t), \quad \text{and} \quad \langle F_i(t)\cdot F_j(0)\rangle,$$

and

$$\phi_{ij}{}^0=\langle V_i(0)\cdot V_j(0)\rangle.$$

The bracket $\langle\cdot\rangle$ denotes an average over an equilibrium ensemble and the dot between the components denotes an ordinary scalar product. With the meaning we have attributed to $\mathbf{R}_0$ and $\mathbf{R}$ it is evident that $\dot{\mathbf{R}}_0(0)$ and $\dot{\mathbf{R}}(0)$ are uncorrelated and so we have

$$\phi^0=\begin{bmatrix}3k_BT/M_0 & 0\\ 0 & 3k_BT/M\end{bmatrix}. \quad (10)$$

The diagonal terms of Eq. (9) give the following fluctuation-dissipation relations:

$$\frac{3k_BT}{M_0}\left[\mu(p)+\frac{\omega_0^2}{p}\right]=F_1(p), \quad (11a)$$

$$\frac{3k_BT}{M}\left[\nu(p)+\frac{\omega_1^2}{p}\right]=F_2(p), \quad (11b)$$

where $\mu(p)$, $\nu(p)$, $F_1(p)$, and $F_2(p)$ are, respectively, the Laplace transforms of $\mu(t)$, $\nu(t)$, $\langle\mathbf{F}_1(t)\cdot\mathbf{F}_1(0)\rangle$, and $\langle\mathbf{F}_2(t)\cdot\mathbf{F}_2(0)\rangle$. It should be noted that $\langle\mathbf{F}_1(t)\cdot\mathbf{F}_2(t')\rangle\neq 0$.

We split each of the stochastic forces $\mathbf{F}_1(t)$ and $\mathbf{F}_2(t)$ in Eqs. (4a) and (4b) into two terms as below:

$$\mathbf{F}_1(t)=\mathbf{A}(t)+(\alpha/M_0)(3k_BT)^{1/2}\mathbf{A}', \quad (12a)$$

$$\mathbf{F}_2(t)=\mathbf{B}(t)+(\alpha/M)(3k_BT)^{1/2}\mathbf{A}', \quad (12b)$$

where $\mathbf{A}(t)$ and $\mathbf{B}(t)$ correspond to the two friction terms in Eqs. (11), and $\alpha(3k_BT)^{1/2}\mathbf{A}'/M_0$ and $\alpha(3k_BT)^{1/2}\mathbf{A}'/M$ correspond to the two restoring forces. Consequently, $\mathbf{A}'$ is here a stochastic force with the property $\langle\mathbf{A}'\rangle=0$ and $\langle\mathbf{A}'\cdot\mathbf{A}'\rangle=1$ and is uncorrelated to $\mathbf{A}(t)$ and $\mathbf{B}(t)$. Then the fluctuation-dissipation relations (11) take the following form:

$$(3k_BT/M_0)\mu(p)=A(p), \quad (13a)$$

$$(3k_BT/M)\nu(p)=B(p), \quad (13b)$$

[6] R. Kubo, in *Many-Body Theory*, edited by R. Kubo (Syokabo Publishing Co., Tokyo, 1966), Part I, p. 1.

where $A(p)$ and $B(p)$ are, respectively, the Laplace transforms of $\langle \mathbf{A}(t)\cdot\mathbf{A}(0)\rangle$ and $\langle \mathbf{B}(t)\cdot\mathbf{B}(0)\rangle$. It also follows from the nondiagonal parts of Eq. (9) that $\langle \mathbf{A}(t)\cdot\mathbf{B}(0)\rangle=0$.

It is appropriate to comment here that in contrast to our starting Eq. (4b) for $\mathbf{R}(t)$, the corresponding equation either of Sears or of Nakahara and Takahashi does not contain the restoring force term. That such a term should be there can be seen from the general form of the fluctuation-dissipation relation as given by Eq. (9). Assuming $\phi^0$ to be a diagonal matrix, as was also assumed by these authors, we get from Eq. (9).

$$\begin{bmatrix}\Gamma_{11}(p)\phi_{11}^0 & \Gamma_{12}(p)\phi_{22}^0\\ \Gamma_{21}(p)\phi_{11}^0 & \Gamma_{22}(p)\phi_{22}^0\end{bmatrix}=\begin{bmatrix}F_{11}(p) & F_{12}(p)\\ F_{21}(p) & F_{22}(p)\end{bmatrix},$$

where $\Gamma(p)$ is the Laplace transform of the matrix appearing in Eq. (6) and given explicitly in Eq. (7). Since $F_{12}(p)=F_{21}(p)$, we have

$$\Gamma_{12}(p)\phi_{22}^0=\Gamma_{21}(p)\phi_{11}^0,$$

or

$$\frac{k_BT}{M}\Gamma_{12}(p)=\frac{k_BT}{M_0}\Gamma_{21}(p).$$

Thus the presence of a restoring force term in Eq. (4a) corresponding to a finite value of $\Gamma_{12}(p)$ demands the presence of a similar term in Eq. (4b) corresponding to $\Gamma_{21}(p)$. It also follows from Newton's third law that a restoring force term should appear in Eq. (4b), if present in Eq. (4a). One might argue that in the limit of $M$ very large the restoring force term would vanish, but then $F_{22}(p)$ would also vanish contrary to what was assumed by Sears and Nakahara and Takahashi.

As mentioned in the Introduction, the precise meaning of their $\mathbf{R}(t)$ is not clear. If we interpret their $\mathbf{R}(t)$ as the center of mass of our fictitious center of surroundings and of the atom under consideration, we arrive at the same equations as those of Nakahara and Takahashi. However, now $\langle \dot{\mathbf{R}}_0(0)\cdot\dot{\mathbf{R}}(0)\rangle\neq 0$ and correspondingly $\phi^0$ will not be a diagonal matrix. This will lead to fluctuation- dissipation relations which are different from those given in Eq. (13) and which were used by the above authors. Equations (13) are, therefore, consistent with Eqs. (4) and not with those of Nakahara and Takahashi.

By definition,

$$\phi_{11}(p)=\int_0^\infty e^{-pt}\langle \dot{\mathbf{R}}(t')\cdot\dot{\mathbf{R}}_0(0)\rangle dt'. \tag{14}$$

Using Eqs. (8) and (10) we now get

$$\phi_{11}(p)=\frac{3k_BT}{M_0}\left[p+\mu(p)+\frac{\omega_0^2\{\nu(p)+p\}}{p\{\nu(p)+p\}+\omega_1^2}\right]^{-1}. \tag{15}$$

The spectral function of the normalized velocity autocorrelation function is given by

$$f(\omega)=\frac{2M_0}{3\pi k_BT}\int_0^\infty \langle \dot{\mathbf{R}}_0(t)\cdot\dot{\mathbf{R}}_0(0)\rangle\cos(\omega t)dt$$
$$=\frac{2M_0}{3\pi k_BT}\cdot \mathrm{Re}\,\phi_{11}(i\omega). \tag{16}$$

Since $f(0)=2MD/\pi k_BT$, it follows from (15) and (16) that

$$\mu(0)+(\omega_0^2/\omega_1^2)\nu(0)=k_BT/M_0D, \tag{17}$$

where $D$ is the diffusion coefficient.

We further have

$$\phi_{11}(p)=\int_0^\infty e^{-pt}\{\phi_{11}(0)+t\phi_{11}^{(1)}(0)+\tfrac{1}{2}t^2\phi_{11}^{(2)}(0)+\cdots\}dt$$
$$=\frac{\phi_{11}(0)}{p}+\frac{\phi_{11}^{(1)}(0)}{p^2}+\frac{\phi_{11}^{(2)}(0)}{p^3}+\cdots, \tag{18}$$

where

$$\phi_{11}^{(n)}(0)=(d^n/dt^n)\phi_{11}(t)\,|_{t=0},$$

and particularly[7]

$$\phi_{11}^{(2)}(0)=-\frac{3k_BT}{M_0}\langle\omega^2\rangle, \tag{19}$$

where $\langle\omega^2\rangle$ is the second moment of $f(\omega)$.

Comparing Eq. (18) with the expansion of Eq. (15) for large $p$, and using Eq. (19), we get

$$\langle\omega^2\rangle=p\mu(p)+\omega_0^2, \quad \text{for} \quad p\to\infty. \tag{20}$$

Equations (17) and (20) give two conditions which the chosen parameters of the model should satisfy.

## 3. MEMORY FUNCTION

Following Berne *et al.*,[8] and Singwi and Tosi,[7] the equation for the velocity autocorrelation function is written in the form

$$\frac{d}{dt}\bar{\phi}(t)+\int_0^t \alpha(t-t')\bar{\phi}(t')dt'=0, \tag{21}$$

where

$$\bar{\phi}(t)=\langle \dot{\mathbf{R}}_0(t)\cdot\dot{\mathbf{R}}_0(0)\rangle=\phi_{11}(t),$$

and $\alpha(t)$ is a certain "memory" function. From the above equation, one obtains

$$\phi_{11}(p)=\frac{3k_BT/M_0}{p+\alpha(p)}, \tag{22}$$

where $\alpha(p)$ is the Laplace transform of $\alpha(t)$. Comparing Eq. (22) with Eq. (15) we find

$$\alpha(p)=\mu(p)+\frac{\omega_0^2\{\nu(p)+p\}}{p\{\nu(p)+p\}+\omega_1^2}, \tag{23}$$

[7] K. S. Singwi and M. P. Tosi, Phys. Rev. **157**, 153 (1967).
[8] B. J. Berne, J. P. Boon, and S. A. Rice, J. Chem. Phys. **45**, 1086 (1966).

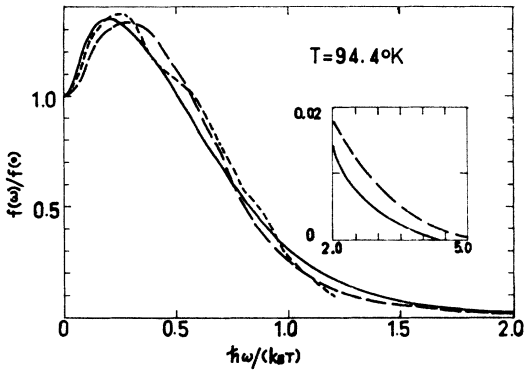


FIG. 1. Frequency spectrum of velocity autocorrelation for liquid argon at 94.4°K. Small dashed curve: as given by A. Rahman, Ref. 3. Long dashed curve: calculation based on exponential correlation in time of the stochastic force. Solid curve: calculation based on the Gaussian correlation in time of the stochastic force.

and we further have

$$f(\omega)=(2/\pi)\ \mathrm{Re}[i\omega+\alpha(i\omega)]^{-1}. \tag{24}$$

Writing for large values of $p$

$$\phi_{11}(p)=\frac{3k_BT}{M_0}\left\{\frac{1}{p}-\frac{C}{p^3}+\cdots\right\}, \tag{25}$$

we find from Eq. (22) that

$$C=\lim_{p\to\infty} p\alpha(p).$$

Comparing this with Eqs. (18) and (19) we get the relation

$$\langle\omega^2\rangle=\lim_{p\to\infty} p\alpha(p). \tag{26}$$

From Eq. (24) it also follows that

$$\alpha(0)=k_BT/MD. \tag{27}$$

The last two conditions on $\alpha(p)$ correspond to those given in Eqs. (17) and (20).

## 4. NUMERICAL CALCULATION

In general the correlation of the fluctuating force terms $\langle\mathbf{A}(t)\cdot\mathbf{A}(0)\rangle$ and $\langle\mathbf{B}(t)\cdot\mathbf{B}(0)\rangle$ may be a very complicated function of time, but the two simple forms one can assume are either exponential or Gaussian. In either case we need two parameters to determine each of these functions. In addition, the effective mass of the fictitious center of mass of the surrounding and the frequency $\omega_0$ will occur as parameters. Thus, in all, we have in the present model six parameters out of which only four are independent because of the restraints imposed by Eqs. (17) and (20).

We shall consider two cases, one in which the correlation of the fluctuating force term is exponential and the other in which it is Gaussian and then examine the relative merits of the two.

**Case (i): Exponential Correlation**

$$\langle A_\alpha(t)A_\beta(0)\rangle=\delta_{\alpha\beta}\langle A_\alpha^2\rangle\exp(-\gamma|t|), \tag{28a}$$

$$\langle B_\alpha(t)B_\beta(0)\rangle=\delta_{\alpha\beta}\langle B_\alpha^2\rangle\exp(-\eta|t|), \tag{28b}$$

and

$$\langle A_\alpha(t)B_\beta(t')\rangle=0.$$

From Eqs. (13) and (28), we have

$$\mu(p)=a/(\gamma+p), \tag{29a}$$

and

$$\nu(p)=b/(\eta+p), \tag{29b}$$

where

$$a=\frac{M_0}{3k_BT}\sum_\alpha\langle A_\alpha^2\rangle,$$

and

$$b=\frac{M}{3k_BT}\sum_\alpha\langle B_\alpha^2\rangle.$$

Using Eqs. (29a) and (29b) in Eqs. (17) and (20), we get the following two restraints on the parameters:

$$a/\gamma+(\omega_0^2/\omega_1^2)(b/\eta)=k_BT/MD, \tag{30}$$

and

$$a+\omega_0^2=\langle\omega^2\rangle, \tag{31}$$

where the right-hand side of the above equations is known.

The choice of the values of the parameters appearing in the model has been made as follows. Consider first the denominator of the right-hand side of Eq. (15),

$$\{p+\mu(p)\}+\frac{\omega_0^2[\nu(p)+p]}{p[\nu(p)+p]+\omega_1^2}.$$

It has been found that the terms in the parentheses in the above expression give the dominant contribution for large frequencies and is even sufficient to reproduce Rahman's $f(\omega)$ curve[3] up to the main peak. Hence the first choice of the parameters $a$ and $\gamma$ appearing in $\mu(p)$ was made so as to give the main peak at the correct place and with the right height. The value of $a$ so obtained was larger than the known value of $\langle\omega^2\rangle$. $\omega_0^2$ was then chosen so as to violate the second moment relation (31) as little as possible without spoiling the agreement with Rahman's data. We were left with three parameters $b$, $\eta$, and $\omega_1^2$ with the condition (30) to be satisfied. The essential feature, which was now needed, was to reproduce a correct behavior of $f(\omega)$ for small $\omega$ values. We thought, as a first trial, that the parameters were more than necessary. We therefore chose $\eta$ to be very large so as to give for $\nu(p)$ the constant value $b/\eta$ for all $p$ values of interest. The parameters $b/\eta$ and $\omega_1^2$ were then chosen to give a good fit with $f(\omega)$ for small $\omega$'s consistent with Eq. (30). Having thus made a preliminary choice of the values of these parameters, they were substituted back into Eq. (15) and $f(\omega)$ was calculated from Eq. (16). It was found that the resultant curve for $f(\omega)$ did not differ much from that computed

by Rahman. Slight changes in the values of the parameters were then made to give a better fit and the resultant curve (long dashed) is shown in Fig. 1 for liquid argon at $T=94.4°K$. It was found that only a very slight change in the calculated curve arose by choosing $\eta$ of the same order as $\gamma$.

### Case (ii): Gaussian Correlation

As in the exponential case, we have assumed that the spectrum of the stochastic force $\mathbf{B}(t)$ is white, whereas the correlation $\langle \mathbf{A}(t)\cdot\mathbf{A}(0)\rangle$ is given by

$$\langle A_\alpha(t)A_\beta(0)\rangle=\delta_{\alpha\beta}\langle A_\alpha{}^2\rangle e^{-Bt^2}, \tag{32}$$

where $B$ is some constant. It is then straightforward to show that

$$\mu(p)=a(\pi/4B)^{1/2}\exp(p^2/4B)\,\mathrm{erf}(p/(4B)^{1/2}). \tag{33}$$

In this case, corresponding to Eqs. (30) and (31), we have the following conditions:

$$a(\pi/4B)^{1/2}+(\omega_0{}^2/\omega_1{}^2)\nu(0)=k_BT/M_0D, \tag{34}$$

$$a+\omega_0{}^2=\langle\omega^2\rangle, \tag{35}$$

where $\nu(0)=b/\eta$.

Here too, in choosing the values of the parameters we have followed the same procedure as in the exponential case. The calculated curve for $f(\omega)$ is shown as a solid curve in Fig. 1, and the values of the parameters are given in Table I. In this case, $f(\omega)$ tends to zero faster than in the exponential case as shown in the indent of the figure.

## 5. COMMENTS

In the present model, the choice of either an exponential or a Gaussian correlation for the stochastic force $\mathbf{A}(t)$ has been made for mathematical simplicity. The choice of a Gaussian correlation is, however, to be preferred for two reasons: (a) It gives a classical velocity autocorrelation function which, when expanded in powers of $t$, contains only even powers as it should,[9] and (b) the choice of the value of the parameter $a$ is such that it satisfies the second moment relation much better than it does in the exponential case. In the latter case, the moment relation was violated by as much as 33%, whereas in the Gaussian case the violation was only 7%, which is probably within the computational error of $\langle\omega^2\rangle$. For long times, an exponential correlation for the stochastic force might be more appropriate. Based on the linear dynamical theory of macroscopic fluctuations, Berne *et al.*[8] obtained a strictly exponential decay of an autocorrelation function of the type considered here. It is, however, not clear whether this theory is applicable to microscopic correlations we are dealing with. Also, this exponential decay can only hold in the asymptotic limit of large times and it is not evident that the asymptotic region is reached for times which are of importance here. It is worth remarking here that in the earlier work of Berne *et al.*[8] and Singwi and Tosi,[7] in which only two parameters appear whose values were uniquely fixed by the diffusion coefficient $D$ and the second moment $\langle\omega^2\rangle$, it was impossible to obtain a reasonable fit with Rahman's $f(\omega)$. The fit was particularly poor for small values of $\omega$ and besides the broad peak in $f(\omega)$ was not reproduced correctly. In the present model this defect is compensated by the last term in the square bracket in Eq. (15). The two-parameter models of Berne *et al.* and Singwi and Tosi described the liquid as more "solidlike" than it really is. This defect has been rectified in the present model, but at the expense of introducing more parameters.

TABLE I. Values of the parameters for liquid argon at 94.4°K.[a]

| Parameters | Exponential correlation | Gaussian correlation |
|---|---|---|
| $a$ | $71.5\times10^{24}$ sec$^{-2}$ | $57.7\times10^{24}$ sec$^{-2}$ |
| $\gamma, B$ | $\gamma=1.14\times10^{13}$ sec$^{-1}$ | $B=0.78\times10^{26}$ sec$^{-2}$ |
| $\nu(0)=b/\eta$ | $0.25\times10^{13}$ sec$^{-1}$ | $0.31\times10^{13}$ sec$^{-1}$ |
| $\omega_0{}^2$ | $1.5\times10^{24}$ sec$^{-2}$ | $1.5\times10^{24}$ sec$^{-2}$ |
| $\omega_1{}^2$ | $2.1\times10^{24}$ sec$^{-2}$ | $2.1\times10^{24}$ sec$^{-2}$ |

[a] $\langle\omega^2\rangle=55\times10^{24}$ sec$^{-2}$, $D=2.43\times10^{-5}$ cm$^2$ sec$^{-1}$. (From Rahman's machine computation.)

We have shown in Sec. 2 that the basic equations of Nakahara and Takahashi[4] are inconsistent with the fluctuation-dissipation relations, and, hence, the agreement with Rahman's $f(\omega)$ curve obtained by these authors does not prove the correctness of the model. These authors as well as Sears have identified $\omega_0{}^2$ with the second moment $\langle\omega^2\rangle$ of $f(\omega)$, but as we have seen here in Eq. (31) this identification is incorrect. In fact, the second moment of their $f(\omega)$ is not equal to $\omega_0{}^2$. We have found that it is the parameter $a$ which is more nearly equal to $\langle\omega^2\rangle$. Also their auxiliary relation corresponding to our Eq. (30) is different. It corresponds to neglecting $a/\gamma$ and putting $\omega_0=\omega_1$, whereas we find that $a/\gamma$ is of the same order of magnitude as $k_BT/MD$.

It should be mentioned that the value of the mass $M$ corresponding to the fictitious center of the surrounding that we obtain is about 0.7 times the mass of an argon atom. This value is much smaller than what one would have intuitively expected. We are unable to comment on this because of our lack of precise understanding of the fictitious center, which in the present model represents in some fashion the dynamical effect of the surroundings.

A final remark regarding the memory function $\alpha(t)$ will not be out of place here. We believe that it is a useful function in terms of which it is perhaps simpler to understand the self-motion of an atom in a liquid. In the present model we have computed its Laplace transform $\alpha(p)$, and we find it to agree reasonably well with that given by Rahman.[10] The corresponding $\alpha(t)$ of Rahman has two very characteristic features. It drops

[9] P. Schofield, in *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1961), p. 39.

[10] A. Rahman (private communication).

very sharply from its value at $t=0$ to a value which is smaller by a factor of almost forty in a time range of $3\times10^{-13}$ sec. It then remains almost constant for a time of the order of $10^{-12}$ sec, and then gradually tends to zero. We have found that Rahman's $\alpha(t)$ curve can be reasonably well reproduced by a four-parameter function. Out of these four parameters, only two are independent because of the diffusion and second moment restraints. It seems, therefore, obvious that in the Sears model there are more parameters than necessary to fit Rahman's data. In a later paper we propose to account for these characteristic features of the memory function from more basic statistical considerations.

## ACKNOWLEDGMENTS

This work was done while one of the authors (K.S.S.) was on leave of absence from the Argonne National Laboratory, and he wishes to thank NORDITA for sponsoring his visit and the U. S. Atomic Energy Commission for partial support. One of us (P.S.D.) would also like to thank SIDA for the award of a scholarship through the International Seminar for Physics, Uppsala. Our thanks are due to Dr. G. A. Kharadze of the Institute of Physics of the Academy of Sciences of Georgian SSR, Tbilisi, USSR, for interesting discussions and to Dr. A. Rahman for sending us the results of his machine computations. Comments from Dr. V. F. Sears and Dr. Y. Nakahara are gratefully acknowledged.

## APPENDIX

Here, following Kubo,[6] we shall show how the relations (8) and (9) of the text can be obtained from Eq. (6).

Consider the equation

$$(d/dt)V(t)+\int_{t_0}^{t}\Gamma(t-t')\cdot V(t')dt'=F(t). \quad \text{(A1)}$$

We assume that $F(t)$ is independent of the initial velocities $V(t_0)$, so that

$$\langle F(t)\cdot\tilde{V}(t_0)\rangle=0,$$

where $\tilde{V}(t_0)$ is the transposed matrix of $V(t_0)$. We can therefore write Eq. (A1) as

$$\frac{d}{dt}\langle V(t+t_0)\cdot\tilde{V}(t_0)\rangle+\int_0^t\Gamma(t-t')\cdot\langle V(t'+t_0)\cdot\tilde{V}(t_0)\rangle dt'=0, \quad \text{(A2)}$$

and we introduce

$$\phi(p)=\int_0^\infty e^{-pt}\langle V(t+t_0)\cdot\tilde{V}(t_0)\rangle dt$$

and

$$\Gamma(p)=\int_0^\infty e^{-pt}\Gamma(t)dt.$$

Taking the Laplace transform of Eq. (A2), we get

$$[p\mathbf{I}+\Gamma(p)]\cdot\phi(p)=\phi^0,$$

which gives

$$\phi(p)=[pI+\Gamma(p)]^{-1}\cdot\phi^0, \quad \text{(A3)}$$

where

$$\phi^0=\langle V(0)\cdot\tilde{V}(0)\rangle.$$

Since from Eq. (A1), $\dot{V}(t_0)=F(t_0)$, we can rewrite Eq. (A1) as

$$(d/dt)\langle V(t+t_0)\cdot\tilde{V}(t_0)\rangle+\int_0^t\Gamma(t-t')\cdot\langle V(t'+t_0)\cdot\tilde{V}(t_0)dt'=\langle F(t+t_0)\cdot\tilde{F}(t_0)\rangle. \quad \text{(A4)}$$

Remembering that correlation functions appearing in the above equations depend only on the difference of their time arguments, we can write (A4) as

$$-(d^2/dt^2)\langle V(t+t_0)\cdot\tilde{V}(t_0)\rangle-\int_0^t\Gamma(t-t')\cdot(d/dt')\langle V(t'+t_0)\cdot V(t_0)\rangle dt'=\langle F(t+t_0)\cdot\tilde{F}(t_0)\rangle. \quad \text{(A5)}$$

Taking the Laplace transform of Eq. (A5) and using the fact that $\langle\dot{V}(t_0)\cdot\tilde{V}(t_0)\rangle=0$, we get

$$[p\mathbf{I}+\Gamma(p)]\cdot\phi^0-p[p\mathbf{I}+\Gamma(p)]\cdot\phi(p)=F(p), \quad \text{(A6)}$$

where $\mathbf{I}$ is the unit matrix and

$$F_{ij}(p)=\int_0^\infty e^{-pt}\langle F_i(t+t_0)\cdot\tilde{F}_j(t_0)\rangle dt.$$

Making use of Eq. (A3) in Eq. (A6), we obtain the following fluctuation-dissipation relation:

$$\Gamma(p)\cdot\phi^0=F(p). \quad \text{(A7)}$$

# Statistical Mechanics of Ideal Fermions in a Thin Film

R. L. DEWAR AND N. E. FRANKEL
*School of Physics, University of Melbourne, Parkville, Victoria, Australia*
(Received 25 August 1967)

Starting from the partition function for ideal fermions in a thin film with box boundary conditions, the influence of size effects on the specific heat is examined both numerically and analytically. For fairly thin films the specific heat is depressed at low temperatures and raised at high temperatures. In the very thin case, the behavior is that of a two-dimensional gas at low temperatures and that of a three-dimensional Boltzmann gas at high temperatures. The relevance to $^3$He thin-film experiments is briefly discussed.

## 1. INTRODUCTION

BECAUSE of the widespread applicability of the ideal Fermi gas, or liquid,[1] as a model in physics, it is of interest to investigate the effect of finite geometry on the properties of such systems.

Although thin films of conducting materials may well be amenable to experiment, the investigation was primarily motivated by recent work on liquid helium,[2,3] for which reason the specific heat was chosen as the quantity for detailed investigation. We note that the corresponding case of ideal bosons has recently been studied numerically.[4]

## 2. THEORY

### A. The Model

We take as our model a system of ideal fermions of mass $m$ and spin $S$ confined within a boxlike potential well of dimensions $L\times L\times D$ and volume $V$.

Since $L$ is allowed to approach infinity it is valid to use the grand canonical ensemble thus obtaining the partition function $Z$ given by

$$\ln Z=\sum_{k,s}\ln(1+ze^{-\beta\epsilon_{k,s}}). \tag{1}$$

We take the energy to be

$$\epsilon_{k,s}=(\hbar^2/2m)(k_\perp^2+k_3^2), \tag{2}$$

where $\mathbf{k}_\perp$ is any wave vector perpendicular to the normal to the film and $k_3$ is given by

$$k_3=n\pi/D, \quad n=1, 2, 3, \cdots. \tag{3}$$

The partition function is now

$$\ln Z=\frac{(2S+1)V}{(2\pi)^2D}\sum_{k_3}\int d^2k_\perp \times\ln\left\{1+z\exp\left[-\frac{\beta\hbar^2}{2m}(k_\perp^2+k_3^2)\right]\right\}. \tag{4}$$

The $k_\perp$ integral may be done using the function $f_s(z)$ defined in the Appendix, thus yielding

$$\ln Z=\frac{(2S+1)mV}{2\pi\beta\hbar^2D}\sum_{k_3}f_2(ze^{-\beta\hbar^2k_3^2/2m}). \tag{5}$$

To determine the thermodynamic functions of interest for the specific heat, namely, the number of particles $N$ and the internal energy $U$, we use the standard relations

$$U=-\partial\ln Z/\partial\beta, \quad N=z\partial\ln Z/\partial z. \tag{6}$$

$z$ is to be eliminated by the requirement that $N$ be a constant given by

$$N=n_0V, \tag{7}$$

where $n_0$ is the number density.

For convenience we define the specific heat to be dimensionless:

$$c_V=(1/N)\partial U/\partial(kT). \tag{8}$$

### B. Calculations

To clarify the mathematics it is convenient to introduce the new temperature variable $\theta$ defined by

$$\theta=2mD^2kT/\pi^2\hbar^2. \tag{9}$$

This gives, using Eqs. (3) and (5),

$$\ln Z=\frac{(2S+1)\pi V}{4D^3}\theta\sum_{n=1}^{\infty}f_2(ze^{-n^2/\theta}) \tag{10}$$

or

$$\ln Z=[(2S+1)\pi V/4D^3]\ln\vartheta, \tag{11}$$

where we have defined the new partition function $\vartheta$ by

$$\ln\vartheta=\theta\sum_{n=1}^{\infty}f_2(ze^{-n^2/\theta}). \tag{12}$$

We also define parameters corresponding to $U$ and $N$ by

$$\mathfrak{U}=\theta^2\partial\ln\vartheta/\partial\theta, \quad \mathfrak{N}=z\partial\ln\vartheta/\partial z. \tag{13}$$

From (6) and (7) it is easily seen that the physical value of $\mathfrak{N}$, which will later be seen to play the role of the principal size-effect parameter, is given by

$$\mathfrak{N}=[4/(2S+1)\pi]n_0D^2. \tag{14}$$

[1] For a collection of papers on Fermi liquid theory, see D. Pines, *The Many-Body Problem* (W. A. Benjamin, Inc., New York, 1962).
[2] D. F. Brewer, in *Superfluid Helium*, edited by J. F. Allen, (Academic Press Inc., New York, 1966), p. 159.
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